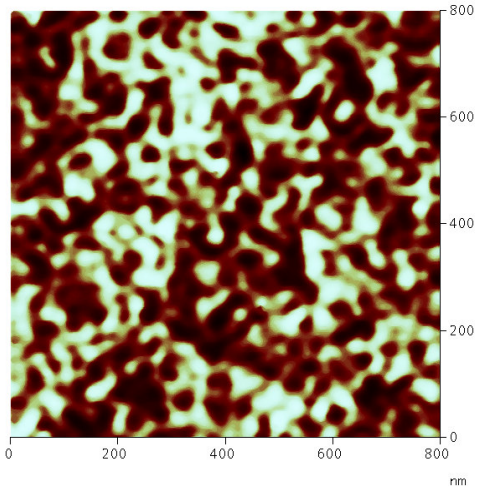
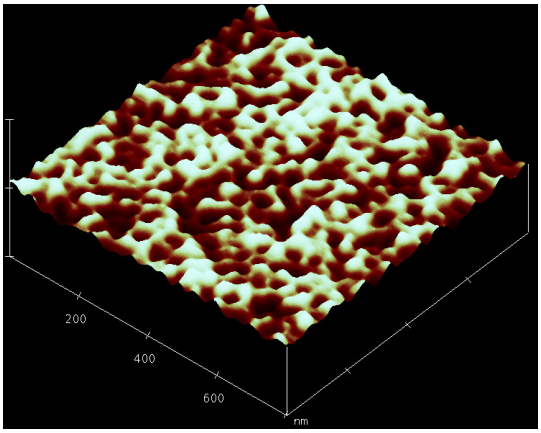
Synthesis and Controlled Radical Polymerization of Multifunctional Monomers





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June 2004

Synthesis and Controlled Radical Polymerization of Multifunctional Monomers

DISSERTATION

zur Erlangung des akademischen Grades
Doctor rerum naturalium
(Dr.rer.nat.)

vorgelegt
der Fakultät Mathematik and Naturwissenschaften
der Technischen Universität Dresden

von
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eingereicht am:	29.03.2004
Tag der Verteidigung:	08.06.2004

谨献给：

我的父母：尹宜志 和 陈文英

dedicated to

my parents *Wenying Chen* and *Yijie Yin*

1. INTRODUCTION AND OBJECTIVES

1.1. Introduction

It is very hard to imagine today's life without plastics, better referred to scientifically as *polymers*. For instance, polystyrene, poly(ethylene), poly(propylene), poly(vinyl chloride) (PVC), poly(methyl methacrylate), polyurethane polyamide and polyester are only a few examples of the polymers employed in everyday life. In the USA alone the last year's plastic resin production was nearly 50 million tons. Among these polymers, synthetic polymers obtained from multifunctional acryl and methacryl derivatives, such as acrylates, methacrylates, acrylamides and methacrylamides, have found wide use in industry, agriculture, and medicine owing to their remarkable properties such as water solubility and potential biocompatibility. They are also used as coatings, adhesives, surfactants, blood coagulants, polymeric antioxidants and photopolymers.[1,2]

Where do the polymers come from? *Polymers* are macromolecules built up by the linking together of large numbers of much smaller molecules. The small molecules that combine with each other to form polymer molecules are termed *monomers* and the reactions by which they combine are termed *polymerizations*.

Free radical polymerization is one of the most common synthetic methods for industrial production of polymers worldwide because of its high tolerance in relation to many monomer families, functional groups and impurities. In fact, radical polymerization is considered a mature technology with millions of tons of vinyl-based homo- and copolymers being produced annually. However, traditional free radical procedures have a significant drawback in that unlike ionic reaction intermediates, the growing radical species usually suffer from bimolecular termination reactions such as radical recombination and disproportionation. Therefore, free radical polymerization does not generally allow the achievement of well-defined architectures.

One of the most effective methods for the synthesis of well-defined polymers is *"living" polymerization*. Living polymerization is free from side reactions such as termination and chain transfer and can thus generate polymers of well-defined architectures and molecular

weights, i.e., one polymer chain per molecule of initiator. The first example of which was discovered in the *anionic polymerization* of styrene with sodium naphthalenide in 1956.[3,4] In general, however, living ionic polymerizations (anionic or cationic) are the only "living" techniques available that efficiently control the structure and architecture of vinyl polymers. However, they are not useful for the polymerization and copolymerization of a wide range of functionalized vinylic monomers. This limitation is due to the incompatibility of the growing polymer chain end with numerous functional groups and certain monomer families.[5] In addition; these polymerization techniques require stringent reaction conditions, such as ultrapure reagents and absolutely dry and oxygen free solvents. The necessity to overcome all these limitations urged synthetic polymer chemists to develop new concepts, which would permit a free-radical polymerization procedure possessing a living characteristic, termed *living radical polymerization* (LRP) or *controlled radical polymerization* (CRP). This field has witnessed explosive growth, especially in the 1990s. There are numerous systems and proposed methodologies for controlling radical polymerizations, even in comparison to some of the “classical” anionic living polymerizations.[6-9]

Among CRP systems *nitroxide-mediated radical polymerization* (NMP),[10-13] *atom transfer radical polymerization* (ATRP)[14-16] and *reversible addition-fragmentation chain transfer polymerization* (RAFT)[17-19] have attracted attention as synthetic routes to well-defined polymers with narrow molecular weight distribution and active chain ends. Great progress has been made in the synthesis of precision polymers in the last years. Huge, well-defined structures with narrow molar mass distribution can be achieved and particularly important parameters, such as the chain length, can be controlled. However, most research has focused primarily on styrene systems.[20-24] Unlike styrene-based systems, there is a lack of published material on the multifunctional acryl and methacryl derivative systems, mostly due to the difficulty in obtaining “living” qualities, although recently research groups at Xerox and IBM have had some success in polymerizing simple acrylates.[25-27] There are only few examples[28-30] for controlled radical polymerization of methacrylates and methacrylamides. For this reason it is of great interest to search for new procedures to improve the living character of the polymerization of multifunctional acryl and methacryl derivatives.

How can the recently achieved knowledge about the synthesis of well-defined architectures be used to synthesize homo- and block-copolymers on the basis of multifunctional acrylic and methacrylic monomers and in particular to customize block-copolymers with phase separation? With this work a contribution to the polymerization of multifunctional acryl and methacryl derivatives using different polymerization technique is presented.

1.2. Aim of the Work

The aim of this work was the synthesis of functional acryl- and methacryl derivatives with free (**I**) and protected functional groups (**II**), which are shown in Figure 1.1, and their homopolymerization starting with the traditional free radical polymerization initiated by AIBN. The deprotection of the protective groups in the polymers was also investigated after the polymerization. Especially the new methods of controlled radical homo-polymerization, as well as block co-polymerzations with styrene, were applied and investigated concerning their applicability for the selected functional monomers.

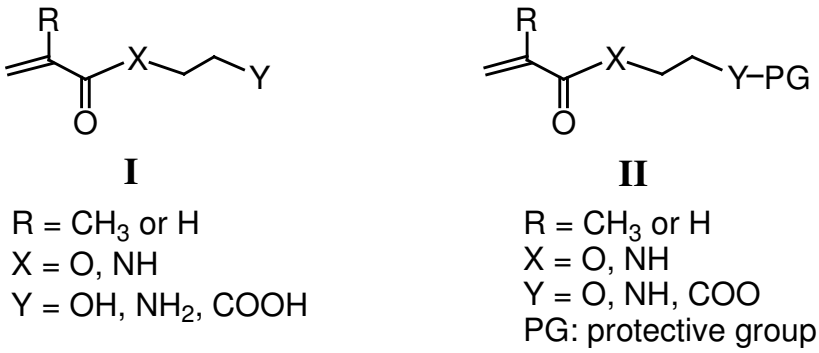


Figure 1.1. General structure of the monomers.

The applicability of NMP, ATRP and RAFT on the controlled polymerization of functional monomers as well as on styrene had to be thoroughly investigated and compared. In addition, *n*-butyl acrylate was used as a model monomer in order to compare the differences between monomers with and without functional groups.

Subsequently, suitable initiators for NMP of mentioned monomers had to be synthesized and an optimization of the reaction conditions was required.

The various aspects of this work can be summarized as follows:

- Synthesis of multifunctional monomers
  - o Synthesis of acryl- and methacryl derivatives with free functional groups (-NH_2, -OH and -COOH)
  - o Synthesis of acryl- and methacryl derivatives with protective groups
  - o Removal of the protective groups by chemical and photochemical methods
- Preparation of suitable initiators for NMP
  - o Synthesis of initiators
  - o Characterization of the initiators

  - o Verification of their applicability to the polymerization of functional monomers
- Synthesis of homopolymers by NMP, ATRP and RAFT
  - o Adjustment of the conditions for each method
  - o Optimization of the reaction conditions for well-defined homopolymers
  - o Confirmation of the "living" characters of the polymerization
- Synthesis of a series of special block-copolymers by NMP, ATRP and RAFT
  - o Optimization of the reaction conditions for block-copolymerization
  - o Synthesis of poly(styrene-*b*-functional monomer) copolymers
  - o Synthesis of poly(protected monomer-*b*-free functional monomer) copolymers
- Investigation of phase behavior of block-copolymers
  - o Study of thermal bulk behavior of block-copolymers
  - o Test of surface behavior of block-copolymers

The focus of the work was to investigate the possibility of a controlled radical polymerization of functional monomers on the basis of acryl- and methacryl derivatives to appropriate homopolymers and block copolymers with a narrow molecular weight distribution.

2. THEORETICAL PART

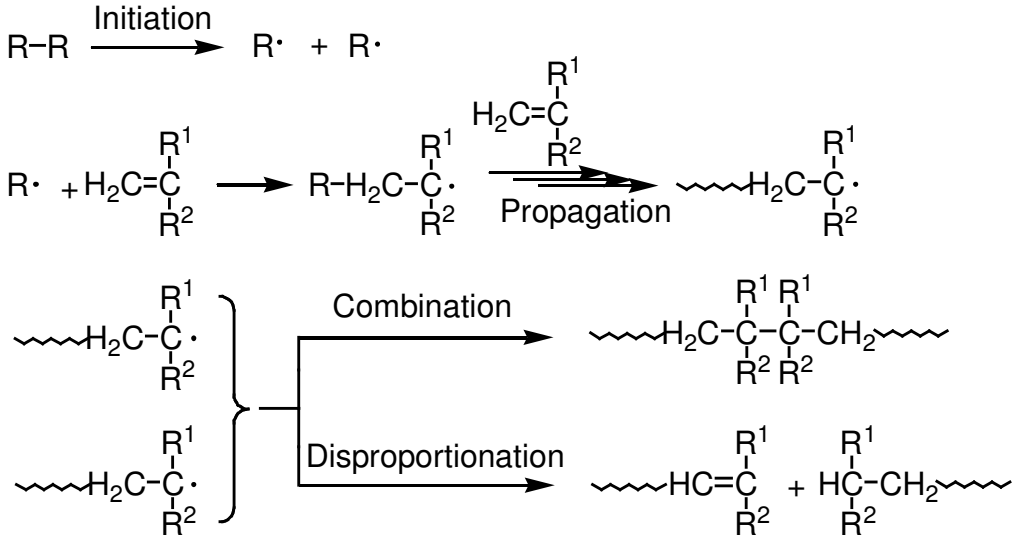
2.1. Free Radical Polymerization (FRP)

Free-radical chain reactions have been known for a long time, but free-radical polymerization was recognized only in the mid-1930s. The topic of free radical polymerization has been repeatedly discussed in numerous reviews and books.[8, 31-35]

2.1.1. Mechanism

The mechanism of free-radical polymerization is composed of three primary process *initiation, propagation,* and *termination*, as shown in Scheme 2.1. Generally, the *initiation* takes place by cleavage of a weak bond; often azo or peroxide compounds are used as initiator to yield the "primary radical". The *propagation*, or growth reaction, occurs when monomers add to the primary radical or to the radical at the end of a growing polymer chain. *Termination* occurs primarily by bimolecular reaction of two growing polymer radicals. The two primary mechanisms observed are radical-radical combination and disproportionation in which one radical abstracts a hydrogen atom from another radical resulting in one saturated chain end and one olefinic chain end.

In addition to these primary reactions, there are a variety of other reactions that occur. There may be very low levels of *chain transfer* to monomer, a reaction that leads to termination of one chain with simultaneous initiation of another new chain so that there is no change in the number of radical species present.

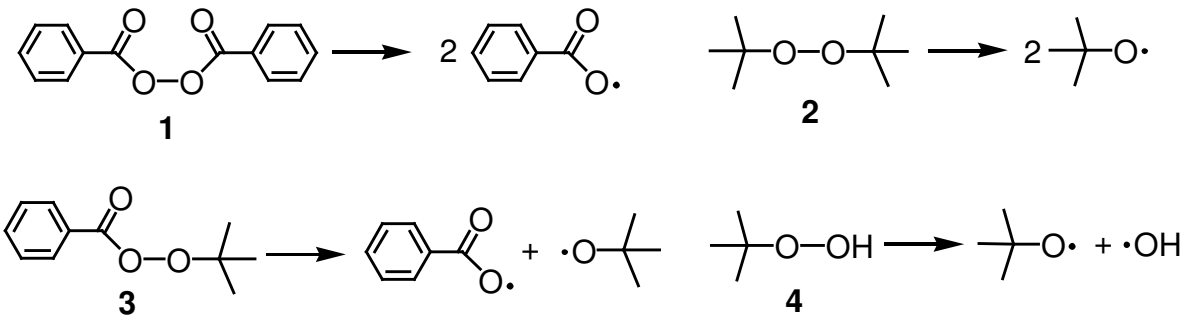


Scheme 2.1. Elementary reactions for conventional radical polymerization.[36]

2.1.2. Initiator

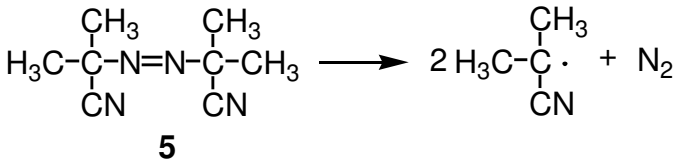
The *thermal, homolytic dissociation* of initiators is the most widely used mode of generating radicals for polymerization. In general, the initiators for free-radical polymerization are peroxides and azo compounds.

Peroxides contain an O-O bond with dissociation energies in the range of 100-170 kJ/mol and have found extensive use as radical sources. Several different types of peroxy compounds are widely used.[37] Examples include acyl peroxides such as benzoyl peroxide (**1,** Scheme 2.2), alkyl peroxides such as *t*-butyl peroxide (**2**), peresters such as *t*-butyl perbenzoate (**3**) and hydroperoxides such as *t*-butyl hydroperoxide (**4**).



Scheme 2.2. *Thermal, homolytic dissociation* of peroxide initiators.

2,2'-Azobisisobutyronitrile (AIBN, **5**, Scheme 2.3) is the most important member of azo compound initiator, although other azo compounds such as 2,2'-azobis(2,4-dimethylpentanenitrile) and 1,1'-azobis(cyclohexanecarbonitrile) are also used.[38]



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Scheme 2.3. *Thermal, homolytic dissociation* of AIBN.

Various initiators are used at different temperatures depending on their rates of decomposition. The value of the decomposition rate constant k_d varies in the range of 10^{-4}-10^{-9} sec^{-1} depending on the initiator and temperature. Most initiators are used at temperatures where k_d is usually 10^{-4}-10^{-6} sec^{-1}. Thus AIBN is commonly used at 50-70°C, acetyl peroxide at 70-90°C, benzoyl peroxide at 80-95°C, and dicumyl or di-*t*-butyl peroxide at 120-140°C.[39]

The differences in the rates of decomposition of the various initiators are related to differences in the structure of the initiators and of the radicals produced. The k_d for a compound depends on the bond energy and the stability of the formed radical and the byproduct (as CO_2, N_2 etc). For R-N=N-R, k_d increases in the order R = allyl, benzyl > tertiary > secondary > primary.[40]

The differences in the decomposition rates of various initiators can be conveniently expressed in terms of the initiator *half-life time* ($t_{1/2}$), defined as the time to decrease the concentration of I to one half its original value. $t_{1/2}$ is obtained as $t_{1/2} = 0.693/k_d$ by setting $[I] = [I_0]/2$.[39]

2.1.3. Monomer and polymer

Monomers show varying degrees of selectivity with regard to the type of reactive center that will cause their polymerization. Although radical, cationic, and anionic initiators are used in chain polymerizations, they cannot be used indiscriminately, since all three types of initiation do not work for all monomers. Most monomers will undergo polymerization with a radical initiator, although at varying rates. Today, free-radical polymerization finds application in the synthesis of many important classes of polymers including those based upon methacrylates, methacrylamides, styrene, chloroprene, acrylonitrile, ethylene, and the many copolymers of these vinyl monomers.

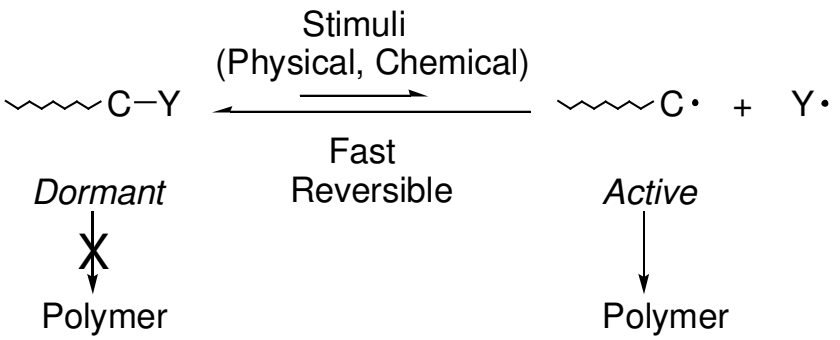
Generally, there are several advantages to radical polymerization, such as its tolerance to protonic compounds like water, compatibility with a wide variety of functional groups, a high reaction rate and a polymerization temperature usually higher than ambient. All of these factors have led to the use of radical polymerization as the most widely employed industrial and laboratory-scale process for polymer synthesis.[32]

One important feature of free radical polymerization is that high molecular weight polymers are formed even at very low levels of monomer conversion. Molecular-weight distribution can be easily calculated for polymerizations restricted to low conversions where all of the kinetic parameters ([M], [I], k_d, k_p, k_t) are approximately constant. Under these conditions, the polymer molecular weight does not change with conversion.[39] The theoretical limiting polydispersity of a conventional free-radical process is 1.5. However, ionic polymerizations, including anionic and cationic polymerization, may perform in a living fashion with special initiators and monomers, which give a lower molecular-weight distribution.

In the preparation of well-defined macromolecules, traditional free radical procedures have a significant drawback, which is related to the reactivity of the propagating free radical chain end and its propensity to undergo a variety of different termination reactions. Free radical polymerization had therefore been considered unsuitable for precision polymer synthesis.[32]

2.2. Controlled/Living Radical Polymerization (CRP)

It is known that "living" polymerization is one of the most effective methods for precision polymer synthesis. Typically, living polymerization techniques are employed where the polymerizations proceed in the absence of irreversible chain transfer and chain termination.[3, 4, 41] Much of the academic and industrial research on living polymerization has focused on anionic, cationic, coordination, and ring-opening polymerizations. The development of *controlled/living radical polymerization* (CRP) methods has been a long-standing goal in polymer chemistry, as a radical process is more tolerant of functional groups and impurities and is the leading industrial method to produce polymer.[42] The past few years have witnessed the rapid growth in the development and understanding of new CRP methods.[8, 43] All of these methods are based on establishing a rapid dynamic equilibration between a minor amount of growth-active radical species and a large majority of the dormant species.



Scheme 2.4. General mechanism of a controlled radical polymerization system.

Scheme 2.4 shows the general outline of a successful living free radical polymerization mechanism.[44] In this general mechanism, the reversible termination of the growing polymeric chain is the key step, because the overall concentration of the propagating radical chain end is reduced. In the polymerization process the mediating radical (Y• is shown in Figure 2.1) is rather stable and there are no other reactions leading to initiation of new polymer chains. The concentration of reactive chain ends is extremely low and minimizes the irreversible termination reactions, such as combination or disproportionation. All chains would be initiated only from the desired initiating species and growth should occur in a living fashion; a high degree of control over the entire polymerization process with well-defined polymers is obtained.

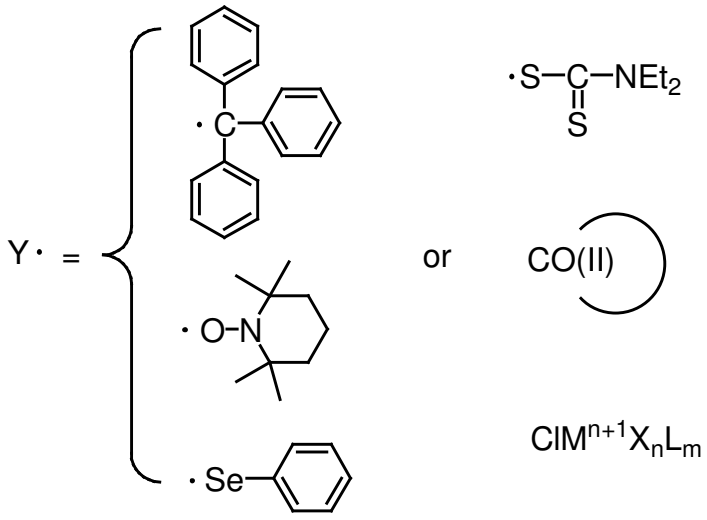


Figure 2.1. Typical mediating radicals.

The dormant species contain a covalent bond, including C-C, C-S, C-Se, C-O, C-Halogen or C-Metal. All of them can reversibly homolyze into the growing radical species and the mediating radical by various stimuli such as heat or light (physical), a metal catalyst

(chemical), or another radical species.[36] In particular, the radicals may be generated in different ways: from a catalyzed process, as in Atom Transfer Radical Polymerization (ATRP)[15, 16, 45, 46] or from a thermochemical process, as in Nitroxide-Mediated radical Polymerization (NMP).[10-13, 47-50] Moreover, the radicals can also be formed reversibly via a degenerative exchange process with dormant species. An example being the Reversible Addition-Fragmentation chain Transfer process (RAFT).[17-19, 51, 52] In principle, the living free radical polymerization techniques are quite similar, yet in practice there are some differences, which affect the feasibility of each technique for specific applications. The following sections focus on the NMP, ATRP and RAFT methods due to the high control of molecular weight and molecular weight distribution, the wide applicability, and the relatively easy access to the catalysts and other components to be employed.

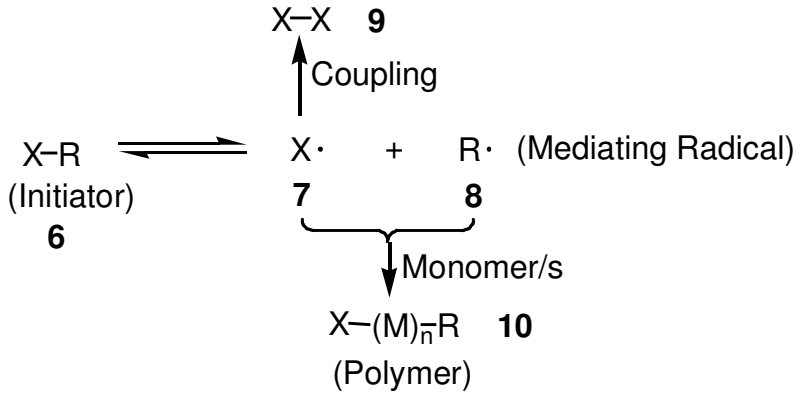
2.2.1. Nitroxide-Mediated Radical Polymerization (NMP)

The first basis for the development of this system dates back to the beginning of 1980s, when, during the free radical polymerization of methyl methacrylate, nitroxides such as TEMPO showed their ability as radical traps.[53] Ten years later, George reported the synthesis of well-defined polystyrene by TEMPO at 130°C, which will be described in detail in section **2.2.1.1.** Shortly afterward, Hawker presented the synthesis of an unimolecular initiator based on TEMPO for controlled radical polymerization.[12, 54] Since then many other initiating compounds have been synthesized in order to optimize the reaction conditions, extending the process to a greater number of monomers and continuously increasing the control over the products.

The key kinetic feature of nitroxide mediated living free radical polymerization, as for all controlled systems, is the operation of a special kinetic phenomenon, termed the Persistent Radical Effect (PRE).[55-58]

In the initial stages of the polymerization a small fraction of the initiating radicals **7** formed from decomposition of the unimolecular initiator **6** undergo radical-radical coupling. This leads to a terminated small molecule **9**, and the resulting elimination of two initiating radicals. At this early stage of the polymerization, this is a facile reaction since the diffusing radicals are sterically uncongested and the reaction medium is not viscous. However, by its nature, the mediating radical or persistent radical **8** does not undergo coupling and so a small increase in the overall concentration of **8** relative to the propagating/initiating radical **7** occurs. This increased level of **8** is self-limiting since a higher concentration leads to more efficient

formation of the dormant chain end **10** and a decrease in the amount of radical-radical coupling (Scheme 2.5). This interplay between termination and mediation leads to a small amount of excess mediating free radical, giving rise to the persistent radical effect and to eventual control over the polymerization process.



Scheme 2.5. General mechanism of the nitroxide mediated polymerization.

2.2.1.1. Initiators for NMP

Nitroxide mediated radical polymerization procedures can be divided into two classes, according to the initiators used. The first class, as introduced by George *et al.*, is a "bimolecular system", in which a conventional free radical initiator, such as 2,2'-azobisisobutyrolnitrile (AIBN) or benzoyl peroxide (BPO) is used in conjunction with TEMPO.[10, 47, 59] The second class is a "unimolecular system", in which alkoxyamine dissociate to produce both the initiating radical and the mediating nitroxide radical.[13, 54, 60]

- **Bimolecular system**

In 1993, George et al[10] tried the polymerizations of styrene derivatives at 130°C in bulk, containing an initiating system composed of benzoyl peroxide and a stable nitroxide (TEMPO) in a molar ratio of 1.3:1. At these elevated temperatures the C-O bond in the formed alkoxyamine becomes unstable, releasing the nitroxide, which can now act as a polymerization mediator, not as an inhibitor as it is at low temperatures. They obtained high molecular weight and low polydispersity materials. A linear increase of molecular weight with conversion typical for a living polymerization procedure was observed. The PD (PD = 1.2-1.3), which was significantly lower than the theoretical lower, limits for a free radical process of 1.5 and the typical values of ca. 2.0 for free radical systems.

- **Unimolecular initiators**

Solomon, Rizzardo, and Moad demonstrated for the first time that the C-O bond in alkoxyamines is unstable and can undergo reversible homolytic cleavage at 100°C, to yield a nitroxide. However, they obtained only low-molecular MMA polymers with bad molecular mass distribution.[53, 61-62]

Borrowing the concept of well-defined initiators from living anionic and cationic procedures, Hawker et al. developed unimolecular initiators for the NMP.[12, 54] The structure of these initiators was based on a specially designed alkoxyamine functionality that is present at the chain end of the growing polymer during its dormant phase. The principle of design of NMP initiators is that the C-O bond of the small molecule alkoxyamine derivatives is thermolytically unstable and decomposes on heating to give initiating and mediating nitroxide radicals in the correct 1:1 stoichiometry. A list of unimolecular initiators synthesized by Hawker and others for the controlled radical polymerizations is included in Figure 2.2.[63-64]

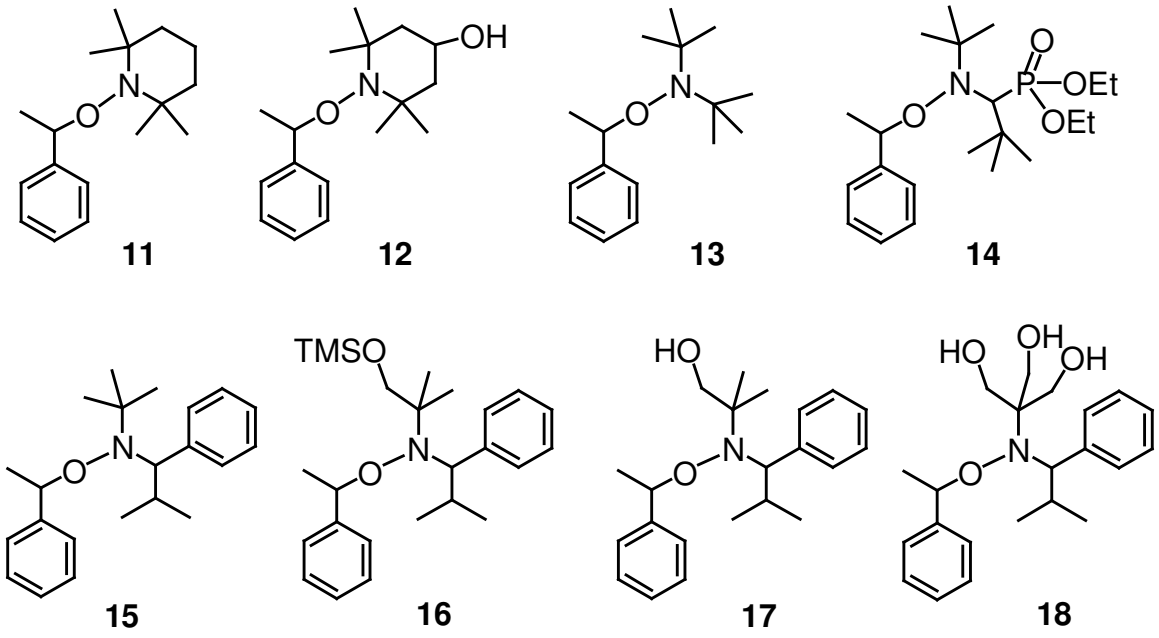


Figure 2.2. Unimolecular initiators for CRP.[63-64]

2.2.1.2. Development of nitroxides

The development of nitroxides as mediators for radical polymerization stems from the pioneering work of standard free radical initiation mechanisms and the desire to efficiently trap carbon-centered free radicals. Among them, TEMPO, **19**, was the standard compound

used as the trapping free radical. However, there were a large number of problems with the use of TEMPO as the mediating radical for a living free radical procedure.[54] For instance, the necessity to use high polymerization temperatures (125-145°C), long reaction times (24-72h) and an incompatibility with many important monomer families.

To overcome the deficiencies of the simple TEMPO system, a modified nitroxide was synthesized. Initial efforts to develop new mediating nitroxides relied on TEMPO-based derivatives. The XEROX groups were able to polymerize acrylates at elevated temperatures (145-155°C) in the presence of 4-oxo-TEMPO **20** as the mediating nitroxide. While the polydispersities were still between 1.40 and 1.67 and the living nature of the polymerization was questionable.[65] The rate of polymerization could be increased by additives such as camphorsulfonic acid[66] or acetic anhydride,[67] however, the improvements were not significant enough to make nitroxide mediated polymerizations a viable competitor to other living polymerization techniques. One terms the TEMPO-derived initiators as " first generation".

The most significant breakthrough in the design of improved nitroxides was the use of alicyclic nitroxides, which bear no structural resemblance to TEMPO. In fact, their most striking difference was the presence of a hydrogen atom on one of the α-carbons, in contrast to the two quaternary α-carbons present in TEMPO derivatives. The best examples of these new materials are the phosphonate derivative **21**, **22** introduced by Gnanou and Tordo[68-69] and compounds **23**, **24** and **25** introduced by Hawker (Figure 2.3).[63-64] The "second generation" initiators have been able to decrease chain end degradation thanks to shorter reaction time and low temperatures permitting the achievement of narrower molar mass distributions, at least for what concerns the styrene family monomers.

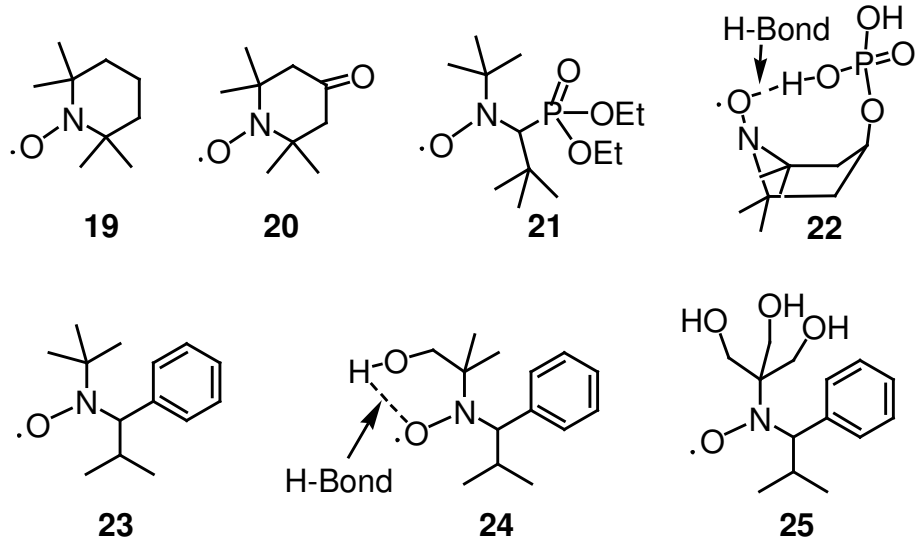


Figure 2.3. Common nitroxides for the NMP.

It must be emphasized that the TEMPO-based systems are not *true* living systems.[70-74] There are some unwanted side reactions that still occur in TEMPO-based systems, such as the generation of additional radicals by styrene auto-polymerization at high temperatures and the decomposition of nitroxide. While the concentration and reactivity of propagating chain radicals has been significantly reduced, it is still not negligible to avoid the unwanted side reactions, and therefore termination reactions can still occur. By the strictest definition nitroxide-mediated, and in fact all versions of CRP are not *living polymerizations*. For an excellent discussion of the many varied opinions on the correct terminology for living free radical polymerizations the reader is directed to a special "living or controlled" thematic issue of Journal Polymer Science.[75] The terms *controlled polymerization*, *living*, *living/controlled*, *pseudo-living*, *living polymerization with reversible deactivation*, and others are scattered throughout the literature. The term *living polymerization* should be recognized when irreversible termination processes such as chain transfer or self-reaction are negligible. In practical terms, in the case of radical polymerization, the irreversible termination processes such as chain transfer or self-reaction are not negligible. We thus prefer to use that the term *controlled radical polymerization* (CRP) rather than *living radical polymerizations* (LRP) throughout this thesis.

2.2.1.3. Applications of NMP

NMP is mainly limited to styrene and its functional derivates.[76-77] Hawker reported that a wide variety of monomer families, such as acrylates, 3-dienes and acrylonitrile based monomers could be polymerized with accurate control of molecular weights and polydispersities as low as 1.1 by using the novel unimolecular initiators.[26, 63-64, 77-78] The acrylates they used are often without functional group, such as n-butyl acrylate, methyl acrylate. Some of the results are still arguable and can not be repeated, we will discuss them later. However, the polymerization of methacrylates and vinyl acetate is still problematic for NMP because of the increased chain end degradation due to hydrogen transfer.[44]

The nitroxide structure plays a crucial role in the success or failure of living free radical polymerizations, and the key to extending the scope of this reaction is in designing more effective nitroxides.[26, 63] The versatile nature of these initiators can also be used to control the formation of random and block copolymers from a wide selection of monomer units. The use of multi-reactive initiators permits the synthesis of complex macromolecular architecture, such

as star and graft polymers, hyper branch polymers, and hybrid dendritic-linear polymers.[48, 63, 79-80]

Besides homogeneous systems, i.e., bulk or solution polymerizations, a considerable amount of effort has been directed to development of NMP under heterogeneous conditions such as suspension, dispersion-seeded emulsion, batch emulsion, and miniemulsion.[81-85]
In conclusion, nitroxide-mediated living free radical polymerizations are simple techniques, as they do not use additional metal complexes, which are required in ATRP. This allows a simple purification of the products.

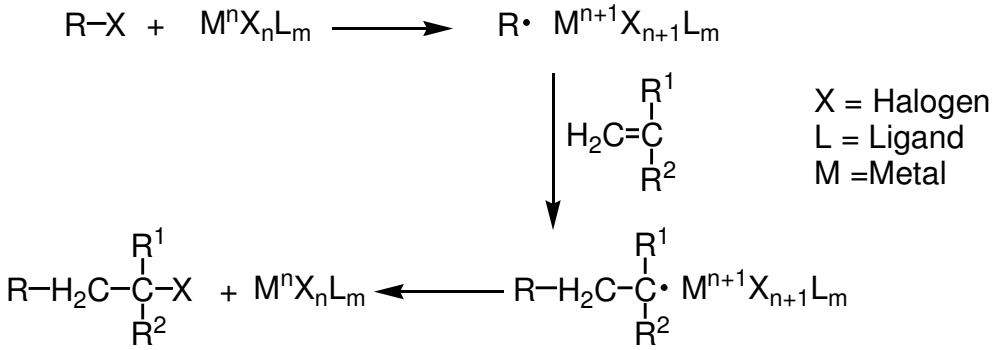
2.2.2. Atom Transfer Radical Polymerization (ATRP)

Up to now, ATRP is the most investigated controlled radical polymerization system due to its wide applicability. The name "atom transfer radical polymerization" was used for the first time in 1995 by Matyjaszewski and his co-workers to describe the controlled synthesis of polystyrene in the presence of transition-metal complexes.[16] Sawamoto reported the first example in 1994, i.e., the living polymerization of methyl methacrylate catalyzed by a ruthenium(II) complex coupled with carbon tetrachloride as the initiator.[14] They called the method "metal-catalyzed living radical polymerization".[15] A very similar mechanism was also applied by Perce and Barboiu to obtain arenesulfonyl chloride initiated polystyrene in the presence of a bipyridine/copper chloride complex.[86] Though classifying them in different ways, the three groups were able to realize controlled polymerization using the same technique. Thus 1995 was the break-through year for ATRP systems.

2.2.2.1. Background: Atom Transfer Radical Addition (ATRA)

The transition metal catalyzed atom transfer radical polymerization (ATRP) can be traced back to the Kharasch, or Atom Transfer Radical Addition (ATRA), reactions (Scheme 2.6).[36]
The classical Kharasch reaction requires high reaction temperatures, long reaction times, and large excesses of the halogenated starting material to ensure efficient propagation and good yields. The process occurs when a radical species generated from an organic halide (R-X, X= halogen) in the presence of a metal catalyst attacks an unsaturated compound to form an adduct with a carbon-halogen bond. The metal catalyst thus undergoes a reversible one-electron redox reaction via abstraction of the halogen from the reactant R-X, followed by a one-electron reduction by release of the halogen back to the resulting radical species (R•). It is

not clear whether this radical is a free radical, a metal-complexed radical, or an organometallic intermediate. However, these features led to scientists to hypothesize the following: if the carbon-halogen bond in the adduct is successively activated by the metal complex, a controlled radical polymerization will similarly proceed via the metal-assisted repetitive activation and formation of the carbon-halogen bond (dormant species) at the polymer chain end.



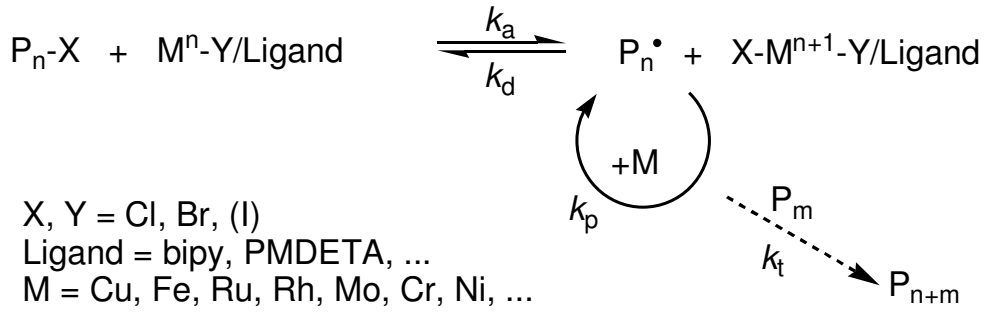
Scheme 2.6. Metal-catalyzed radical addition reactions (Kharasch addition reaction).[36]

2.2.2.2. Mechanism of ATRP

The mechanism of ATRP is illustrated in Scheme 11. To generate a growing radical or an active species (P_n•), a transition metal complex (M^nYL) undergoes one-electron oxidation accompanied by the abstraction of a halogen (X) from an initiator or a dormant species (P_n-X). The active species initiate monomers (CH_2=CH_2R_1) to form new growing radicals, which can continually react with monomers until their halogen atoms are released from the oxidized metal back to form dormant species. The reversible process then switches the polymer chain ends from a dormant state to an active and propagating state. In this process the oxidized metal complexes (X-$M^{n+1}YL$) are used as persistent radicals and reduce the stationary concentration of growing radicals, therefore minimize termination by generating a steady low concentration of short-lived active radical chain ends. The key feature of this mechanism is the constantly low concentration of radical intermediates in the reaction medium due to fast but reversible transformation into non-active species, before adding new monomer units. The fast initiation and the rapid reversible deactivation enable the uniform growth of all chains and subsequently the achievement of narrow polydispersities. It also suppresses termination reactions, like radical coupling and disproportionation.

A successful ATRP will have not only a small contribution of terminated chains, but also a uniform growth of all the chains, which is accomplished through fast initiation and rapid

reversible deactivation.[76] This process is described by Scheme 2.7, which occurs with a rate constant of activation k_a and deactivation k_d. Polymer chains grow by the addition of the intermediate radicals to monomers in a manner similar to a constant of propagation k_p. Termination reactions (k_t) would also occur mainly through radical coupling and disproportionation in ATRP.



Scheme 2.7. Mechanism of metal-catalyzed atom transfer radical polymerization (ATRP).

2.2.2.3. Components of ATRP

ATRP is a rather complicated method, where the choice of the components is of extreme importance for the achievement of the desired products.

As a multicomponent system, ATRP consists of a monomer or monomers, an initiator with a transferable (pseudo) halogen (identified as P_n-X in Scheme 2.11), and a catalyst (composed of a transition metal species (M_t) with any suitable ligand (L)). Sometimes an additive such as oxygen, zerovalent metals and phenol is used. For a successful ATRP, other factors, such as solvent and temperature, must also be taken into consideration.

For each monomer, the suitable initiator with a transferable halogen has to be selected, as well as the appropriate catalyst system. Furthermore, the solvent, the reaction temperature and the reaction time have to be tailored and the possibility to obtain better results by using additives should also be considered. All these factors have been thoroughly investigated and a wide range of convenient systems has been developed for many monomers as exhaustively reported by Matyjaszewski[76] and Sawamoto.[36]

- **Monomers for ATRP**

Various monomers have been successfully polymerized via ATRP: styrene, acrylates, methacrylates, dienes, acrylonitriles, etc.[87-109] In particular, a wide range of styrene derivatives with different substituents on the aromatic ring and acrylates and methacrylates with various

side chains have been also polymerized in a well-controlled fashion. However, there are only a few reports on the attempted ATRP of acrylamides,[102, 110] such as *N*,*N*-dimethylacrylamide. It was subsequently confirmed by Rademacher et al[109] that these systems were not "living".

There are currently two major classes of monomers, which have not yet been successfully polymerized by ATRP. Acidic monomers fail since they can protonate ligands and form the corresponding carboxylate salts. Halogenated alkenes, alkyl-substituted olefins, and vinyl ester are presently resistant to polymerization by ATRP. Nevertheless, the range of monomers polymerizable by ATRP is greater than that accessible by nitroxide-mediated polymerization, since it includes the entire family of methacrylates.

- **Initiators for ATRP**

The role of the initiator in ATRP is to form an initiating radical species via homolytic cleavage of its labile bond such as C-halogen by the metal catalysts.

The number of the available initiators for ATRP is much larger than for other CRP methods. A variety of initiators, typically alkyl halides, have been used successfully in ATRP. Halogens (X) in the initiators (R-X) include chlorine, bromine, and iodine, where the reactivity of the C-X bond increase in the order Cl < Br < I, with concomitant decrease in the stability of the C-X bond. Chlorides and bromides have thus been widely employed. Common initiators are shown in Figure 2.4.

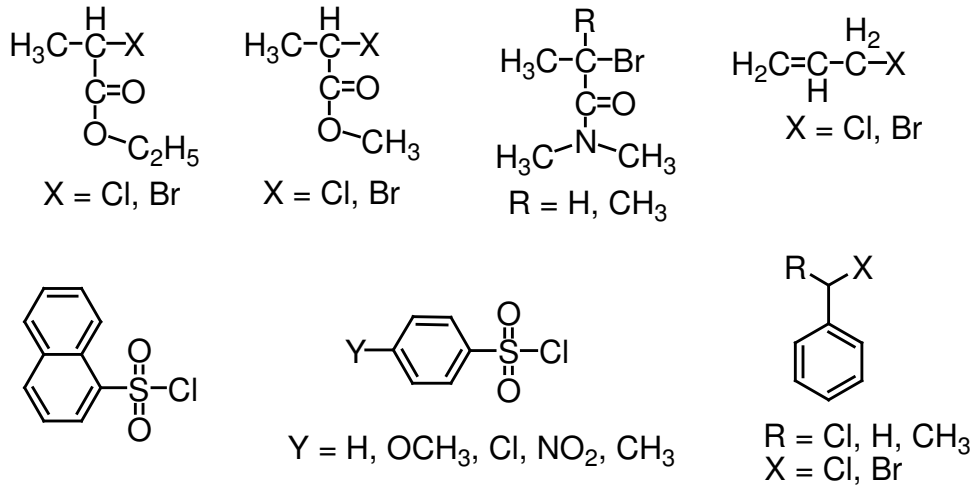


Figure 2.4. Common initiators for ATRP.

The design of initiators has been a challenging task for the optimization of products. Many different types of halogenated compounds such as sulfonyl halides,[111] functionalized phenolic

ester halides,[112] modified cholesterol,[113] and glucose[114] have been successfully used to initiate ATRP.

- **Catalysts for ATRP**

One of the most important components of ATRP is the transition-metal complex. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species. The role of the transition metals (such as Cu(I)) is to abstract halogen atoms from the halogen-terminated inactive polymer chains and is oxidized to Cu(II) via a single electron transfer to generate a growing radical species.[76] After then the oxidized metal center returns back to the more stable lower oxidation state, by donating the halogen back to the radical growing species and deactivating the propagating polymer chains. In this way it establishes an extremely low concentration of the radical species as well as a fast reversible reaction with halogen.
Many transition-metal complexes are used as catalysts for ATRP. Among these, copper catalysts are superior in ATRP in terms of versatility and cost. Styrene, (meth)acrylate, and acrylonitrile have been successfully polymerized using copper-mediated ATRP.[88, 115, 116]

- **Ligand**

The main role of the ligand in ATRP is to control the solubility of a transition metal in the reaction mixtures. Furthermore ligands serve several purposes: they tune the atom transfer equilibrium constants and dynamics, adjust the selectivity of the catalysts, and ensure the stability of the complexes in different monomers, solvents, and at different temperatures.

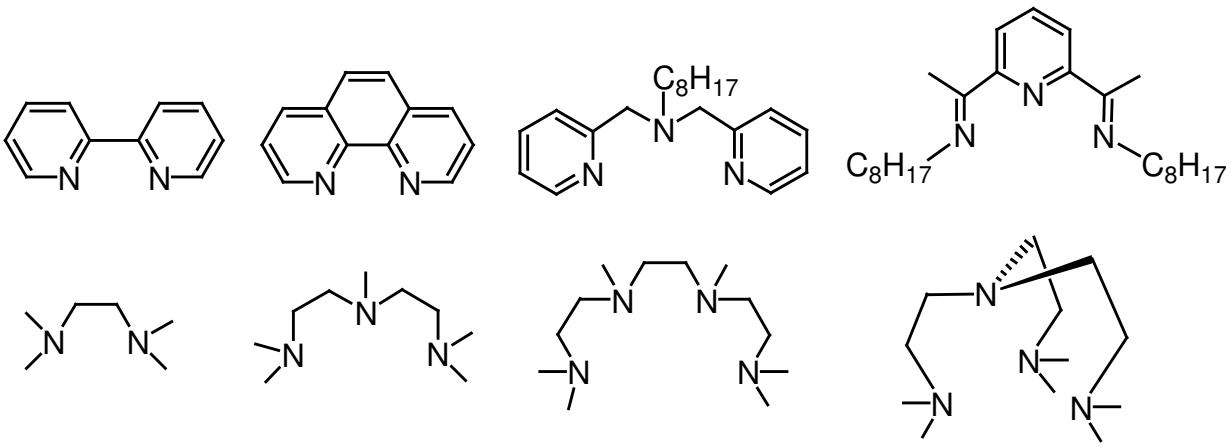


Figure 2.5. Examples of ligands used in copper-mediated ATRP.[76]

Several different ligands that have been used for ATRP are described in the literature.[76] The common ligands used in copper-mediated ATRP are shown in Figure 2.5. Nitrogen ligands are usually used to complex copper and iron transition metals in ATRP.[117-121] Phosphorous ligands are employed for rhenium-, ruthenium-, iron-, rhodium-, nickel- and palladium-mediated ATRP.[122-128]

- **Additives in ATRP**

The effects of different additives on ATRP have been studied.[23, 129] Additives are sometimes essential for a successful ATRP. When a small amount of a zerovalent metal, such as copper or iron, was added to some ATRP systems, a significant rate enhancement was observed.[76, 130] In contrast, when a small amount of Cu(II) halide was added to a copper-based ATRP, the polymerization was slower but could be better controlled.[131] The reason could be Cu(0) reduces "excess" Cu(II), which is generated primarily during the early stages of the polymerization through irreversible radical termination to form *in situ* Cu(I) by a single electron transfer (SET) process. This process reduces the concentration of Cu(II) and simultaneously increases the concentration of Cu (I).

Haddleton and coworkers found that various phenols accelerated the polymerization rate of methyl methacrylate, at no expense to molecular weight control or to the resulting polydispersities.[132] Further additives such as carboxylic acids[133] enhanced the polymerization rate, but the polydispersities are also increased with an increase in the acid-to-copper ratio.

- **Solvent influence on ATRP**

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (e.g., emulsion, suspension). The use of a solvent is sometimes necessary, especially when the polymers formed are not soluble in their monomers. Different solvents (benzene, toluene, xylene, diphenyl ether, ethyl acetate, DMF, ethylene carbonate, alcohol, water, and others) have been used for various monomers.[76, 93, 103]

Several factors affect the solvent choice. Minimal chain transfer to solvent is one of the basic requirements for selecting a solvent. In addition, interactions between solvent and the catalyst or other components in the ATRP system should be considered. Catalyst poisoning by the solvent (e.g., carboxylic acids or phosphines in copper-based ATRP[23] and solvent-assisted side reactions, which are more pronounced in a polar solvent[134] should be minimized.

- **Reaction temperature and reaction time**

In general increasing the temperature in an ATRP accelerates the polymerization due to the increase of both the radical propagation rate constant and the atom transfer equilibrium constant. Furthermore, the solubility of the catalyst increases at higher temperatures. However, at high temperature the chain transfer and other side reactions, such as catalyst decomposition, become more pronounced.[125, 126, 134, 135] Thus, the optimal temperature for the reaction should be pre-determined based on the particular ATRP system (monomer, catalyst and targeted molecular weight). The range of useful reaction temperatures is broad, from 20°C to 150°C.
At high monomer conversions the rate of propagation slows down considerably; however, the rate of side reactions does not change significantly, as most of them are monomer concentration independent. Prolonged reaction times leading to higher monomer conversion may not increase the polydispersity of the final polymer but will cause the obtained polymer to lose end groups,[136] which are important for the subsequent synthesis of block copolymers. To avoid end group loss, it is suggested that the conversion not exceed 95%.[76]

2.2.2.4. Polymeric materials by ATRP

A basic understanding of the mechanism and kinetics of this process has enabled the synthesis of various polymeric materials with novel functionalities, compositions, and architectures. Many polymeric materials prepared using ATRP have been listed in the recent review.[76] They include functional polymers, gradient/statical copolymers, block copolymers, inorganic/organic hybrids, graft copolymers, comb polymers, star polymers, hyperbranched polymers and well-defined networks.

- **Functionality**

ATRP is the most versatile CRP technique to control precisely and inexpensively chain-end functionality. Halogen end groups are much less expensive than nitroxides or dithioesters. Due to commercial availability of many activated alkyl halides with various functionalities, it is very easy to prepare end-functional polymers. Moreover, the activated alkyl halides can be incorporated to the chain ends of many polymers and be used for novel block copolymers.
Halogen end groups may be replaced using many different organic transformations such as nucleophilic substitution, electrophilic addition, radical addition, etc. Especially important may be the synthesis of well-defined mono-, di-, and multifunctional oligomers with hydroxyl,

amino, and acid functionalities for coatings and as segments for polyesters, polyamides, and polyurethanes.

Attachment of initiator fragments to organic or inorganic surfaces can be used as a method to modify the surface. This modification can be performed under very undemanding conditions of free radical polymerization to yield biocompatible surfaces, and surfaces with high lubrication or scratch resistance.[76]

2.2.3. Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization

The reversible addition-fragmentation chain transfer process is certainly the most recent of the controlled radical systems. Even if the concept of atom/group transfer is well-known in organic chemistry,[137] the first reports about the possibility of performing controlled radical polymerization using dithiocarbonyl compounds only appeared in 1998.[17] The interest in developing new radical processes with living character for the synthesis of well-defined architectures has allowed an unbelievable growth of this reversible chain transfer mediated process, as shown by the increasing number of publications on the subject.[18, 19, 51, 52, 138-142]

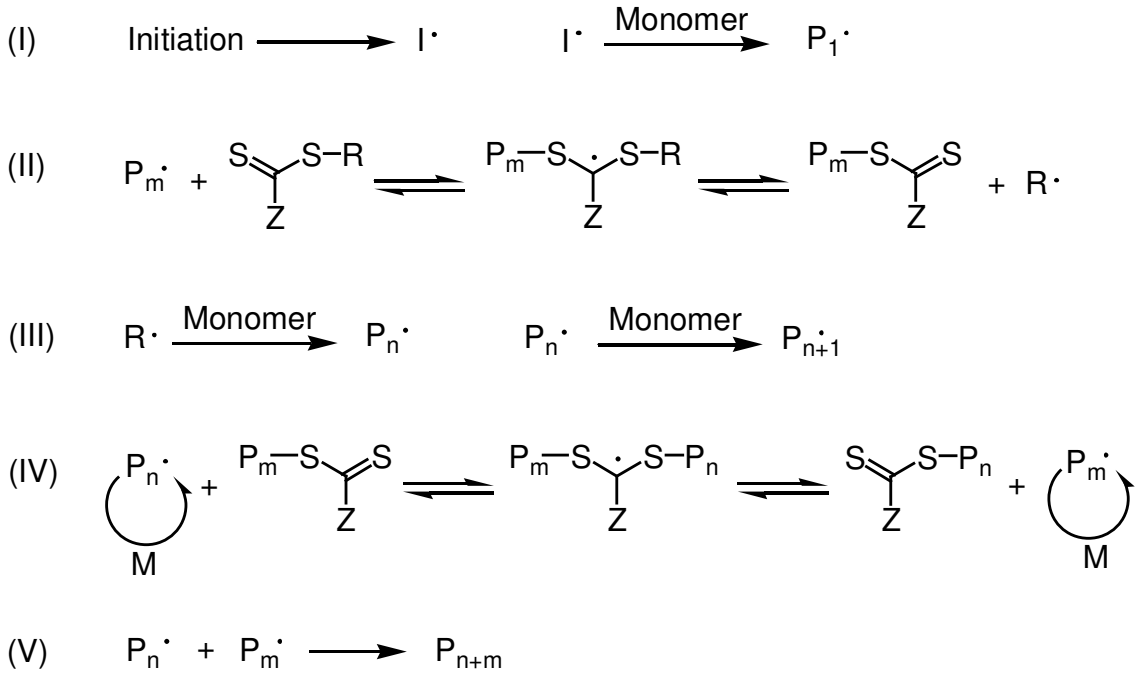
2.2.3.1. Mechanism of RAFT

Rizzardo first demonstrated that dithiocarbonyl compounds, with a weak carbon-sulphur bond, confer living characteristics to radical polymerization,[143-144] which they termed RAFT polymerization. The technique employs dithiocarbonyl compounds in order to mediate the polymerization via a reversible chain transfer process. This leads to an equilibrium under which all the propagating chains grow proportionally with conversion.

The widely accepted mechanism for the RAFT process is shown in Scheme 2.8.[17] The scheme consists of the initiation processes (I), a preequilibrium involving the initial RAFT agent (II), propagation and reinitiation processes (III), the addition–fragmentation equilibrium (IV), and bimolecular termination reactions (V).

In essence, the mechanism relies on an initial release of initiating radicals through chain transfer (II) and a reversible addition fragmentation step (IV) through which irreversible termination events are minimized. During a particular transfer event the chain-propagating end is converted to a polymeric transfer agent, which can then undergo transfer itself, re-releasing

the propagating radical. Through this equilibrium, chains convert from propagating radicals to polymeric transfer agents enabling the incremental growth of the chains with conversion.



Scheme 2.8. Mechanism of reversible addition-fragmentation chain transfer polymerization.

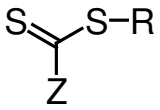
These RAFT process results in living radical behavior, characterized by a predictable, linear evolution of molecular weight with conversion, narrow molecular weight distribution, and pseudo-first order kinetics.

As concerns the mechanism of RAFT, the chain equilibrium process is based on a transfer reaction, no radicals are formed or destroyed and, when the chain transfer agents behave ideally, the kinetics can be compared to the one of a conventional free radical polymerization. A correct understanding of its mechanistic and kinetic features is essential for its successful application. Many mechanistic and kinetic studies of RAFT polymerization have been reported.[145-150]

2.2.3.2. Chain Transfer Agents for RAFT

After Rizzardo demonstrated that dithiocarbonyl compounds performed as Chain Transfer Agents (CTA) in RAFT process,[143-144] dithioester,[17] trithiocarbonates,[18] and certain aromatic dithiocarbamates[52,151] were successfully employed as CTA to obtain narrow polydispersity for styrene and (meth)acrylates in batch polymerization.

The general structure of CTA is shown in Figure 2.6. Z is a group such as phenyl or methyl that governs the reactivity of the C=S moiety toward radical addition and R is a free-radical homolytic-leaving group that is capable of reinitiating the polymerization.



Z = aryl, alkyl, NR'_2, OR', SR'
R = homolytic leaving group

Figure 2.6. The general structure of CTA.

The effectiveness of the RAFT process in terms of molecular weight control and polydispersity is governed by the nature of the groups Z and R. Thus, the choice of CTA is very important for the achievement of well-defined products. The first requirement for the CTA is that they should have a high transfer constant relative to the monomers being polymerized, which means a high rate of addition and a suitable leaving group for the propagating radical. The second important quality of the CTA is the ability of forming intermediates that fragment rapidly, giving no side reactions. In addition, the expelled radicals (R•) should be able to efficiently reinitiate the polymerization.[152] The first requirement ensures the rapid consumption of the initial CTA and fast equilibration of the dormant and active species while the second ensures the continuity of the chain process.

The common leaving groups (R) used for RAFT are $-CH_2Ph$, $-CH(CH_3)Ph$, $-C(CH_3)_2Ph$, $C(CH_3)_2(CN)$, $CH_2(Ph)COOH$, $C(CH_3)(CN)(CH_2CH_2CH_2OH)$, and $-C(CH_3)(CN)(CH_2CH_2COOH)$. The leaving group ability of R increases with increasing stability and bulk of the radical R•. Thus, CH_3 and $C(CH_3)_2CN$ are examples of very poor and very good homolytic leaving groups, respectively.

One other effective CTA is xanthate,[153] which is used as a chain transfer agent to control the free radical polymerization of styrene, alkyl acrylates and vinyl acetate.[154] This technique has also been successfully employed to obtain well-defined copolymers based on acrylic acid and acrylamide monomer units.[155]

With appropriate choice of chain transfer agent, a wide range of polymers of predetermined molecular weight and a narrow polydispersity can be prepared.[17, 51, 143, 144, 151, 156] The versatility and convenience of this process offers distinct advantages over other forms of living radical polymerization.[143] Of course, not all the chain transfer agents are suitable for every circumstance, and each new system must be optimized to reduce side reactions and maximize

the living character of the RAFT-process.

2.2.3.3. Application of RAFT

The RAFT polymerization distinguishes from all other methods of controlled radical polymerization, that it can be used with a variety of monomer types, including those which are difficult to polymerize by CRP, such as unprotected (meth)acrylic acids, [155, 157] acrylamides[155, 158, 159] vinyl acetate.[154]

The procedure is one of the most forgiving, allowing a wide range of polymerization conditions to be used. For example, it has been successfully performed over the temperature range 20 to 150°C in a broad range of solvents, including water, and in different performance processes (bulk, emulsion, suspension, etc.). RAFT polymerization is also unique in allowing polymerization conditions close to those used in conventional radical polymerization.

The use of the RAFT process allows the control over the polymer molecular weight, film thickness, and polymer brush structure. Further the synthesis of comb and graft polymers[160] as well as of star polymers, functional isoporous materials and micro patterned thin films[142] have also been reported.

However, in comparison to the other controlled radical polymerization systems, the following shortcomings have been noted. The polymerization rate is not very fast, because it is based on the chain transfer between propagating centers and dormant chain transfer agent (CTA). Almost each CTA is toxic, malodorous and red in color.

2.3. Functional monomers

2.3.1. General background of functionality

Functionality can refer to many different aspects when describing a polymer. Those components relevant to polymerization are functional monomers, initiator fragments, and polymer termini.[161] The initiator fragments and polymer termini have already been discussed previously, so the focus here is directed to functional monomers.

A functionalized monomer may provide the material used directly to exploit the properties provided by the functional group (hydrophilicity, polarity, metal complexation, etc.) or via a

derivative (i.e. a protecting group) of a monomer when the free functional group is not polymerizable by specific mechanism.[76]

Polymers of (meth)acrylamides and (meth)acrylates and its derivatives have found wide use in industry, agriculture, and medicine owing to their remarkable properties such as water solubility and potential biocompatibility. Functional (meth)acrylamide and (meth)acrylates have been grafted onto numerous substrates for the purpose of increasing hydrophilicity, reducing susceptibility to degradation, especially by microorganisms, or providing a reactive site. Grafts are initiated by chemical radical sources, ultraviolet light with a photosensitizer, or X-rays. Substrates used include cellulose, polysaccharides, proteinaceous materials, polyolefins, polyvinyl alcohol, polyesters, polyamides, and urethanes.[162] Yang et al. reported that *N,N*-bis(2-hydroxyethyl)acrylamide was grafted onto a segmented polyether-polyurethane film to increase the hydrophilicity and blood anti-coagulability of the grafted surface.[163]

Up to now, although (meth)acrylamide and (meth)acrylates derivatives and their polymers have been prepared or produced, there are continuously increasing needs for functional monomers and better properties. The synthesis and polymerization of these new monomers has become more important and has been of great interest to both academic and industrial polymer chemists.[164-166] The functional monomers required in our research are acryl- and methacryl derivatives with free and protected functional groups (NH_2, OH and COOH).

2.3.2. Protection of the functional groups

- **Properties of a protective agent**

When a chemical reaction is to be carried out selectively at one reactive site in a multifunctional compound, other reactive sites must be often temporarily blocked. Many protective groups have been, and are being, developed for this purpose.[167] A protective group must fulfill a number of requirements. It should be selectively introduced in a given substrate and should be stable to the projected reactions. The protective group must be selectively removed in good yield by readily available, preferably nontoxic reagents that do not attack the regenerated functional group. The protective group should form a derivative that can easily be separated from side products associated with its formation or cleavage. The protective group should have a minimum of additional functionalities to avoid further sites of reaction.

- **Selection of a protective group**

As chemists proceeded to synthesize more complicated structures, they developed more satisfactory protective groups and more effective methods for the formation and cleavage of protected compounds. To select a specific protective group, one must consider in detail all the reactants, reaction conditions, and functionalities involved in the proposed synthetic scheme. First one must evaluate all functional groups in the reactant to determine those that will be unstable to the desired reaction conditions and require protection. The reactivities of possible protective groups have to be examined to determine the compatibility of the protective group and the reaction conditions. When several protective groups are to be removed simultaneously, it may be advantageous to use the same protective group to protect different functional groups (e.g., a benzyl group, removed by hydrogenolysis, to protect an alcohol and a carboxylic acid). When a selective removal is required, different classes of protective groups must be used. A very useful compilation of functional group protection and deprotection has been published recently.[167]

2.3.2.1. Protection of amino groups

A great number of protective groups have been developed for the amino group, including carbamates (>NCOOR), used for the protection of amino acids in peptide and protein synthesis,[168] and amides (>NCOR), used more widely in synthesis of alkaloids and for the protection of the nitrogen bases adenine, cytosine, and guanine in nucleotide synthesis.[169]

- **Carbamates**

Carbamates are often used as protective groups for amino acids to minimize racemization in peptide synthesis. Many carbamates have been used as protective groups.[167] The most useful groups are the Boc (*t*-butyloxycarbonyl), Cbz and Z (benzyloxycarbonyl) groups.

The Boc group is used extensively in peptide synthesis for amine protection.[170] One of the more common methods for introduction of the Boc group is via reaction of the amine with $(Boc)_2O$ (di-*tert*-butyl dicarbonate) in basic conditions at room temperature. It has the advantage that the by-products are innocuous and easily removed.[171] The Boc group can be readily cleaved by acidic hydrolysis, commonly performed with 50% TFA/CH_2Cl_2.[172]

The Z group can be introduced by reacting with $PhCH_2OCOCl$ or $(PhCH_2OCO)_2O$ in the presence of a base. The latter reagent was reported to give better yields in preparing amino

acid derivatives than when $PhCH_2OCOCl$ was used.[173] The Z group is often cleaved by catalytic hydrogenolysis (H_2/Pd-C) and under strongly acidic conditions. If hydrogenation is carried out in the presence of $(Boc)_2O$, the released amine is directly converted to the Boc derivative.[174]

- **Amides**

Simple amides are generally prepared from acid chlorides or anhydrides. They are exceptionally stable to acidic or basic hydrolysis and are classically hydrolyzed by heating in strongly acidic or basic solutions. Among simple amides, hydrolytic stability increases from formyl to acetyl to benzoyl. Lability of the haloacetyl derivatives to mild acid hydrolysis increases with substitution: acetyl < chloroacetyl < dichloroacetyl < trichloroacetyl < trifluroacetyl.[175] Note that amide hydrolysis under acidic or basic[176] conditions is greatly facilitated by the presence of a neighboring hydroxyl group that can participate in the hydrolysis.[177] Although a number of imaginative amide-derived protective groups have been developed, most are not commonly used because they contain other reactive functionality or because other more easily introduced and cleaved groups, such as the Boc and Cbz groups, serve more adequately for amine protection.

2.3.2.2. Protection of hydroxyl groups

The protection/deprotection protocol of free hydroxyl groups has become commonplace in organic synthesis. Hydroxyl groups are present in a number of compounds of biological and synthetic interest, including nucleosides, carbohydrates, steroids, macrolides, polyethers, and the side chain of some amino acids.[169, 178] During oxidation, acylation, halogenation with phosphorus or hydrogen halides, or dehydration reactions of these compounds, a hydroxyl group must be protected. In general the formation of ether, ester and carbonate is available for the protection of hydroxyl functions by means of organic synthesis. The ester protective group is recommended to see chapter 2.3.2.3, on the preparation of esters as protective groups for carboxylic acids).

- **Ethers**

Ethers are among the most used protective groups in organic synthesis and vary from the simplest, most stable methyl ether to the more elaborate, substituted trityl ethers developed for

use in nucleotide synthesis.[179] Ethers are formed and removed under a wide variety of conditions. Some of the ethers that have been used extensively to protect alcohols include substituted methyl ethers, substituted ethyl ethers, substituted benzyl ethers and various silyl ethers.

Among ethers, silyl ethers are the most frequently used protective groups for the alcohol function.[180] The selective cleavage of numerous silyl derivatives has been investigated.[181] This stems largely from the fact that their reactivity (both formation and cleavage) can be modulated by a suitable choice of substituents on the silicon atom. Both steric and electronic effects are the basic controlling elements that regulate the ease of cleavage in multiply functionalized substrates. In planning selective deprotection, the steric environment around the silicon atom, as well as the environment of the protected molecular framework, must be considered. Electron-withdrawing substituents on the silicon atom increase its susceptibility toward basic hydrolysis, but decrease its sensitivity toward acid. For some of the more common silyl ethers, such as trimethylsilyl (TMS), triethylsilyl (TES), *t*-butyldimethylsilyl (TBDMS), triisopropylsilyl (TIPS), *t*-butyldiphenylsilyl (TBDPS), the stability toward acid increases in the order: TMS < TES < TBDMS < TIPS < TBDPS, and the stability toward base increase in the order: TMS < TES < TBDMS ~TBDPS < TIPS. One of the properties that have made silyl groups so popular is the fact that they are easily cleaved by fluoride ion, which is attributed to the high affinity that fluoride ion has for silicon.

- **Carbonates**

Organic carbonates are also used as protective groups and can be cleaved by basic hydrolysis, but are generally much less susceptible than esters because of the resonance effect of the second oxygen. In general, carbonates are cleaved by taking advantage of the properties of the second alkyl substituent (e.g., zinc reduction of the 2,2,2-trichloroethyl carbonate). The reagents used to introduce the carbonate onto alcohols react readily with amines as well. As expected, basic hydrolysis of the resulting carbamate is considerably more difficult than hydrolysis of a carbonate.

2.3.2.3. Protection of carboxyl groups

Carboxylic acids are protected for a number of reasons: (1) to mask the acidic proton so that it does not interfere with base-catalyzed reactions, (2) to mask the carbonyl group to prevent

nucleophilic addition reactions, and (3) to improve the handling of the molecule in question (e.g., to make the compound less water soluble, to improve its NMR characteristics, or to make it more volatile so that it can be analyzed by gas chromatography).

Besides stability to a planned set of reaction conditions, the protective group must also be removed without affecting other functionalities in the molecule. For this reason, a large number of protective groups for acids have been developed that are removed under a variety of conditions, even though most can be readily cleaved by simple hydrolysis. Hydrolysis is an important means of deprotection, and the rate of hydrolysis is, of course, dependent upon steric and electronic factors that help to achieve different deprotection in polyfunctional substrates. These factors are also important in the selective protection of compounds containing two or more carboxylic acids.[182]

- **Esters**

A wide range of methods is available for the protection of carboxyl functions by means of methyl, ethyl, substituted methyl and ethyl, *t*-butyl, allyl, benzyl, substituted benzyl, diphenyl methyl and silyl esters among others.

The preparation of esters can be classified into two main categories: (1) carboxylate activation with a good leaving group and (2) nucleophilic displacement of a carboxylate on an alkyl halide or sulfonate. The latter approach is generally not suitable for the preparation of esters if the halide or tosylate is sterically hindered, but there has been some success with simple secondary halides[183] and tosylates (ROTs, DMF, K_2CO_3, 69-93 % yield).[184]

An ester has two sites that can be potentially attacked by a nucleophile. In general, the approach of cleaving ester groups can be employed under acidic, basic or hydrogenolytic conditions.[185]

3. RESULTS AND DISCUSSION

3.1. Synthesis, protection and deprotection of multifunctional acryl- and methacryl derivatives

The object of the work present here was to synthesize acryl- and methacryl derivatives containing additional functional groups (-NH_2, -OH and -COOH) and their protected species. The general structure of the monomers selected for synthesis and further investigation are given in Figure 3.1.1. As functional groups the -NH_2, -OH, and -COOH groups were chosen. For the protection of their functional groups appropriate protective groups, such as the *tert*-butyloxycarbonyl (Boc), the *tert*-butyldimethylsilyl (TBDMS) and *tert*-butyl (TB) groups were used. After polymerization the protective groups could be deprotected by different methods.

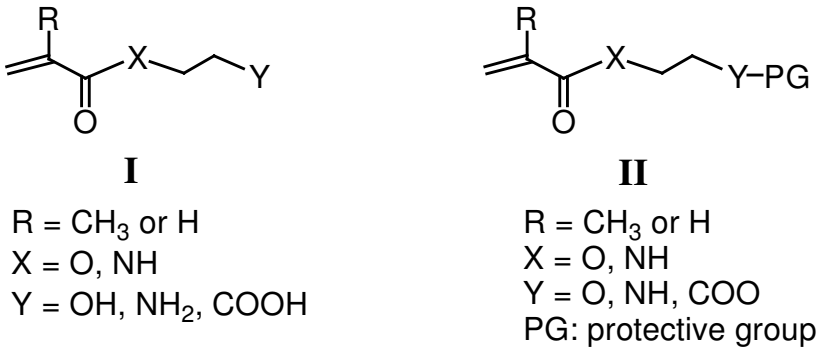


Figure 3.1.1. General structure of the monomers.

3.1.1. Syntheses of acryl- and methacryl derivatives with free and protected functional groups

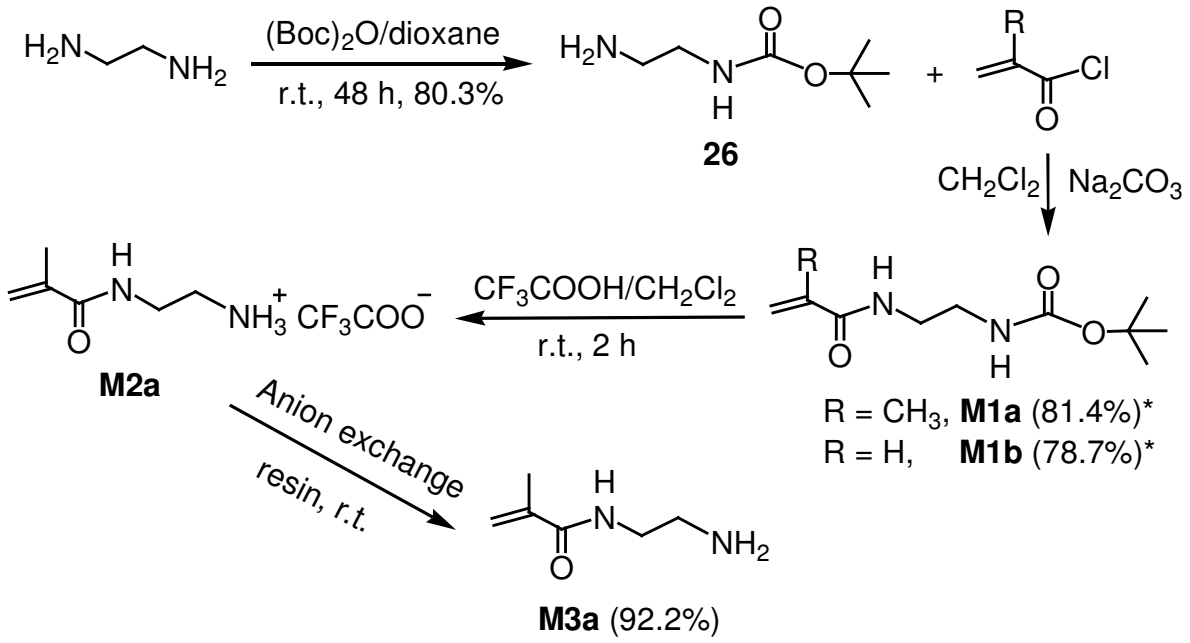
The reaction of acryloyl and methacryloyl chlorides or esters with diamines, dialcohols or aminoalcohols is a versatile method for preparing functional acryl- and methacryl

derivatives.[186-188] In our laboratory, we have focused on the use of acryloyl and methacryloyl chlorides reacting with diamines, dialcohols or aminoalcohols as the synthesis of monomers.

3.1.1.1. Synthesis of acryl- and methacrylamides with a free and a protected amino group (M1a, M1b, M2a and M3a)*

N-(2-aminoethyl)-2-methylacrylamide **(M3a)** was synthesized in three steps as shown in Scheme 3.1.1. *tert*-Butyl [2-(methacryloylamino)ethyl]carbamate **(M1a)** and [2-(methacryloylamino)ethyl] ammonium trifluoroacetate **(M2a)** were obtained as intermediates during the synthesis of **M3a**.

Since the reaction of acryloyl chloride with excess 1,2-diaminoethane gave a very poor yield[189] due to the preferential formation of bis (*N,N'*-acryloyl)-1,2-diaminoethane, the key step in the synthesis of **M3a** is the protection of one of the amino groups of 1,2-diaminoethane by a readily removable group, e.g., the *tert*-butyloxycarbonyl (Boc) group.[190, 191]



Scheme 3.1.1. Synthesis of *N*-(2-aminoethyl)-2-methylacrylamide **(M3a)**.

The known *tert*-butyl (2-aminoethyl)carbamate (**26**) was reacted with methacryloyl chloride in the presence of anhydrous sodium carbonate to yield **M1a** as a white solid. Acryloyl chloride instead of methacryloyl chloride under the same basic conditions yielded *tert*-butyl [2-(acryloylamino)ethyl]carbamate **(M1b)**. The Boc group in **M1a** is readily removed by

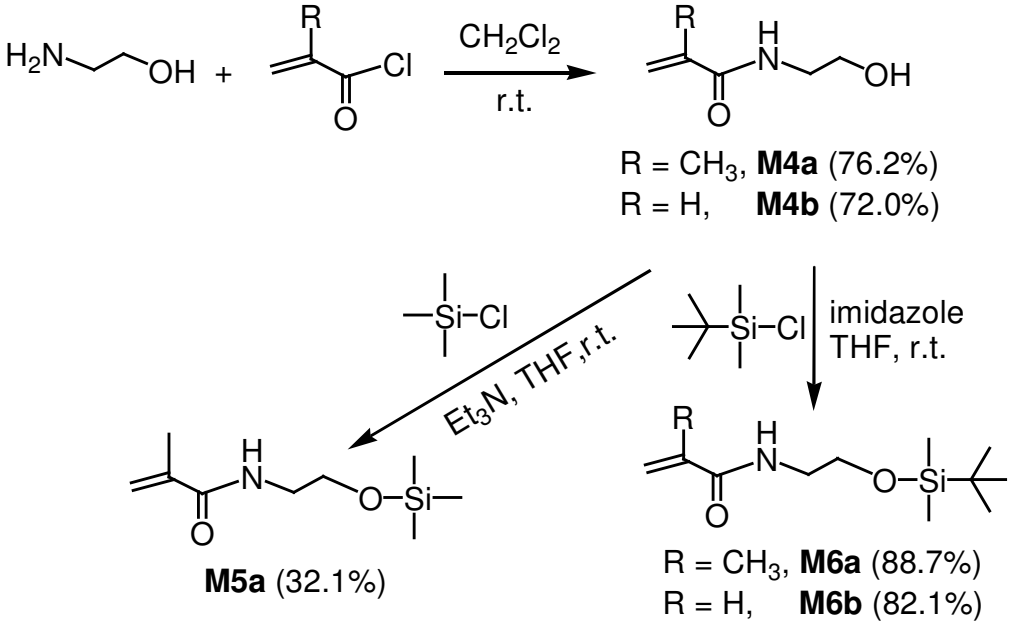
* **a)** always corresponds to the methacryl derivatives, i.e. R = CH_3; and **b)** to acryl derivatives, i.e. R = H, throughout this thesis.

CF_3COOH/CH_2Cl_2 to give the ammonium salt **M2a** in quantitative yield. Conversion into the free base **M3a** (92.2%) by treatment with anion exchange resin gave the product as colorless oil. We found this procedure advantageous in comparison to the known use of EtOH/NaOEt[192] or Et_3N[193] to afford the free amines from ammonium salts.

M3a is rather reactive and tends to auto-polymerize even at room temperature, thus requiring storage at low temperature (-25°C) in an argon atmosphere. The ammonium salts, such as **M2a**, stabilize the methacrylamide. Therefore, CF_3COOH was used as a protective group for the amine.

3.1.1.2. Synthesis of acryl- and methacrylamides with a hydroxyl group (M4a, M4b) and their protected analogues (M5a, M6a, M6b)

Preparation of **M4a** and **M4b** according to literature procedures[194] afforded the desired monomers in high yields.



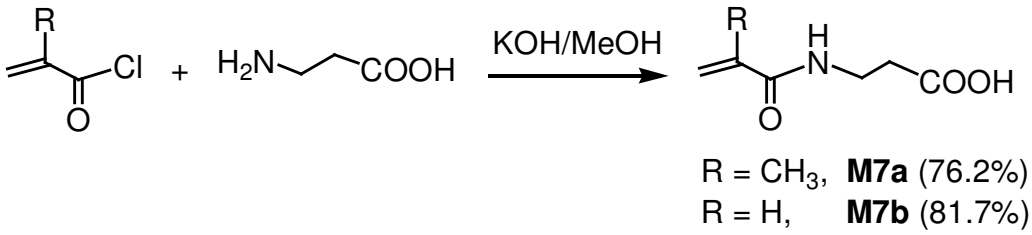
Scheme 3.1.2. Synthesis of **M5a**, **M6a** and **M6b**.

The hydroxyl group of monomer **M4a** was protected with trimethylsilyl (TMS) chloride under basic conditions to yield *N*-{2-[(trimethylsilyl)oxy]ethyl}-2-methylacrylamide (**M5a**) in low yield (32.1%, Scheme 3.1.2). We believe this is due to facile hydrolysis when exposed to air. This implies that the trimethylsilyl group is not a suitable protective group for the further envisaged application.

Considering the low yield of **M5a**, a more stable protective group,[167, 180] namely the *tert*-butyldimethylsilyl (TBDMS), was chosen as protective group of the hydroxyl function in **M4a** and **M4b**. Ratifyingly, these reactions proceeded to give the desired monomers **M6a** and **M6b** in much higher yield (88.7% and 82.1%, respectively). To our knowledge monomer **M6a** is a new compound, no reference reported about this compound for reactant and product.

3.1.1.3. Synthesis of acryl- and methacrylamides with a carboxyl group (M7a, M7b) and their protected analogues (M8a, M9a, M9b, M10a, M11a)

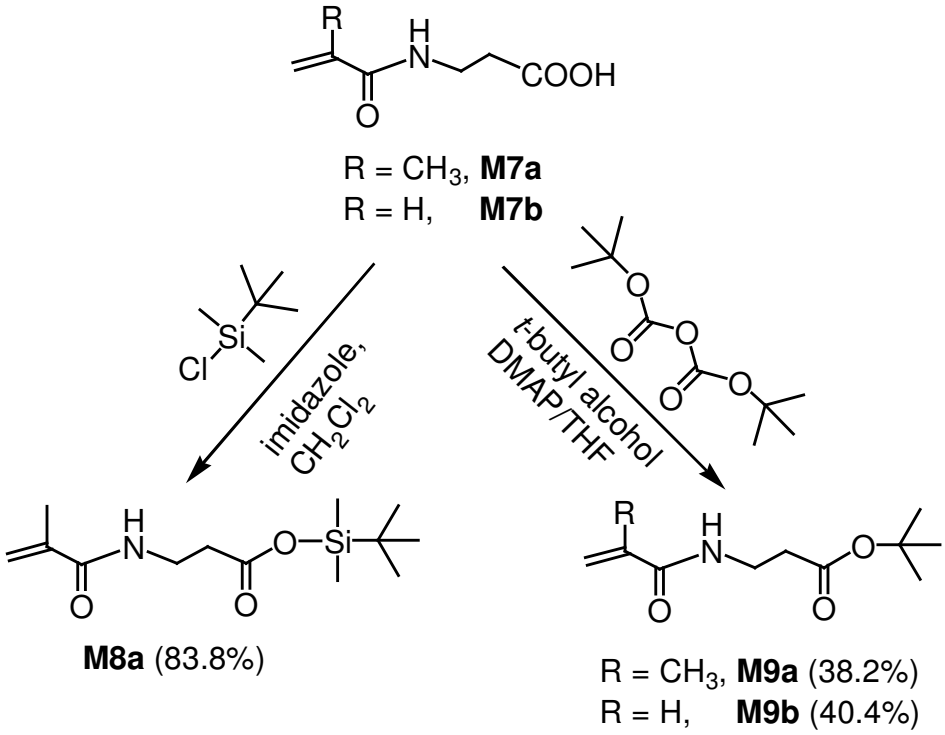
Preparation of the monomers *N*-methacryloyl-*β*-alanine (**M7a**) and *N*-acryloyl-*β*-alanine (**M7b**) by Contino's procedure[195] gave the desired monomers in high yield (Scheme 3.1.3). These products are quite stable and can be stored at room temperature for a long time.



Scheme 3.1.3. Synthesis of *N*-methacryloyl-*β*-alanine (**M7a**) and *N*-acryloyl-*β*-alanine (**M7b**).

- **Chemically removable protecting groups**

TBDMS was selected for the protection of the carboxyl group of **M7a**.[196] However, silyl esters are not as stable as the corresponding silyl ethers. Accordingly some precipitate was observed in the liquid monomer after three weeks, which presumably resulted from the hydrolysis of the silyl ester. The reaction product of the hydrolysis bearing a free carboxylic acid group accelerates the further ester cleavage. Thus the reaction product **M8a** must be stored in dry atmosphere and at low temperature. This instability might account for the fact that this compound was, heretofore, unknown.



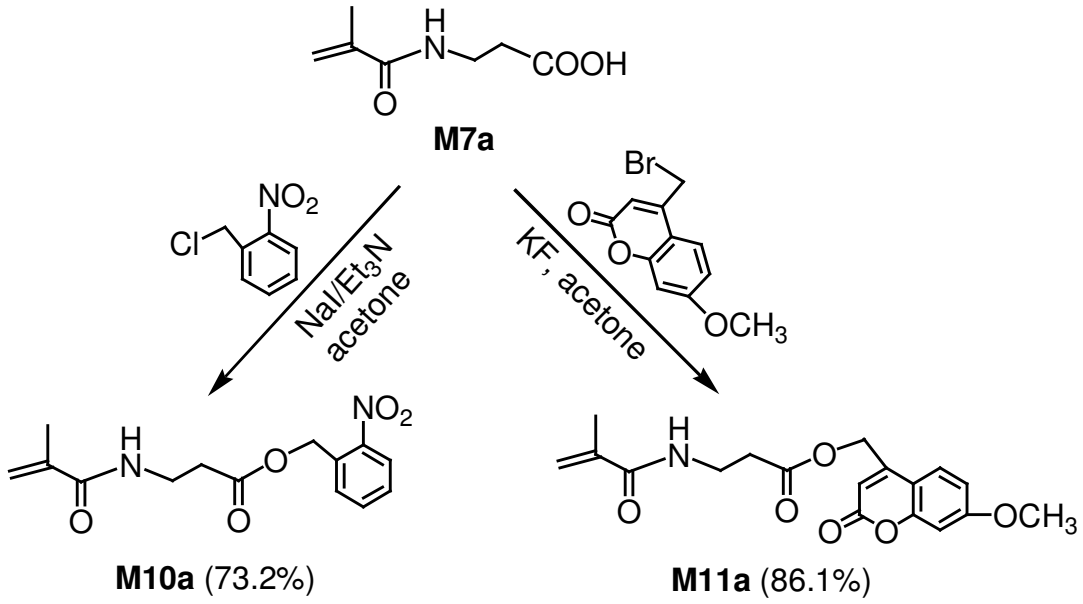
Scheme 3.1.4. Synthesis of *tert*-butyl(dimethyl)silyl *N*-methacryloyl-*β*-alaninate (**M8a**) and *tert*-butyl *N*-methacryloyl-*β*-alaninate (**M9a**) and *tert*-butyl *N*-acryloyl-*β*-alaninate (**M9b**).

tert-Butyl esters can be selectively hydrolyzed in the presence of primary alkyl esters,[197, 198] and are available via the 4-dimethylaminopyridine (DMAP) catalyzed reaction of commercially available dicarbonates and carboxylic acids.[199] Thus, the protection of carboxylic acid **M7a** was carried out with di-*tert*-butyldicarbonate ($(Boc)_2O$) in the presence of a catalytic amount of DMAP at room temperature to give ester *tert*-butyl *N*-methacryloyl-*β*-alaninate (**M9a**) in reasonable yield (31.4%, Scheme 3.1.4). While the yield increased slightly (38.2%) at elevated temperature (50°C), it was still much lower than the reported yield.[199] We believe this is due to the much larger scale of our reactions. *tert*-Butyl *N*-acryloyl-*β*-alaninate (**M9b**) was similarly synthesized from compound **M7b**, with a higher yield of 40.4% at 60°C. Compounds **M9a** and **M9b** were previously unknown.

- **Photoremovable protective group**

In addition to the previously described, chemically labile protective groups, we were also interested in a photochemical option.[167, 200] Photoremovable protecting groups are sensitive to light but relatively stable to most chemical reagents.[200, 201] The *o*-nitrobenzyl (OBN) group, a

common photoremovable group, and the (7-methoxy-2-oxo-2*H*-chromen-4-yl)methyl (MCM) group,[202, 203] a quite active photolabile group, were selected for such a purpose.



Scheme 3.1.5. Synthesis of 2-nitrobenzyl *N*-methacryloyl-*β*-alaninate (**M10a**) and (7-methoxy-2-oxo-2*H*-chromen-4-yl)methyl *N*-methacryloyl-*β*-alaninate (**M11a**).

As shown in Scheme 3.1.5, the protection of the carboxylic acid **M7a** was realized by esterification of the carboxylic acid with 1-(chloromethyl)-2-nitrobenzene in the presence of triethyl amine and sodium iodide in dried acetone. The ester 2-nitrobenzyl *N*-methacryloyl-*β*-alaninate (**M10a**) was obtained as a yellow solid in 73.2% yield after flash chromatography. Sodium iodide worked as a catalyst to yield 1-(iodomethyl)-2-nitrobenzene, which as intermediate readily reacts with carboxylic acid.

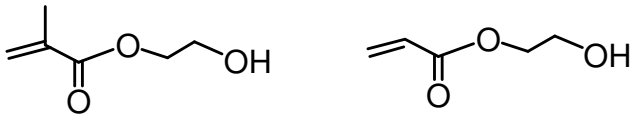
The MCM carboxylic acid ester was synthesized via reaction of 4-(bromomethyl)-7-methoxycumarin and compound **M7a**,[204] giving the desired (7-methoxy-2-oxo-2*H*-chromen-4-yl)methyl *N*-methacryloyl-*β*-alaninate (**M11a**) as a yellow solid in high yield (86.1%). To the best of our knowledge monomers **M10a** and **M11a** are new compounds.

3.1.1.4. Synthesis of acryl- and methacrylates with a protected hydroxyl group (M13a, M13b, M14a, M14b)

2-Hydroxyethyl 2-methylacrylate (**M12a**) is a monomer with numerous applications and a large number of publications and patents have been devoted to this product and its

corresponding polymer.[2, 205] This popularity is due to several factors, such as the primary alcohol function, which allows substitution reactions in the monomer and the corresponding polymer. It is a major component in materials for contact lenses and drug delivery compounds. The monomer, which is soluble in water, forms a hydrogel, which has applications in biomedical fields.[2, 205]

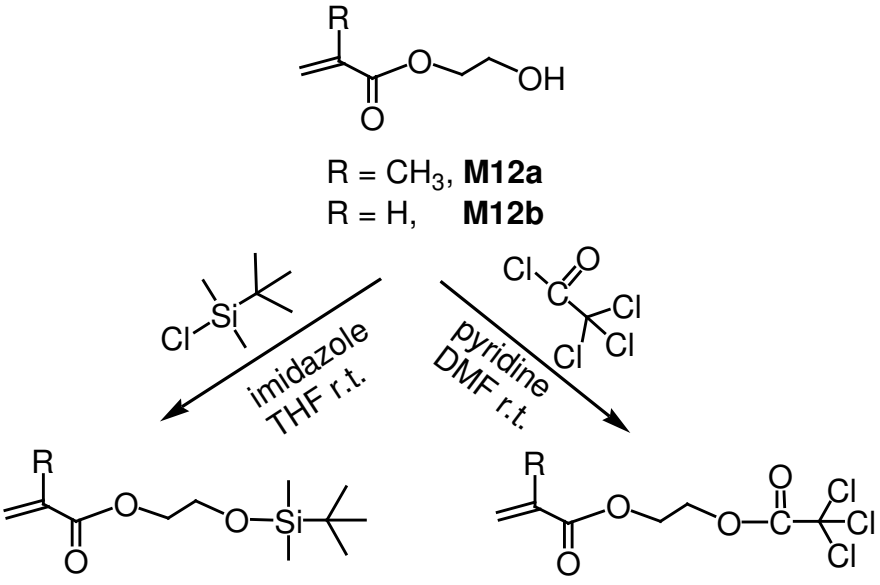
This monomer, as well as the analogous acrylate 2-hydroxyethyl acrylate (**M12b**), both of which are commercially available, was selected for further investigation of controlled radical polymerization.



M12a **M12b**

- **Protection of the hydroxyl group**

The TBDMS moiety was again used to protect the hydroxyl group in **M12a** and **M12b**. The synthesis of the monomers 2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl 2-methylacrylate (**M13a**) and 2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl acrylate (**M13b**) are shown in Scheme 3.1.6.



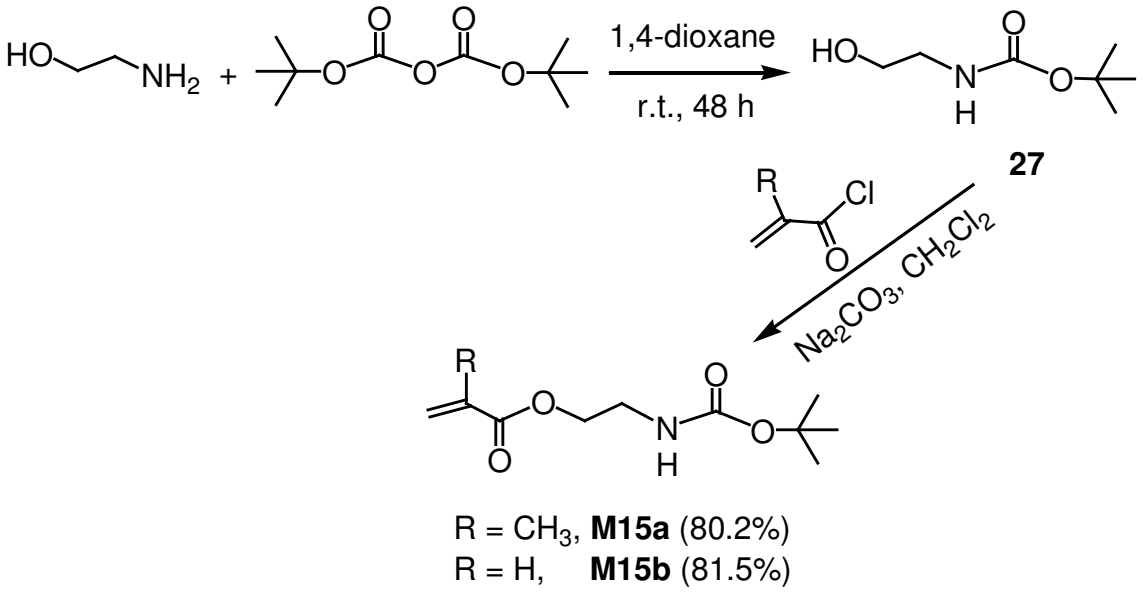
Scheme 3.1.6. Protection of compounds **M12a** and **M12b** using TBDMS and TCA as protective groups.

In order to try different cleavage conditions, 2,2,2-trichloroacetyl (TCA) was used as protective group for the protection of the hydroxyl group in **M12a** and **M12b**. The electron withdrawing trichloromethyl group allows facile hydrolysis with NH_3 in MeOH.[206, 207] Protection of **M12a** and **M12b** with trichloroacetyl chloride under basic conditions gave 2-[(2,2,2-trichloroacetyl)oxy]ethyl 2-methylacrylate (**M14a**) and 2-[(2,2,2-trichloroacetyl)oxy] ethyl acrylate (**M14b**) as pale yellow oils in good yield.

Despite the large number of publications, which include compounds **M12a** and **M12b**, the protected derivatives **M13b** and **M14b** have not been described yet.

3.1.1.5. Synthesis of acryl- and methacrylates with a protected amino group (M15a, M15b)

Since amino groups are more nucleophilic than hydroxyl groups, the active amine group must be protected when using 2-aminoethanol as a reactant in the synthesis of esters. Use of the Boc group for protection of the amine, the protected *tert*-butyl (2-hydroxyethyl)carbamate (**27**) was obtained as colorless oil in 90.2% yield (Scheme 3.1.7).



Scheme 3.1.7. Synthesis of 2-[(*tert*-butyloxycarbonyl)amino]ethyl 2-methylacrylate (**M15a**) and 2-[(*tert*-butyloxycarbonyl)amino]ethyl acrylate (**M15b**).

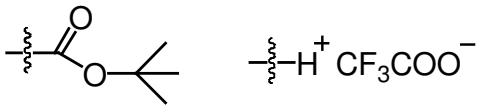
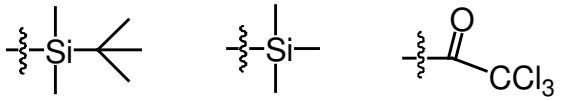
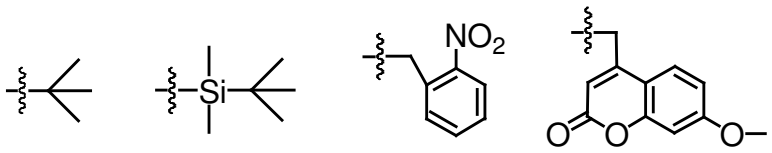
Compound **27** was then reacted with 2-methacryloyl chloride or acryloyl chloride under strong basic conditions to produce 2-[(*tert*-butyloxycarbonyl)amino]ethyl 2-methylacrylate (**M15a**) (80.2%) or 2-[(*tert*-butyloxycarbonyl)amino]ethyl acrylate **(M15b)** (81.5%) as white solids.

In comparison to the synthesis of **M1a**, **M1b** and **M4a**, (meth)acryloyl chloride reacts with amines (2 h) much faster than with alcohols (48 h).

3.1.2. Deprotection of the protected functional groups

The different protective groups are summarized in Table 3.1.1.

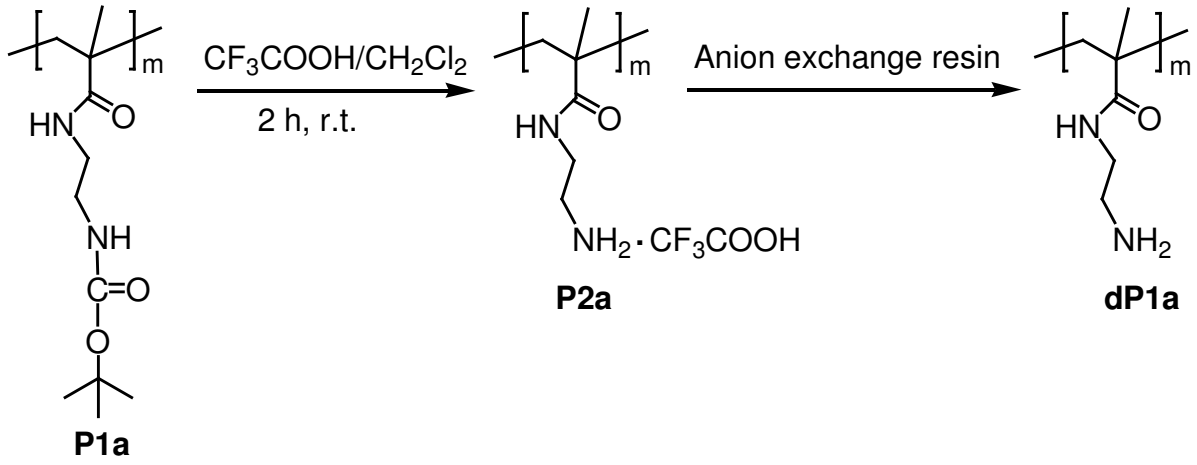
Table 3.1.1. Protective groups used for the synthesized functional monomers.

FG (functional group)	**PG** (protective group)
-NH_2	 **Boc**
-OH	 **TBDMS** **TMS** **TCA**
-COOH	 **TB** **TBDMS** **ONB** **MCM**

3.1.2.1. Deprotection of the protected amino groups

As was reported the Boc group is the most useful protective group for amines, and it is readily cleaved by acidic hydrolysis.[190, 191] Deprotection of the Boc group in polymer **P1a** was accomplished by treatment with 1:1(v/v) solution of CF_3COOH/CH_2Cl_2 to give the ammonium salts with trifluoroacetic acid in quantitative yield, which can be transformed into **dP1a**[¢] after treating with anion exchange resin, the same way as the deprotection of the Boc group from monomer **M1a** to monomer **M3a**.

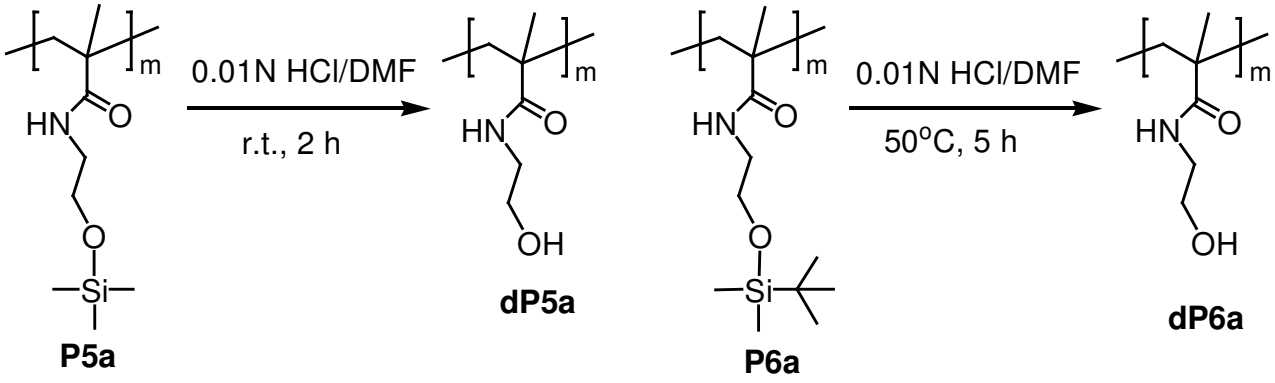
[¢] **P1a)** corresponds to the polymer of **M1a**
dP1a) to the polymer after the deprotection of **P1a**



Scheme 3.1.8. Deprotection of the Boc group in the polymer **P1a**.

3.1.2.2. Deprotection of the protected hydroxyl groups

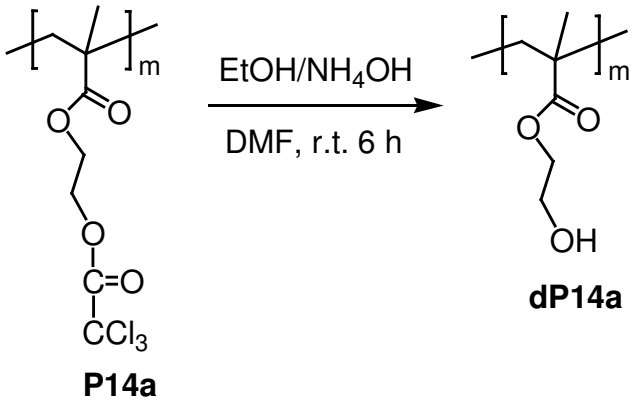
The TMS group is less stable than the TBDMS under acidic and basic conditions.[167] Though the same concentrations of acid were used to cleave TMS and TBDMS protective groups, the TMS group was removed at a lower temperature in a shorter amount of time (see Scheme 3.1.9).



Scheme 3.1.9. Deprotection of the TMS group in polymer **P5a** and the TBDMS group in polymer **P6a**.

The purification of the deprotected polymers was easily accomplished by precipitation in ether. The TBDMS protected monomers were used in our investigation of different radical polymerization reactions due to the observed stability.

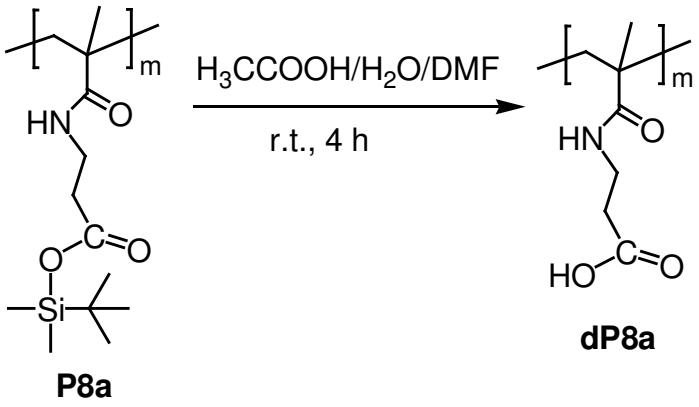
Use of 2,2,2-trichloroacetyl (TCA) as a protecting group allowed for chemoselective deprotection of the terminal ester under basic condition (Scheme 3.1.10). Again, the polymer was easily purified by precipitation from ether.



Scheme 3.1.10. Deprotection of the TCA group in polymer **P14a**.

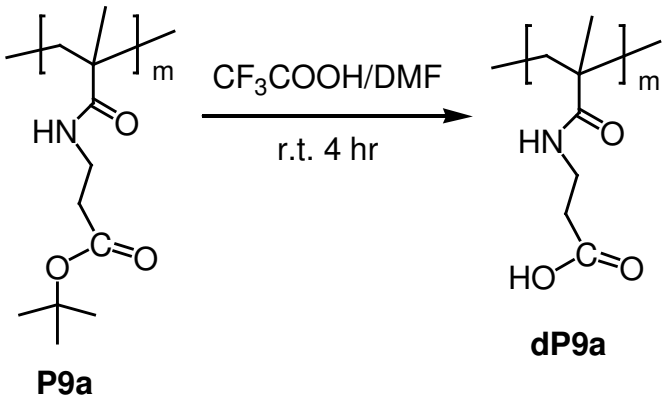
3.1.2.3. Deprotection of the protected carboxyl groups

Homopolymer **P8a** was deprotected by the use of acetic acid to give the free carboxyl acid product **dP8a**,[196] which was, again, easily purified by precipitation (Scheme 3.1.11).



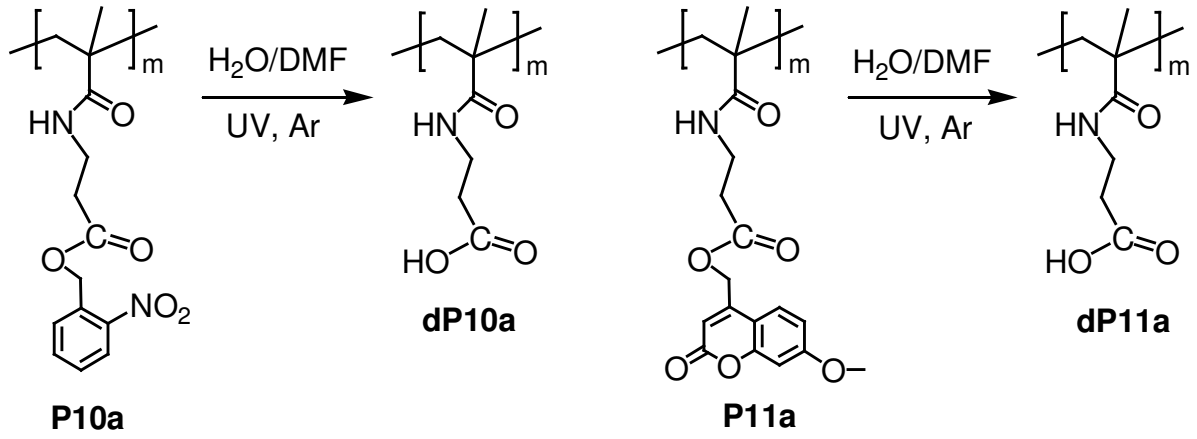
Scheme 3.1.11. Deprotection of the TBDMS group in polymer **P8a**.

t-Butyl esters are stable to mild basic hydrolysis conditions. They are cleaved, however, by moderate acidic hydrolysis, with the release of the *tert*-butylene.[208] In our case *t*-butyl groups in polymer **P9a** were cleaved by CF_3COOH (Scheme 3.1.12). The deprotection product **dP9a** was purified by precipitation from ether.



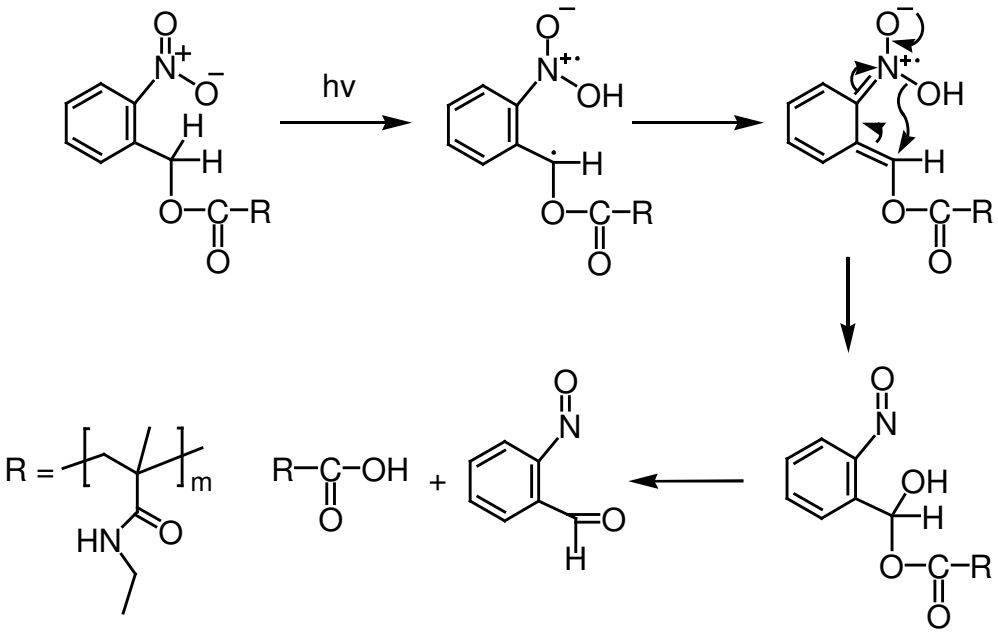
Scheme 3.1.12. Deprotection of the *t*-butyl group in polymer **P9a**.

Apart from the acidic cleavage of protective ester groups, the photolytic cleavage of protecting ester groups has been investigated. As shown in Scheme 3.1.13, the ONB and MCM protective group in homopolymers **P10a** and **P11a** can be removed by photolysis to yield homopolymers **dP10a** and **dP11a**. The products were purified by precipitation from diethyl ether.



Scheme 3.1.13. Deprotection of ONB in homopolymer **P10a** and deprotection of MCM in homopolymer **P11a**.

The photolysis of the *o*-nitrobenzyl group in polymer **P10a** was carried out by irradiation at a wavelength of 320 nm using a high-pressure mercury lamp (I = 100 W). As shown in Scheme 3.1.14, the irradiation of *o*-nitrobenzyl ester results in the formation of *o*-nitrobenzaldehyde and a carboxylic acid.[200]



Scheme 3.1.14. Mechanism of the deprotection of ONB.

Monitoring the absorption by UV spectroscopy one can see that a complete removal of the ONB groups occurs in six hours (Figure 3.1.2). After one hour the deprotection of the ONB group in **P10a** proceeded only in 22% yield.

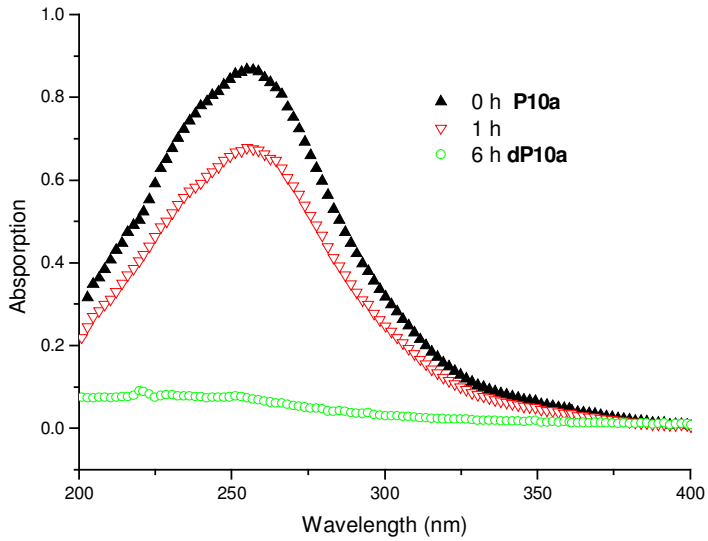


Figure 3.1.2. The UV absorption of ONB in the homopolymer **P10a** and **dP10a**.

Because 6 hours is too long for a photoreaction, the more photolabile group **MCM** was used for the protection of carboxyl groups.[203, 209] Previous investigations have shown the presence of two intense absorption maxima near λ = 325 nm and λ = 217 nm. **P11a** showed the same characteristics (Figure 3.1.3).

For our investigation the longer wavelength 320 nm was selected and a mixture of water and DMF was used as the solvent. Irradiation of the MCM protected polymer **P11a** gave the desired polymer **dP11a** within 60 min (Figure 3.1.3).

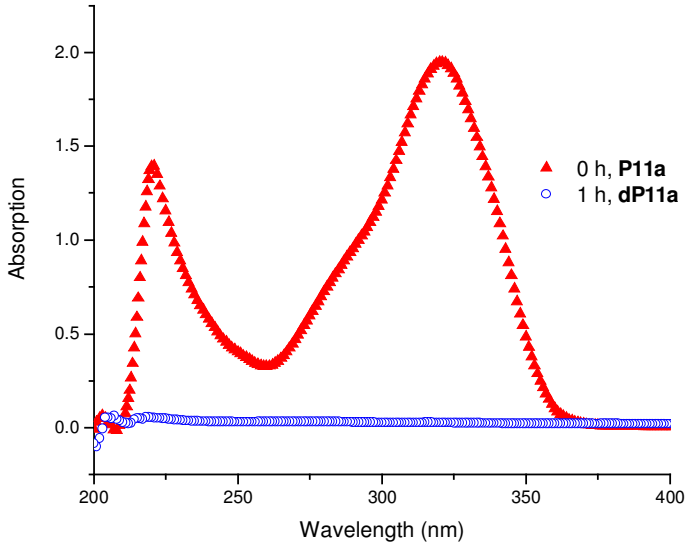


Figure 3.1.3. The UV absorption of MCM in the homopolymer **P11a** and **dP11a**.

Comparing of Figure 3.1.2 and Figure 3.1.3, which show the UV-spectra of the polymers after one hour irradiation reveals that the ONB group was only removed in about 22% yield, while the MCM group was completely split off. The result verifies that MCM is more photolabile than ONB. The mechanism of the photolytic cleavage of MCM is outlined in Schade's report.[203]

3.2. Synthesis of initiators for Nitroxide-Mediated Polymerization

Unimolecular initiators have been introduced as an attractive advantage over producing the two relevant radicals in a stoichiometric ratio. They offer the possibility of having a shelf-stable initiator available that can readily initiate polymerization. More importantly, unimolecular initiators afford the means to study the key radical processes that occur during polymerization, as they can be considered as the first unit of the polymer. This mimetic feature allows the thermodynamic, kinetic, and other properties of LFRP to be examined with the

added simplicity of working with small molecules.[12, 210, 211] This is the primary reason for which unimolecular initiators have been drawn a great deal of attention.

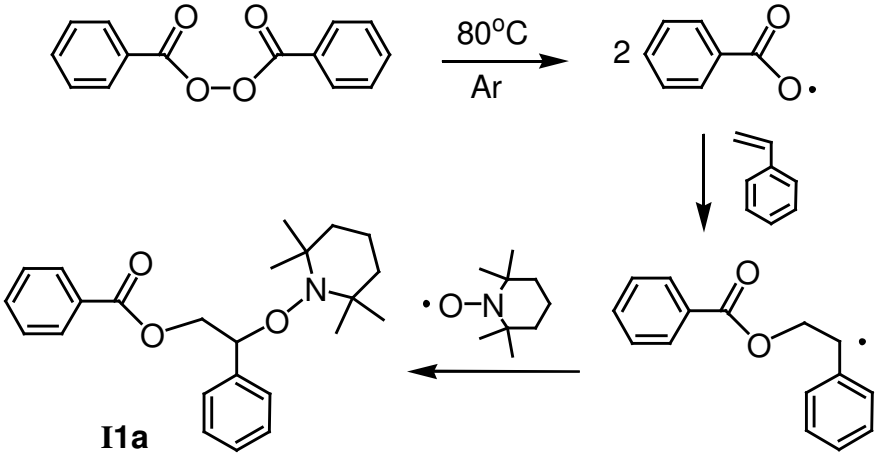
3.2.1. Synthesis of the TEMPO derivatives (I1a, I1b, I1c)

As reported earlier, Georges[10] first showed that low polydispersity (PD) polymers could be prepared under certain reaction condition by free-radical polymerization. This result was based on the use of stable nitroxide radicals, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), as thermally labile "capping" agents for the growing polymer chain, which in turn leads to a control of the polymerization.

TEMPO had been used to trap the initiating radical species in a variety of free-radical polymerizations[212] and to reversibly terminate a growing polymer chain, producing low molecular weight oligomers.[213] Subsequently, Hawker reported the use of a modified TEMPO-based initiator that allows an accurate molecular weight control and the polymer formation with well-defined end groups.[54] On the basis of Hawker's report, different TEMPO derivatives were used in this work for the synthesis of modified free-radical initiators.

- **2-Phenyl-2-[(2,2,6,6-tetramethylpiperidin-1-yl)oxy]ethyl benzoate (I1a)**

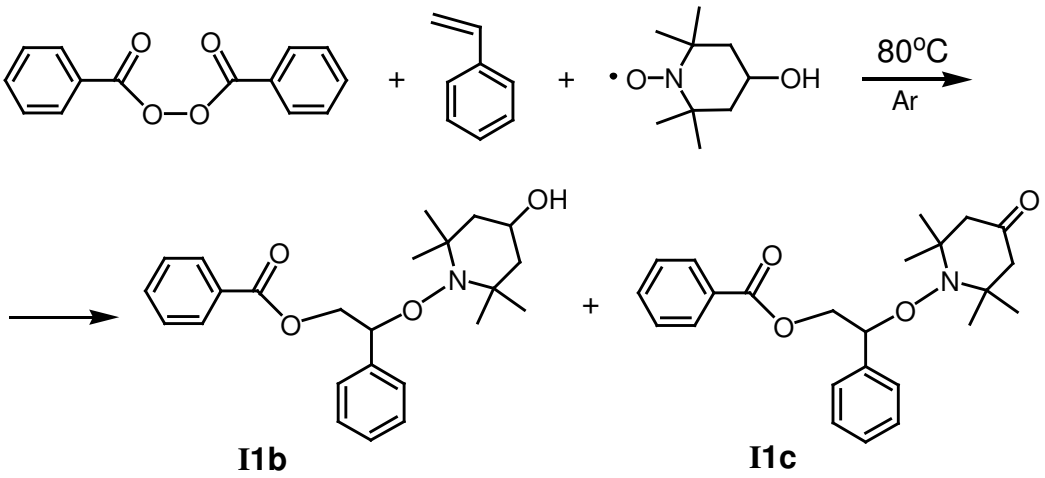
This modified free-radical initiator was received as a mixture with more than 7 other compounds by heating of dibenzoyl peroxide (BPO) and TEMPO in an excess of styrene (Scheme 3.2.1). The desired monoadduct **I1a** could be separated by repeated flash chromatography as a yellow solid. Despite several attempts, the yields were always lower than that reported.[54]



Scheme 3.2.1. Synthesis of alkoxyamine **I1a**.

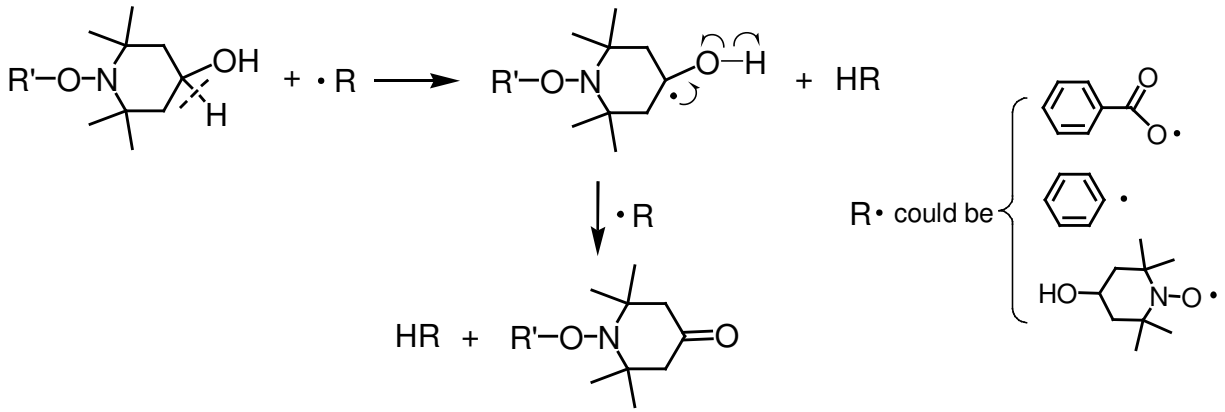
- **2-[(4-Hydroxy-2,2,6,6-tetramethylpiperidin-1-yl)oxy]-2-phenylethyl benzoate (I1b) and 2-phenyl-2-[(2,2,6,6-tetramethyl-4-oxopiperidin-1-yl) oxy]ethyl benzoate (I1c)**

The same reaction was performed, using 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (HTEMPO) (Scheme 3.2.2). The expected product **I1b** was obtained, however, only, in lower yield (8.6 %).



Scheme 3.2.2. Synthesis of TEMPO-based initiator **I1b** and **I1c**.

Another modified TEMPO initiator **I1c** was isolated by flash chromatography from the same reaction mixture and obtained even in higher yield (18.5%). The formation of this compound that occurred in the reaction includes an oxidation of the secondary alcohol. However, it is unknown whether the alcohol oxidation or the radical trapping is running first. A possible mechanism is given in Scheme 3.2.3. Both initiators formed and isolated were identified by ^{1}H-NMR spectra.



Scheme 3.2.3. Mechanism of the oxidation of **I1b** to give ketone **I1c**.

The main difference between the spectra of **I1a** and **I1b** arises from the proton of H_n, which appears as a multiplet (Figure 3.2.1). Compound **I1c**, despite of the presence of a keto group in the piperidine ring, has a similar spectrum.

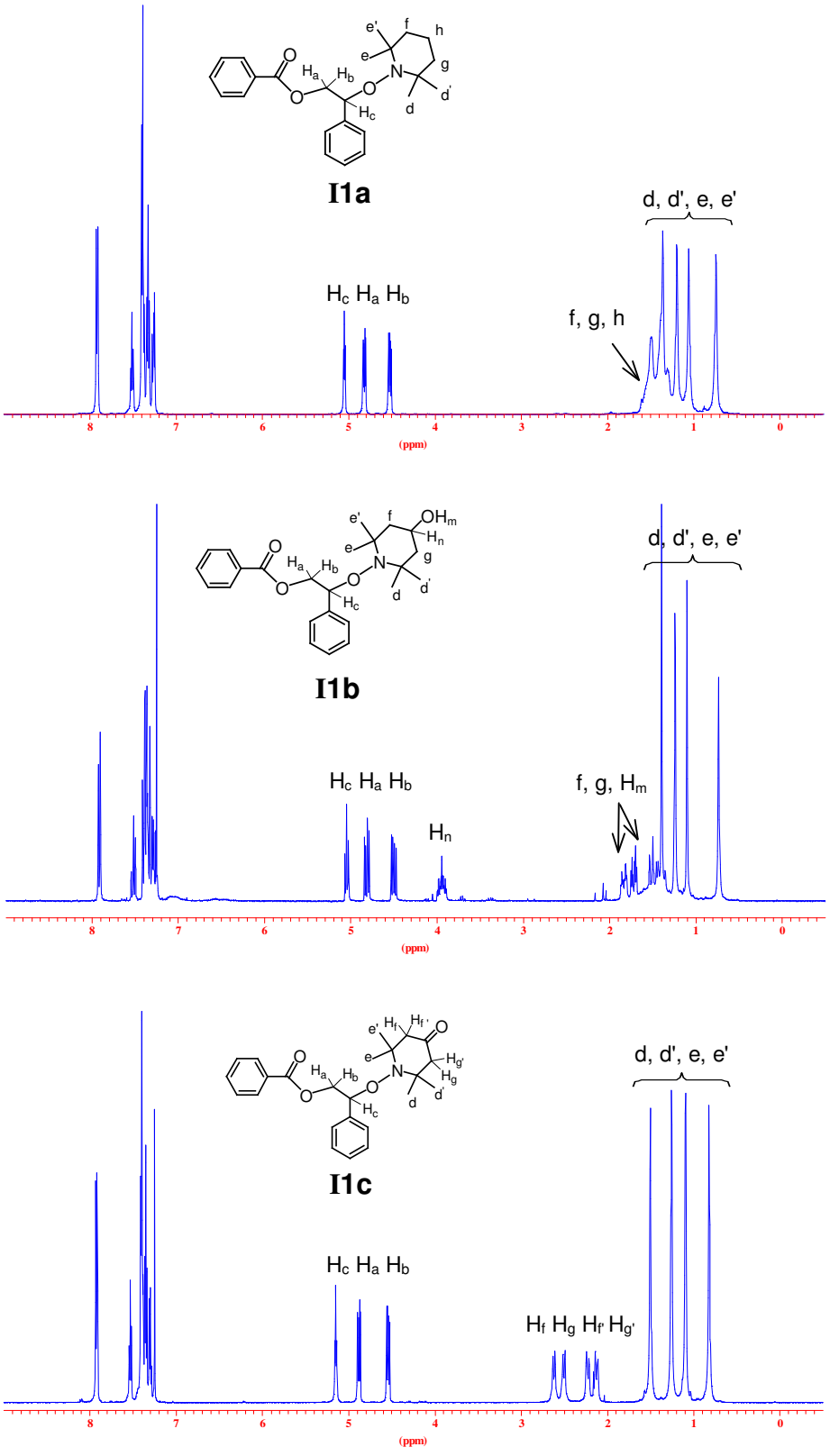


Figure 3.2.1. ^{1}H spectra of initiator **I1a**, **I1b** and **I1c** in $CDCl_3$.

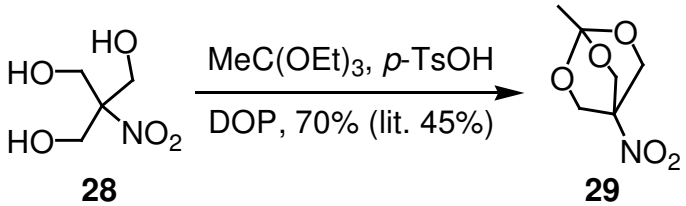
The ^{13}C-NMR spectra of **I1a**, **I1b** and **I1c** show the expected signals for the carbon atoms (e.g. a doublet peak due to the CH-OH group in **I1b** which appears at 63.10 ppm and a peak at 208.02 ppm, typical evidence of existence of the keto group in **I1c**).
The mass spectra of the three compounds are as expected, which the molecular ion of each compound clearly visible. Chemically, **I1b** has a higher up than **I1c**.

3.2.2. Synthesis of Hawker Adduct II (I2a)[#]

The concept of intramolecular H-bonding is very important for the design of new alkoxyamines, since bond homolysis should occur under mild conditions. Hawker et al. reported that a monohydroxyl-substituted derivative of **24** accelerated the polymerization of styrene.[63] It was, thus, decided to maximize the potential of this intramolecular H-bonding effect by examining the initiating ability of the tris-hydroxy derivative **I2a**. Studer[215] and Hawker[64] contributed to the synthesis of alkoxyamine **I2a** as an unimolecular initiator.
The product **I2a** was available in a multistep reaction. The cheap and readily available 2-(hydroxymethyl)-2-nitropropane-1,3-diol (**28**) was protected by 1,1,1-triethoxyethane as its ortho ester **29**, following reductive coupling with 2-methyl-propionaldehyde in the presence of zinc/NH_4Cl to give the nitrone **31**. After reaction with phenylmagnesium chloride, oxidation of the hydroxylamine affords the protected nitroxide radical **33**, which then was coupled with styrene by Jacobsen's catalyst to yield the protected alkoxyamine **36**. Deprotection of either **33** or **36** was accomplished under mild conditions with *p*-toluenesulfonic acid (*p*-TsOH) to give the corresponding tris(hydroxymethyl) derivatives **I2a** and **37** almost in quantitative yields.

- **Synthesis of 1-methyl-4-nitro-2,6,7-trioxabicyclo[2.2.2]octane (29)**

Yokoyama *et al*[216] reported the synthesis of 1-methyl-4-nitro-2,6,7-trioxabicyclo[2.2.2]octane **29** from 2-(hydroxymethyl)-2-nitropropane-1,3-diol **28** by an acid-catalyzed transesterification (Scheme 3.2.4). The reaction was performed without problem even on a larger scale. The yield reached was 70% (lit. 45 %).



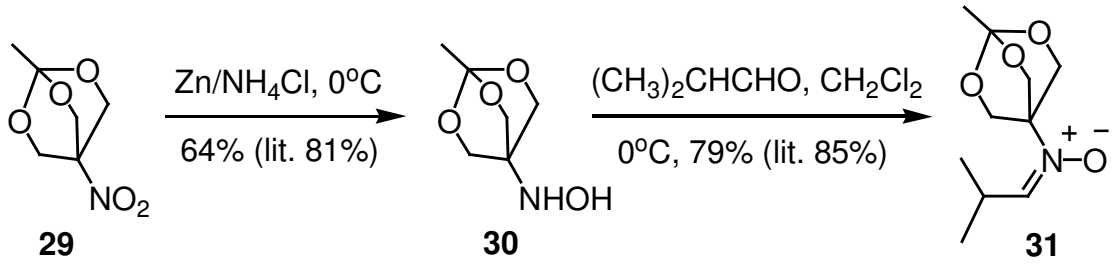
28 **29**

Scheme 3.2.4. Synthesis of 1-methyl-4-nitro-2,6,7-trioxabicyclo[2.2.2]octane (**29**).

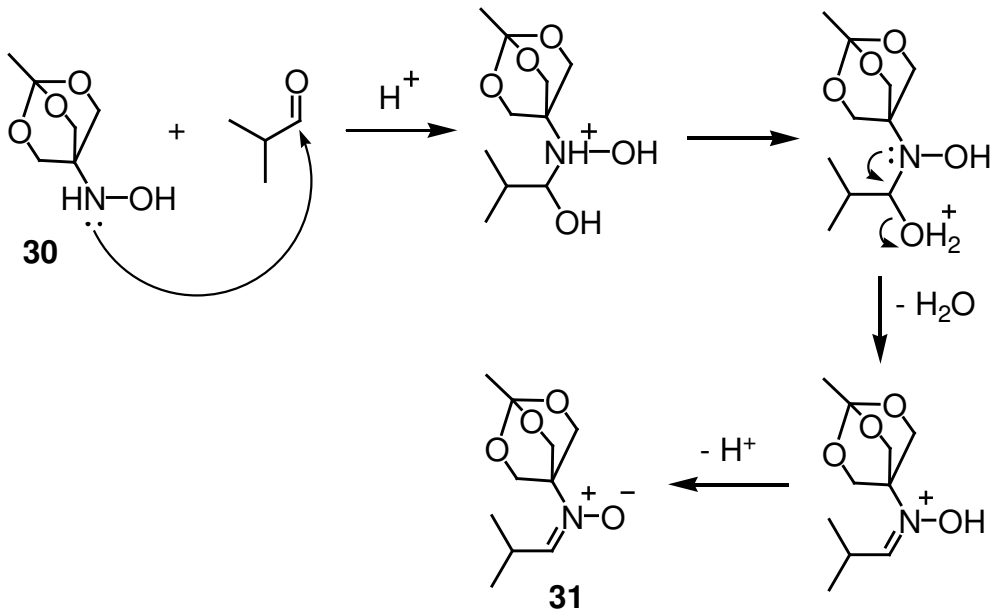
[#] Cooperation with Tilo Krause[214] (TU Dresden)

- **Synthesis of (*E*)-(2-methylpropylidene)(1-methyl-2,6,7-trioxabicyclo[2.2.2]oct-4-yl) azane oxide (31)**

(*E*)-(2-methylpropylidene)(1-methyl-2,6,7-trioxabicyclo[2.2.2]oct-4-yl)azane oxide **31** was synthesized from the nitro compound **29** in two steps (shown in Scheme 3.2.5). First, compound **29** was reduced by Zn to give *N*-(1-methyl-2,6,7-trioxabicyclo[2.2.2] oct-4-yl)hydroxylamine **30**. Subsequently, the hydroxylamine **30** was converted into nitrone **31** via treatment with 2-methyl-propionaldehyde. The mechanism of this addition is shown in Scheme 3.2.6.



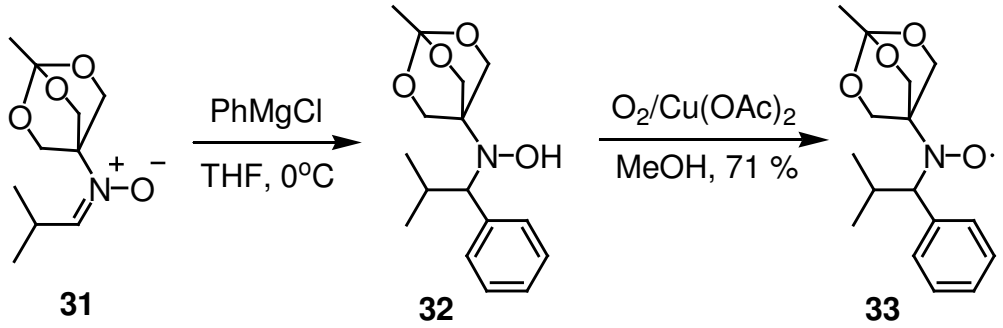
Scheme 3.2.5. Synthesis of (*E*)-(2-methylpropylidene)(1-methyl-2,6,7-trioxabicyclo[2.2.2] oct-4-yl)azane oxide (**31**).



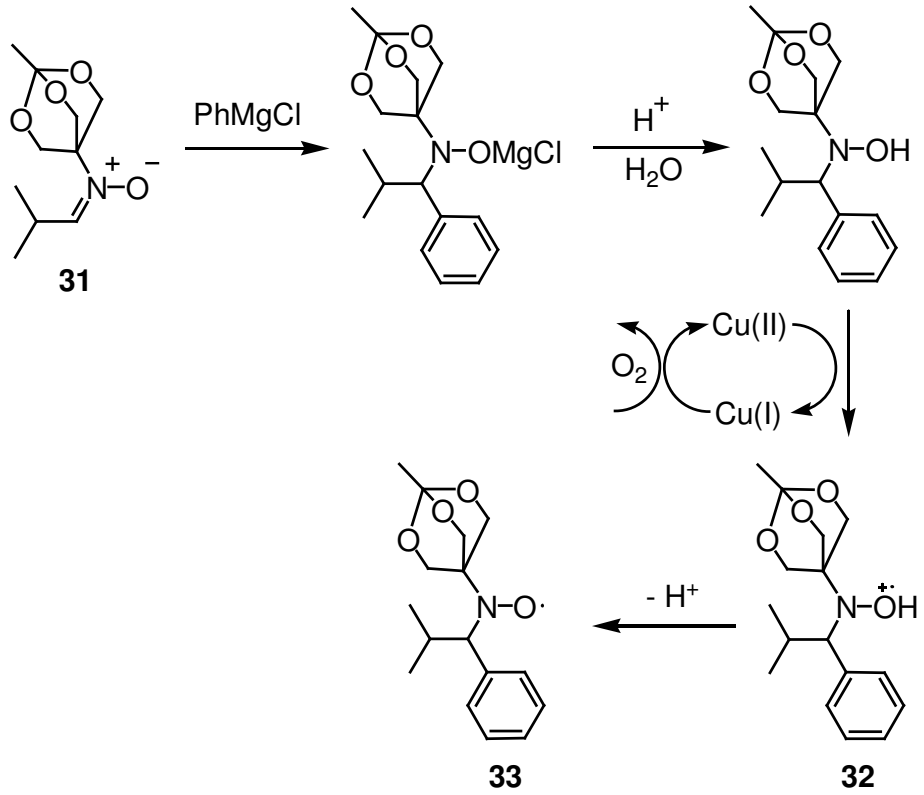
Scheme 3.2.6. Mechanism of the addition of 2-methyl-propionaldehyde to yield nitrone **31**.

- **Synthesis of *N*-(2-methyl-1-phenylpropyl)-*N*-(1-methyl-2,6,7-trioxabicyclo-[2.2.2] oct-4-yl)-amine-*N*-oxyl (33)**

The arylation of nitrone **31** with phenylmagnesium chloride under argon in dry condition resulted in the substituted hydroxylamine **32**, *N*-(2-methyl-1-phenylpropyl)-*N*-(1-methyl-2,6,7-trioxabicyclo[2.2.2]oct-4-yl)hydroxylamine, as an intermediate (Scheme 3.2.7). Hydroxylamine **32** was oxidized without further purification by means of $Cu(OAc)_2$ and air to yield *N*-(2-methyl-1-phenylpropyl)-*N*-(1-methyl-2,6,7-trioxabicyclo-[2.2.2]oct-4-yl)-amine-*N*-oxyl **33** in 71% yield. The yield is not indicated in the literature.[64, 215, 217] While the presence of the α-hydrogen decreases the stability of the nitroxide when compared to TEMPO, all of the above mentioned compounds were stable to storage at room temperature and could be purified by normal procedures, such as flash chromatography.[63] The mechanism of the synthesis of nitroxide **33** is shown in Scheme 3.2.8.



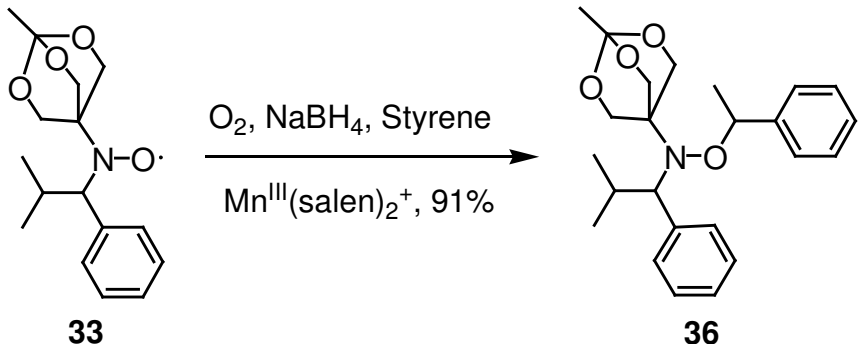
Scheme 3.2.7. Synthesis of *N*-(2-methyl-1-phenylpropyl)-*N*-(1-methyl-2,6,7-trioxabicyclo-[2.2.2]oct-4-yl)-amine-*N*-oxyl **33**.



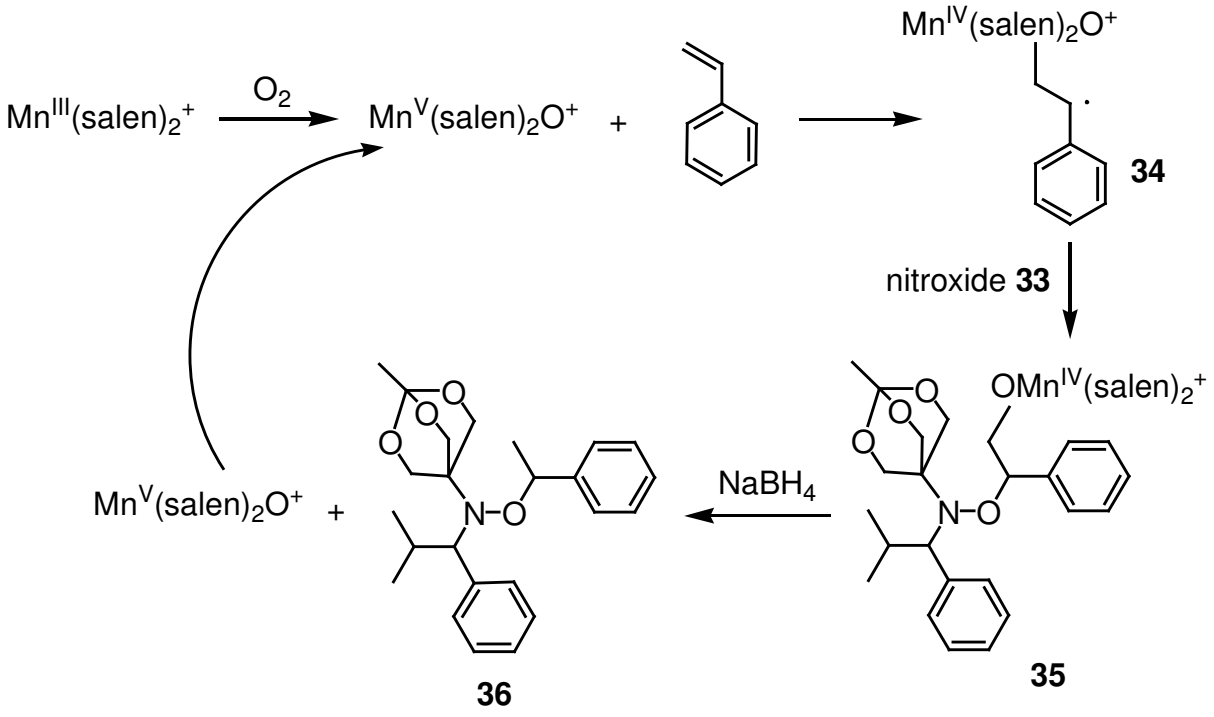
Scheme 3.2.8. Mechanism of the oxidation of nitrone **31** to nitroxide radical **33**.

- **Synthesis of *N*-(2-methyl-1-phenylpropyl)-*N*-(1-methyl-2,6,7-trioxabicyclo[2.2.2] oct-4-yl)-*O*-(1-phenylethyl)hydroxylamine (36)**

According to Hawker's publication,[45] the protected alkoxyamine **36** was synthesized by the use of Jacobsen's catalyst (0.05 equivalent) with an optimized yield of 91% (Scheme 3.2.9).



Scheme 3.2.9. Synthesis of the protected alkoxyamine **36**.



Scheme 3.2.10. Mechanism of the formation of alkoxyamine **36** from nitroxide **33** by use of Jacobsen's reagent.[12, 13]

Jacobsen's reagent, a manganese-(III) salen complex is often used as a catalyst for the addition of nitroxides to the double bond of olefinic derivatives, such as styrene, leading to alkoxyamines suitable for an application as initiators in living free radical procedures.[218, 219] A possible mechanism involves the direct attack of styrene at an *oxo*-manganese center to generate a radical intermediate **34**, which is trapped by nitroxide **33** to give the addition product **35**, followed by reduction with sodium borohydride ($NaBH_4$) to the desired alkoxyamine **36** (Scheme 3.2.10).[217]

There are two chiral carbons in the structure of alkoxyamine **36**, and two diastereomers (1:1) were isolated by flash chromatography. The ^{1}H-NMR spectrum of the mixture of diastereoisomer is shown in Figure 3.2.2.

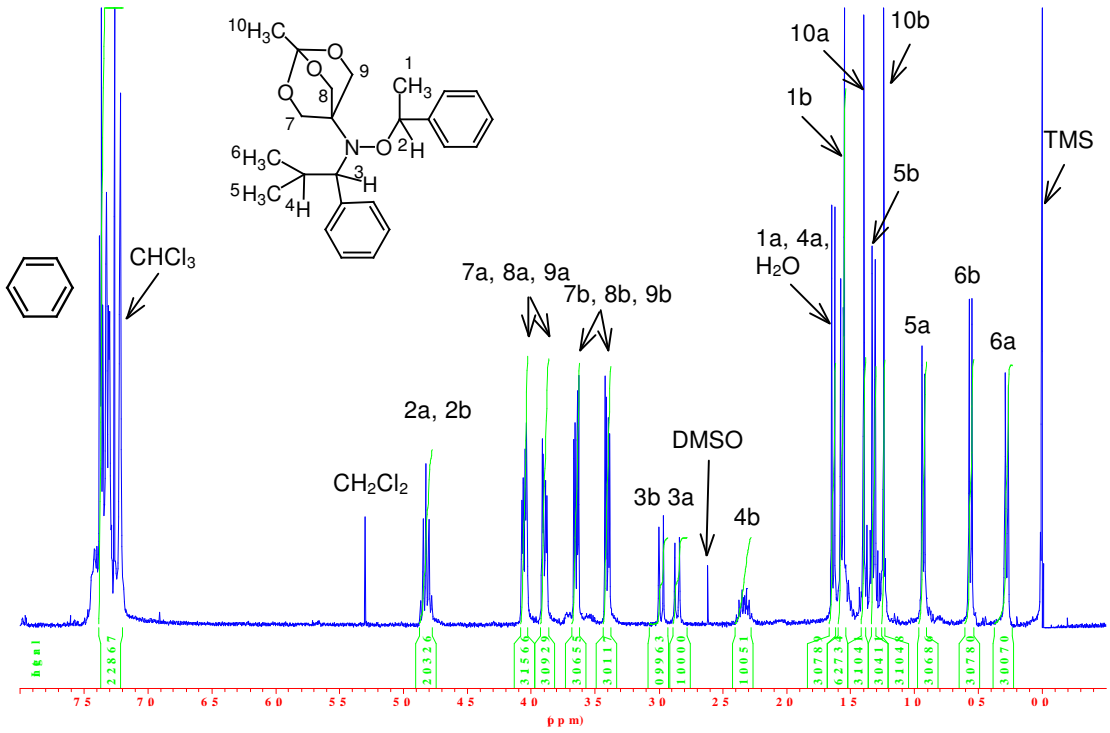
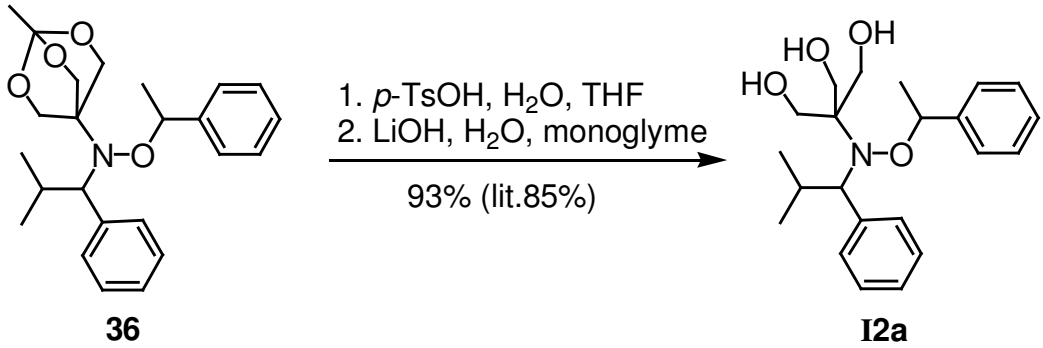


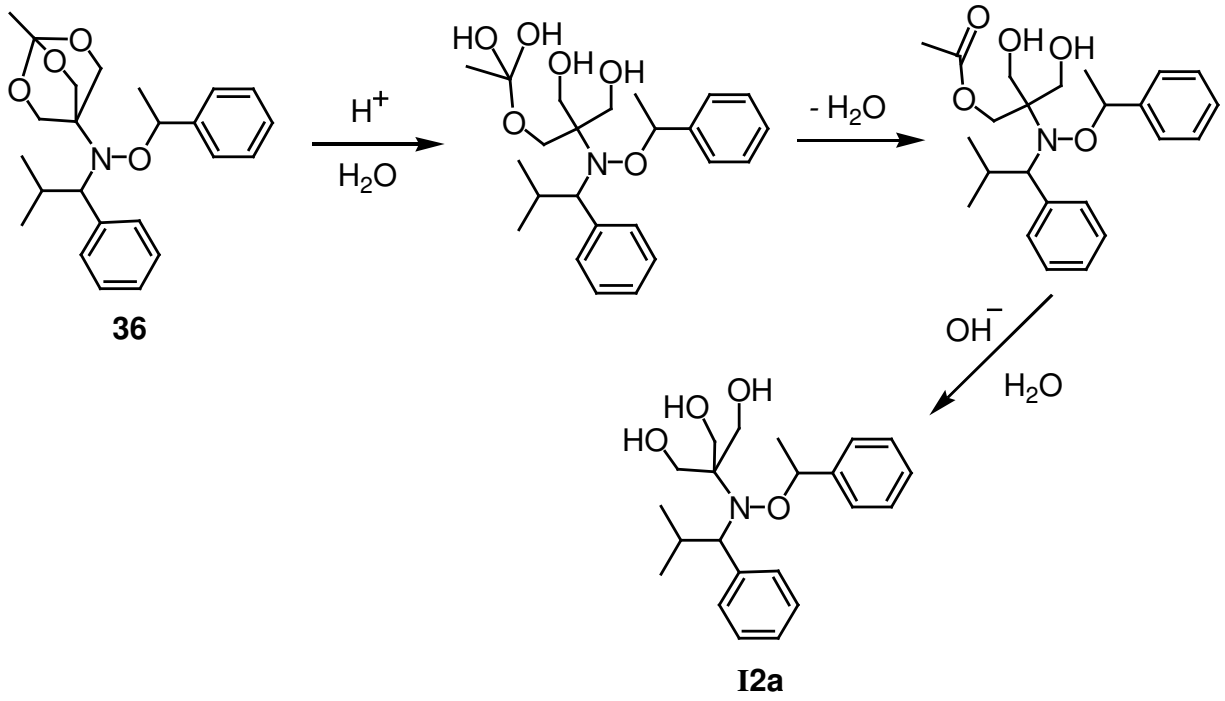
Figure 3.2.2. ^{1}H-NMR spectra of alkoxyamine **36** (a: diastereomer I, b: diastereomer II).

- **Synthesis of 2-(hydroxymethyl)-2-[(2-methyl-1-phenylpropyl)(1-phenylethoxy) amino]propane-1,3-diol (I2a) and free nitroxide *N*-(2-Methyl-1-phenylpropyl)-*N*-[2,2,2-tris(hydroxymethyl)methane] -amine-*N*-oxyl (37)**

In the first step, the alkoxyamine **36** was partially cleaved by *p*-TsOH to yield the corresponding diol ester, which was subsequently treated with LiOH to give rise to the desired initiator **I2a** in high yield (Scheme 3.2.11). The mechanism of the deprotection of alkoxyamine **36** to initiator **I2a** is shown in Scheme 3.2.12



Scheme 3.2.11. Deprotection of alkoxyamine **36** to afford initiator **I2a**.



Scheme 3.2.12. Mechanism of the deprotection of alkoxyamine **36** to obtain initiator **I2a**.

Because a mixture of two diastereomers of alkoxyamine **36** was employed for the deprotection, also two diastereomers of initiator **I2a** were obtained. For each diastereomer the ability to initiate polymerization is nearly the same (see next chapter of controlled radical polymerization). The diastereomeric mixture of initiator **I2a** was directly used for polymerization. ^{1}H-NMR spectra of the two diastereomers (A, B) of initiator **I2a** are shown in Figure 3.2.3.

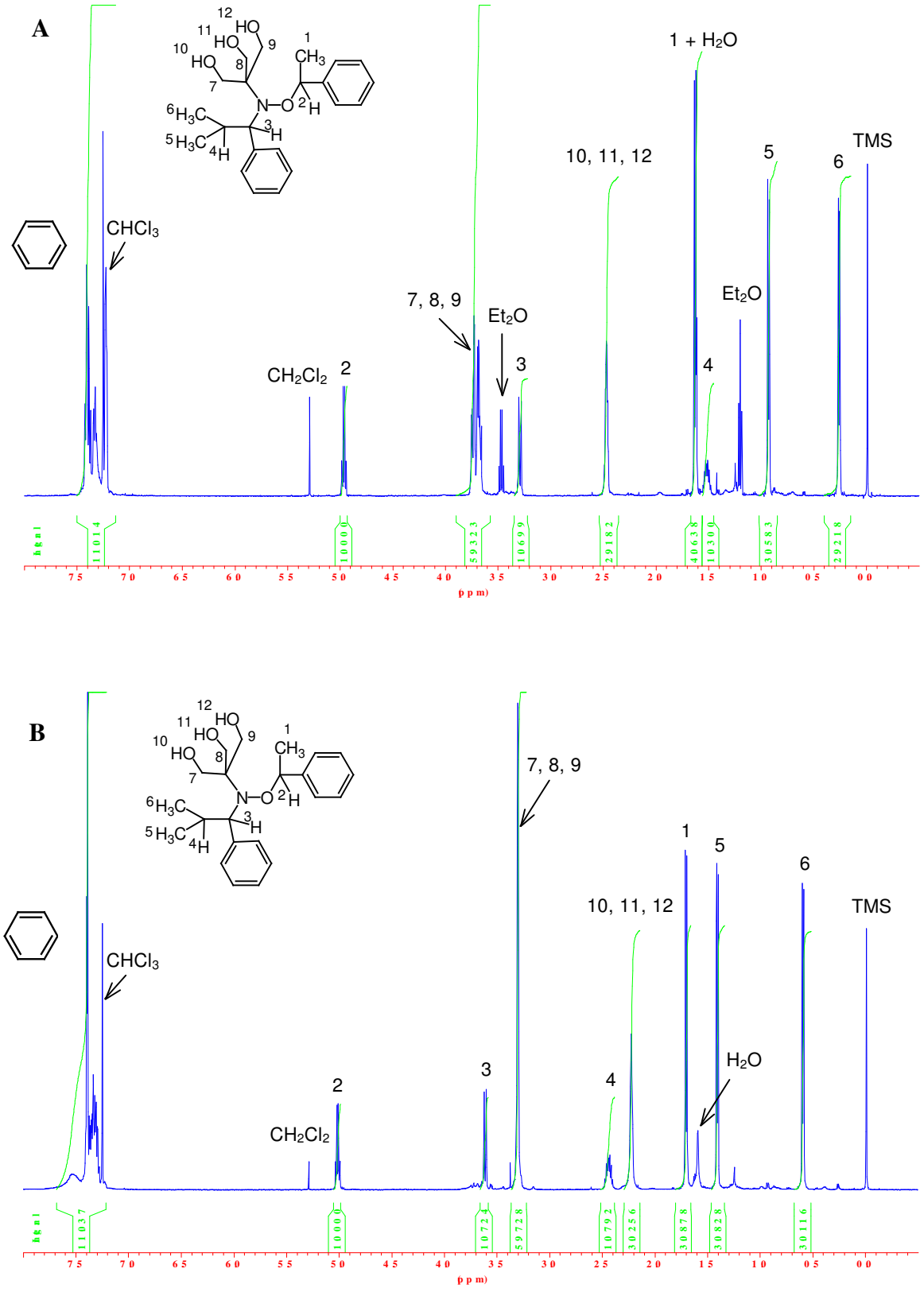
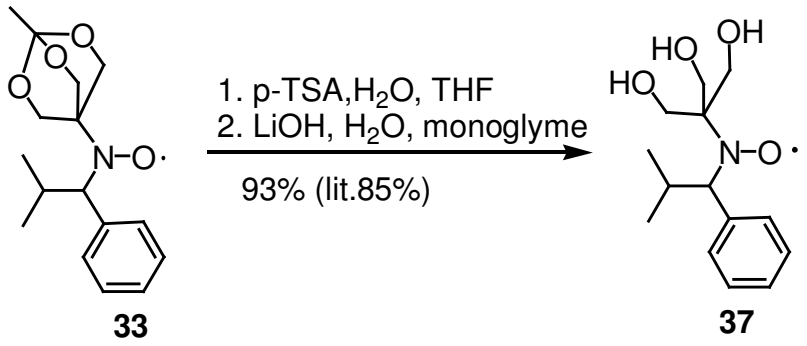


Figure 3.2.3. ^{1}H spectra of initiator **I2a** (A. diastereomer I; B. diastereomer II).

The deprotection of nitroxide **33** processed the same as for alkoxyamine **36** to give the free hydroxyl nitroxide **37** from the protected precursor (Scheme 3.2.13). The free nitroxide **37** is rather unstable and must be stored under N_2 at -15°C.

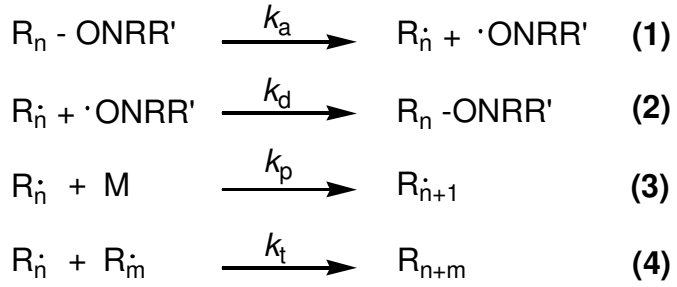


Scheme 3.2.13. Deprotection of protected nitroxide **35** to the free hydroxyl nitroxide **37**.

3.2.3. Kinetics of the C-O bond homolysis of the initiators

3.2.3.1. General background of the alkoxyamine C-O bond homolysis

Alkoxyamines have a relatively unstable C-O bond.[220-222] Upon heating, this bond readily cleaves homolytically to yield a carbon-centered radical species and a nitroxide, which is the prerequisite for alkoxyamines to act as radical initiators. Directly related to this homolysis is the process of trapping a carbon-centered radical with a nitroxide. It generally occurs via coupling of the two radical species to yield the alkoxyamine as a covalent adduct. In this way, the alkoxyamine homolysis can be considered as a reversible process. This reversible homolytic C-O bond cleavage of alkoxyamines has led to the development of a living radical polymerization technique.[10, 223] In terms of a nitroxide-mediated living-radical polymerization, this so-called reversible activation of the dormant alkoxyamines needs to meet two basic requirements. First, the alkoxyamine C-O bond homolysis needs to produce a carbon-centered radical that is able to undergo addition to a monomer (propagation). Second, the nitroxide needs to be a persistent compound, which is only capable of trapping the carbon-centered radical via coupling. (Note that in this thesis the alkoxyamine, carbon-centered radical and nitroxide may be represented by the symbols R_n-ONRR′, R_n•, and R′RNO•, respectively. Scheme 3.2.14).



Scheme 3.2.14. Schematic mechanism of dissociation of the nitroxide-capped alkoxyamine.

The rate constants of the cleavage of the dormant chains into radicals (activation) k_a and of the reverse coupling (deactivation) k_d are crucial for the living radical polymerization process (Scheme 3.2.14). The rate constant k_a and k_d influence the degree of livingness and control of the resulting polymer and the monomer conversion rate.[58] A kinetic treatment[56] with chain-length independent rate constants has shown that the polymerization time decreases with increasing equilibrium constant $K = k_a/k_d$ of the reversible dissociation of the nitroxide-capped polymer alkoxyamine. That is, the polymerization time decreases with increasing k_a. In successful living radical polymerizations, k_a has to be sufficiently large to ensure reasonable conversion times and low polydispersities. However, k_a must not exceed a critical value for which the controlling persistent radical effect breaks down, and the optimum values of k_a and k_d depend on the propagation constant (k_p) and the termination rate constant (k_t). As a rule, $k_a \geq 10^{-3}$ s^{-1} is desirable, and it would be helpful if k_a could be reasonably predicted based on alkoxyamine and nitroxide structure to avoid unnecessary synthetic and experimental work.
In the absence of monomer, i.e. $n = 0$, there is no propagation and only reactions (**1**), (**2**), and (**4**) should occur. The dissociation rate constant k_a of alkoxyamines can be measured conveniently by quantitative CW-ESR spectroscopy from the appearance of the nitroxide radical using a specified scavenger for the transient radicals.[224, 225]

3.2.3.2. Previous results of the kinetics of C-O bond homolysis of alkoxyamines

In 2000, Skene[226] investigated the rate constants for the trapping of various carbon-centered radicals by nitroxides including TEMPO and reported that substitution at the 4-position of TEMPO does not play an important role for the stabilization or destabilization of the radical. Furthermore, the substituent at C-4, despite its bulkiness, is too far away to influence the kinetics, which suggest that the decay rate constants of **I1a**, **I1b** and **I1c** are more or less equal. In 2001, Fischer[58] reviewed that the TEMPO based alkoxyamines give lower dissociation rate

constants k_a (c.a. 1.6×10^{-3} s^{-1}) and lower equilibrium constants K (2.1×10^{-11} M) in comparison with other developed alkoxyamines. These data explain the deficiencies of simple TEMPO systems, such as higher polymerization temperature (125-145°C) and long reaction time. In connection with this work there was an interest in the kinetic behavior of the adduct II (**I2a**, **I2b**).

The decay kinetics of the alkoxyamines **I2a**[227] and **I2b**[225] have previously been analyzed by Marque *et al*. They reported activation parameters and rate constants for the dissociation of the C-O bond in initiator **I2a** (T = 115-124°C, $k_a = 5.6\times10^{-3}$ s^{-1}, E_a = 125.1 kJ·mol^{-1} in *tert*-butyl benzene) and initiator **I2b** (T = 60-131°C, $k_a = 3.3\times10^{-3}$ s^{-1}, E_a = 129.6 kJ·mol^{-1} in *tert*-butyl benzene).

3.2.3.3. Electron Spin Resonance-spectroscopic (ESR) measurement of initiator I2a[#]

Because most polymerizations of the synthesized monomers should be carried out with initiator **I2a** in polar solvents such as DMF, we, therefore, investigated the dissociation rate constant of the C-O bond homolysis in initiator **I2a** in the same solvent. For comparison, this was carried out in *tert*-butyl benzene as well.

Initiator **I2a** was dissolved in the inert solvent *tert*-butylbenzene (1×10^{-3} mol/l). The sample solution was degassed with nitrogen for 20 minutes before ESR measurement. Afterwards, the sample solution was heated up slowly and a trace of the signal of nitroxide **37** was performed. The signals (appearance) of the nitroxide **37** correctly reflect the decomposition of initiator **I2a**. At room temperature, there is no signal of any radical. The signal of nitroxide **37** only appeared at a temperature of 60°C, i.e. the C-O bond in initiator **I2a** starts to homolyze at 60°C. A representative ESR spectrum of nitroxide **37** is shown in Figure 3.2.4.

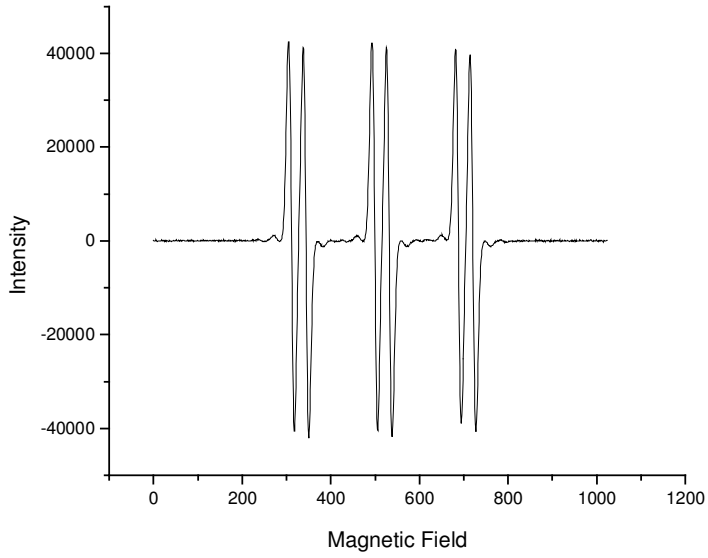
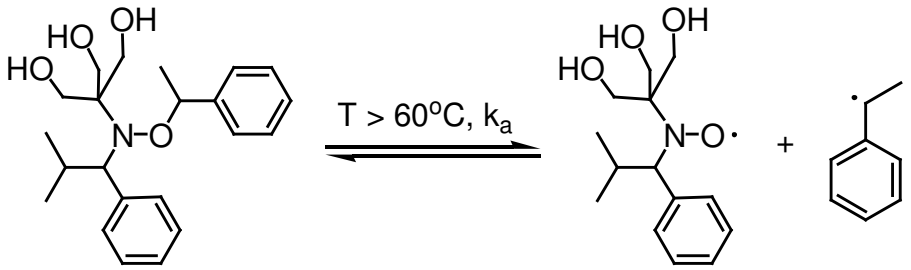


Figure 3.2.4. ESR spectrum of nitroxide **37** at 120°C (1×10^{-3} mol/l in *tert*-butylbenzene).

As shown in Scheme 3.2.15, the decomposition of alkoxyamine **I2a** formed two radicals, the persistent nitroxide **37** and the more reactive 1-phenylethyl radical **38**. To avoid a recombination of nitroxide **37** and 1-phenylethyl radical **38**, which would affect the signal of nitroxide **37**, it is necessary to trap the reactive species by a scavenger.



Scheme 3.2.15. Thermal decomposition of the initiator **I2a**.

Oxygen has been reported as a suitable trapping agent for ESR-studies at higher temperature (T > 110°C).[225] Therefore, air was used as a scavenger for initiator **I2a** in the following experiments. The experimental cleavage rate constants k_a were calculated using Equation **3.2.1** of the growing ESR nitroxide signal.[225, 227]

$$\ln\left(\frac{[NO\cdot]_{eq} - [NO\cdot]_t}{[NO\cdot]_{eq}}\right) = -k_a t \qquad \text{Equation } \mathbf{3.2.1}$$

3.2.3.4. Effect of solvents on the C-O bond homolysis of initiator I2a

The ESR experiments with initiator **I2a** were carried out in *tert*-butylbenzene, DMF and 1,2,4-trichlorobenzene using initiator concentrations of 1×10^{-3} mol/l. All the sample solutions were measured directly without degassing with nitrogen. The nitroxide concentrations were determined by double integration of the ESR signals.

- **Kinetics of C-O bond homolysis of the initiator I2a in *tert*-butylbenzene**

The transient concentration of **37** from the thermal homolysis of **I2a** was measured in the inert solvent *tert*-butylbenzene at 85°C and 120°C. The build-up of the nitroxide radical could be monitored until the expected concentration for 100% conversion was approached (Figure 3.2.5). As can be seen in Scheme 3.2.15, the decomposition of initiator **I2a** is much faster at 120°C than at 85°C. The concentration of nitroxide **37** reached the maximum after 2000 s at 120°C and after 10000 s at 85°C.

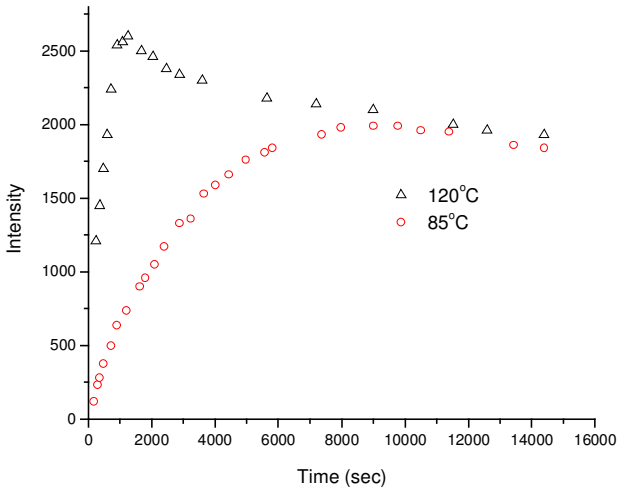


Figure 3.2.5. Time dependence of nitroxide **37** concentrations during thermolysis of initiator **I2a** in *tert*-butylbenzene at 120°C and 85°C.

The concentration-time dependence of the homolysis of **I2a** follows the expected first-order kinetics (Figure 3.2.6), and the thermal decay rate constants k_a of the initiator **I2a** were extracted from plots corresponding to Equation **3.2.1**. At 85°C a constant of $k_a = 3.8\times10^{-4}$ s^{-1} and at 120°C of $k_a = 4.7\times10^{-3}$ s^{-1} were measured. The decay rate constant at 120°C is in good agreement with the reported value ($k_a = 5.6\times10^{-3}$ s^{-1}, T = 115-123°C).[227]

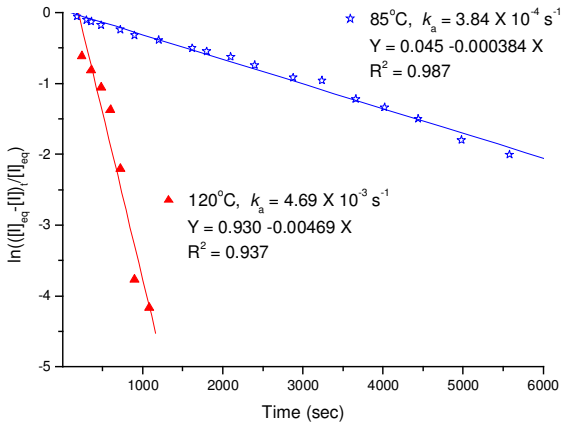
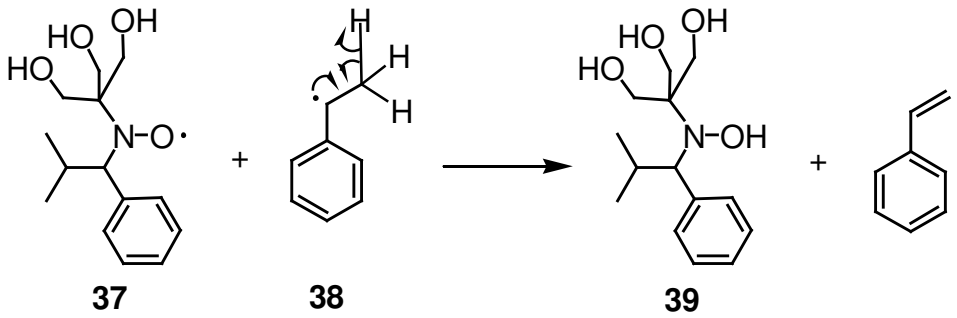


Figure 3.2.6. First-order plot according to Equation 3.2.1 (in *tert*-butylbenzene).

The activation energy of the cleavage of the C-O bond was calculated on the basis of Equation 3.2.2 for the temperatures 85°C and 120°C and gives rise to a value of 84.2 kJ/mol, which is smaller than previously reported value of 125.1 kJ/mol.[227]

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_1}\right) \qquad \text{Equation } \mathbf{3.2.2}$$

The decrease of the signal intensity, especially at 120°C (Figure 3.2.5), can be related to the formation of hydroxylamine **39** (Scheme 3.2.16) by H abstraction of **37** from the 1-phenylethyl radical in *tert*-butylbenzene. The formation of hydroxylamine **39** was proved by LC-MS measurement and the proposed reduction reaction is shown in Scheme 3.2.16.



Scheme 3.2.16. Reduction of the nitroxide radical **37** to give hydroxylamine **39**.

- **Kinetics of C-O bond homolysis of the initiator I2a in DMF**

The thermal decay of **I2a** at 120°C in DMF is shown in Figure 3.2.7. The concentration of **37** increases with time up to a constant value, which indicates that the formed nitroxide **37** is

more stable in polar solvent than in nonpolar solvent, such as *tert*-butylbenzene. The plot of $\ln\{([I]_{eq} - [I]_t)/ [I]_{eq}\}$ versus time gives a rate constant of the bond cleavage of $k_a = 2.1\times10^{-3}$ s^{-1} (Figure 3.2.7.).

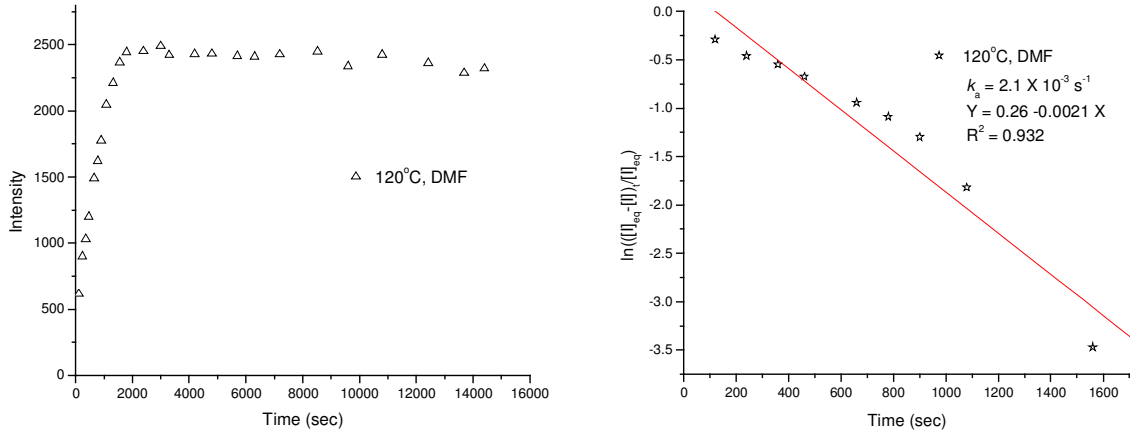
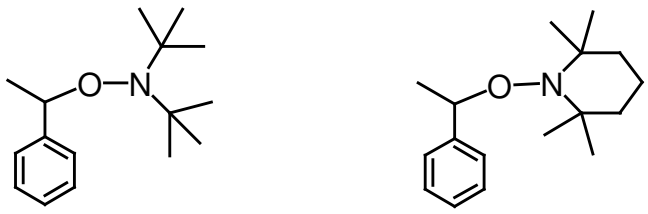


Figure 3.2.7. Time dependence of nitroxide **37** concentrations during thermolysis of initiator **I2a** in DMF at 120°C and the plot of $\ln\{([I]_{eq} - [I]_t)/ [I]_{eq}\}$ vs time.

Marque reported that the rate of C-O bond homolysis is increasing upon increasing the solvent polarity.[227] They used *tert*-butanol and chlorobenzene as polar solvents. The alkoxyamines investigated are shown in Figure 3.2.8. (**40**: T = 100°C, $k_a = 1.9\times10^{-3}$ s^{-1} in *tert*-butyl benzene; T = 100°C, $k_a = 4.0\times10^{-3}$ s^{-1} in *tert*-butyl benzene/*tert*-butanol (1:1). **41**: T = 120°C, $k_a = 5.2\times10^{-4}$ s^{-1} in *tert*-butyl benzene; T = 120°C, $k_a = 1.2\times10^{-3}$ s^{-1} in chlorobenzene). In our case, however, the rate constant of C-O bond homolysis in DMF at 120°C was two times smaller than the values of k_a in *tert*-butylbenzene ($k_a = 4.7\times10^{-3}$ s^{-1}).

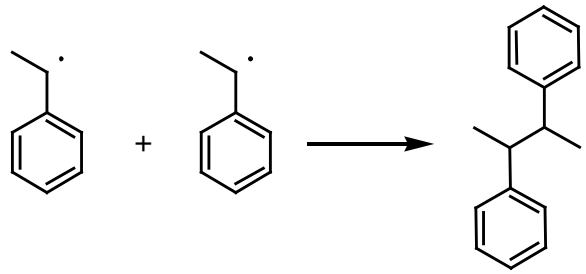


40 **41**

Figure 3.2.8. Structures of alkoxyamines **40** and **41**.

In the case of DMF as solvent the concentration of nitroxide **37** did not decrease after the maximum was reached. That means that nitroxide **37** does not react with the 1-phenylethyl radical **38** to give alkoxyamine **I2a**. The reactivity of the nitroxide radical is obviously reduced in DMF. Since no signal of **38** formed from the decomposition of initiator **I2a** could be

detected during the ESR measurement, it can be concluded that the active radical **38** is either instantaneously trapped by O_2 or dimerized to 2,3-diphenylbutane (Scheme 3.2.17).



Scheme 3.2.17. Dimerization of 1-phenylethyl radical to 2,3-diphenylbutane.

- **Kinetics of C-O bond homolysis of initiator I2a in 1,2,4-trichlorobenzene**

For comparison 1,2,4-trichlorobenzene was also used as another polar solvent for the ESR measurements. As shown in Figure 3.2.9, the thermal homolysis of the C-O bond to give **37** is quite fast, but the concentration of nitroxide **37** also decreased very quickly after reaching the maximum value. It seems that there is no H-bonding effect in this solvent. A probable side reaction arises from a chlorine atom, which often used to quenching radicals.

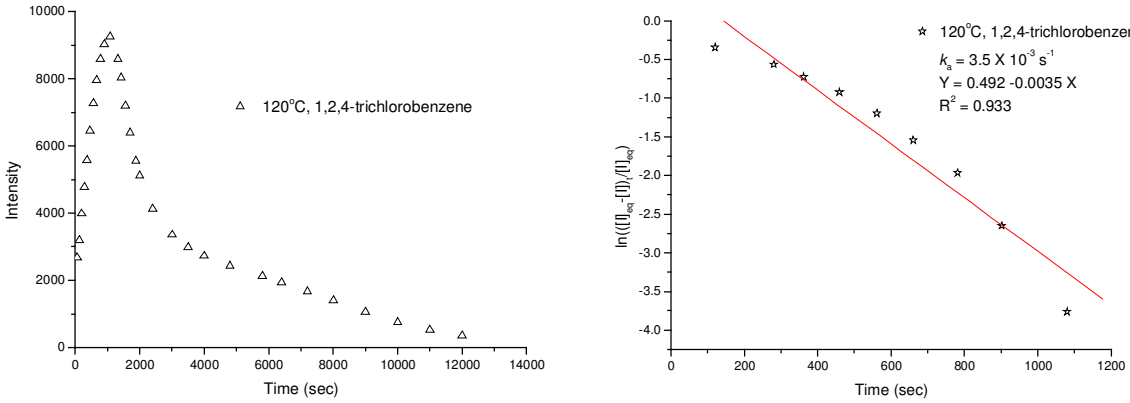


Figure 3.2.9. Time dependence of the concentration of the nitroxide **37** and first-order plot according to Equation 3.2.1. (1,2,4-trichlorobenzene at 120°C).

The linear relationship of the concentration of **37** with time is given in Figure 3.2.9. According to Equation 3.2.1 the calculated rate constant $k_a = 3.5\times10^{-3}$ s^{-1} is still smaller than the decay rate constants of **I2a** in *tert*-butylbenzene.

As mentioned previously, satisfactory living radical polymerizations apparently require rate constants of $k_a \approx 10^{-3}$ s^{-1} for the dissociation of the intermediate polymeric alkoxyamine. Thus, the rates of C-O bond homolysis of **I2a** in the three solvents matches this theoretical value at

120°C. All data of the dissociation of the C-O bond in **I2a** are summarized in Table 3.2.1. The stability of nitroxide **37** shows a dependence on the polarity of the solvent, being more stable in dipolar aprotic DMF than in nonpolar *tert*-butylbenzene or1,2,4-trichlorobenzene.

Table 3.2.1. Activation rate constant k_a, activation energy E_a and the stability of the nitroxide yielded from the dissociation of the C-O bond in alkoxyamine **I2a**.

Alkoxy amine	T °C	Solvent	k_a (s^{-1})	E_a ($kJ \cdot mol^{-1}$)	Stability of nitroxide	Liter
I2a	115-123	*tert*-butylbenzene	5.6×10^{-3}	125.1		227
	85	*tert*-butylbenzene	3.8×10^{-4}	84.2		
	120	*tert*-butylbenzene	4.7×10^{-3}		lower	
	120	DMF	2.1×10^{-3}	-	high	
	120	1,2,4-trichlorobenzene	3.5×10^{-3}	-	lowest	

3.3. Free radical polymerization of multifunctional acryl- and methacryl derivatives

It is well known that radical polymerization is considered a mature technology with millions of tons of vinyl-based homo- and copolymers being produced annually. This perception of maturity is based on the fact that free radical polymerization is so widely used industrially and in research laboratories for the synthesis of a wide variety of polymeric materials. This widespread adoption is due to its versatility, synthetic ease, and compatibility with a wide variety of functional groups, coupled with its tolerance to water and protonic media.

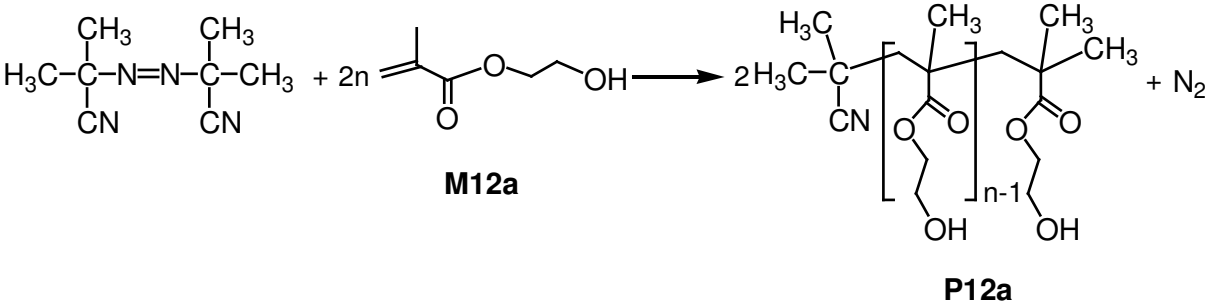
In the preparation of well-defined macromolecules, traditional free radical procedures have a significant drawback, which is related to the reactivity of the propagating free radical chain end and its propensity to undergo a variety of different termination reactions. The materials obtained are therefore polydisperse with very limited control over macromolecular weight and architecture.[32] For the synthesis of well-defined products other polymerization methods have to be taken into account.

In this section the synthesis of polymers on the basis of acryl- and methacryl derivatives via conventional free radical polymerization, such as AIBN initiated polymerization, as well as controlled radical polymerization (NMP, ATRP and RAFT) is described in detail.

3.3.1. AIBN initiated traditional radical polymerization of acryl- and methacryl derivatives

The multifunctional acryl- and methacryl derivatives selected for investigation have three or more functional groups: the double bond, the amide or ester group, and one or more additional functional groups (-NH_2, -OH and -COOH). Since the ester and amide groups are electron withdrawing, the double bond is activated and easy to polymerize. The classical vinyl polymerization involves the normal steps of initiation, propagation, chain transfer, and mutual termination of pairs of growing chains.

In order to have the possibility of comparing the poly(acryl- and methacryl derivatives) produced by conventional free radical polymerization with those obtained with NMP, ATRP and RAFT, the well known AIBN initiated radical polymerization of the selected multifunctional monomers was included in the research program. The conventional radical polymerization of **M12a** initiated by AIBN is represented in Scheme 3.3.1.

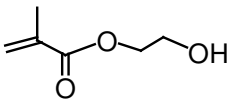


Scheme 3.3.1. Conventional free radical polymerization of **M12a**, using AIBN as initiator.

A comparison of the polymerization makes sense only if the products are similar; therefore the first step was to optimize the conditions in order to produce polymers with relatively narrow molar mass distributions (also termed polydispersity, PD). Because AIBN is commonly used at 50-70°C, in our research work the reaction temperature has been fixed at 70°C. The reaction conditions used for the conventional free radical polymerization of **M12a** are summarized in Table 3.3.1. Different ratios of monomer and initiator have been used, as well as different concentrations of the monomer in the reaction solution. It has been shown that the

concentration of monomer in the solution has a great influence on the product. **R1** is not soluble in DMSO, DMF and DMAc. On the other hand, comparing **R2**, **R3**, and **R4** the ratio of monomer to initiator does not seem to have any influence on the obtained molar masses. As expected for a typical free radical polymerization, the polymers have quite broad molar mass distributions (PD ~ 2), which is a symptom of the uncontrolled mechanism of the reaction. By tailoring all the above mentioned reaction conditions, it was possible to obtain products with a narrow molar mass distribution comparable to that of controlled radical polymerization systems. Because **R3** had a relatively narrow molar mass distribution, these reaction conditions (T = 70°C, ratio of monomer to initiator of 40:1 (mol/mol), concentration of monomer of 0.1 g/ml) were always chosen for the conventional radical polymerization of the other monomers.

Table 3.3.1. Reaction conditions for the AIBN initiated polymerization of **M12a**.

No.	M **M12a**	M : I (mol/mol)	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,GPC}$ (g/mol)	$M_{w,GPC}$ (g/mol)	PD M_w/M_n
R1		100:1	70	1	6	100	-	-	-
R2		100:1	70	0.1	6	100	23600	51600	2.19
R3		40:1	70	0.1	6	100	21700	40300	1.86
R4		20:1	70	0.1	6	100	20300	40300	1.99

^{1}H and ^{13}C-NMR spectra of polymer **P12a** obtained by AIBN initiated free radical polymerizations are shown in Figure. 3.3.1. In comparison with the spectra of the monomer, all the signals in the proton NMR spectra are broad. From the ^{1}H-NMR spectra one sees that the methyl groups of AIBN now are overlapped in the broad signals of -CH_3 and -CH_2- groups of the repetition units. Therefore, it is impossible to calculate accurately the molar mass M_n of these kinds of polymers initiated by AIBN from the NMR spectra. In fact, during an AIBN initiated radical polymerization, a large number of side reactions occur and determination of the number of repetition units from the integration of the –CH_3 groups can be done only assuming disproportional termination and supposing that no transfer and recombination reactions take place. Due to the tacticity of the chain, the signals of the repetition units in the ^{13}C-NMR spectra are broad and some multiple peaks are recognizable, which affirm that the AIBN initiated polymers have an atactic conformation of the chain.

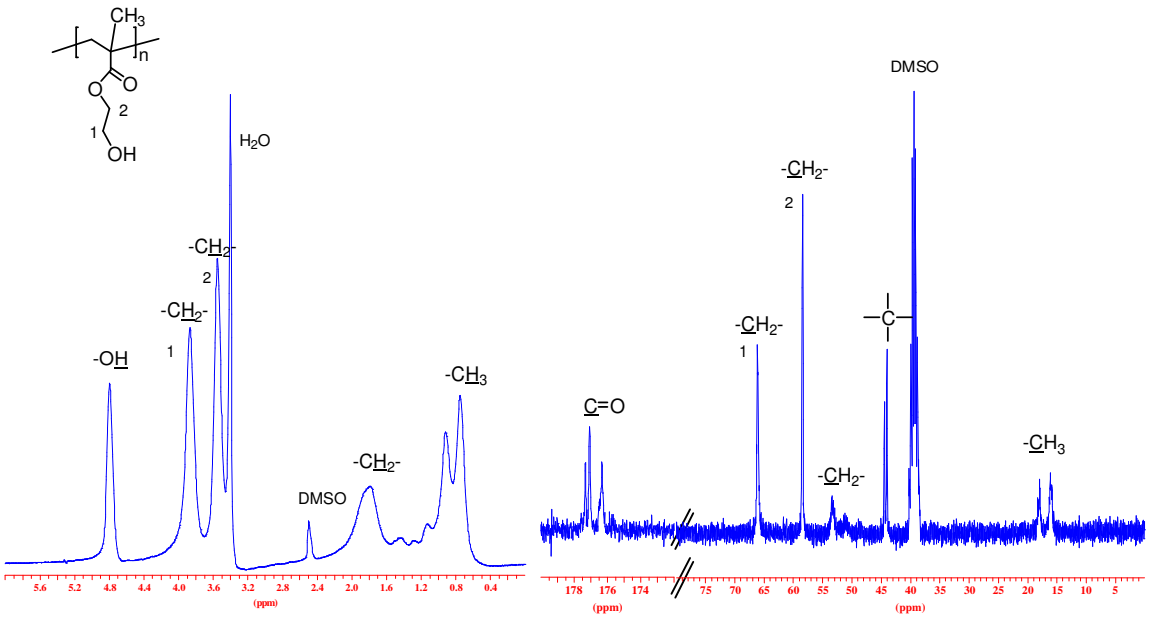


Figure 3.3.1. ^{1}H and ^{13}C-NMR spectra in DMSO-d_6 of polymer, synthesized by conventional free radical polymerization.

In order to obtain some information about the conventional radical polymerization of multifunctional acryl- and methacryl derivatives, similar structures of (meth)acrylate and (meth)acrylamide monomers (**M1a**, **M1b**, **M15a** and **M15b**) were selected and the difference of their free radical polymerization rates was investigated. As shown in Figure 3.3.2 acryl derivatives (**M1b** and **M15b**) polymerized much faster than corresponding methacryl derivatives (**M1a** and **M15a**), and the acrylamide **M1a** and methacrylamide **M1b** proceeded at faster rates than the corresponding acrylate **M15a** and methacrylate **M15b**.

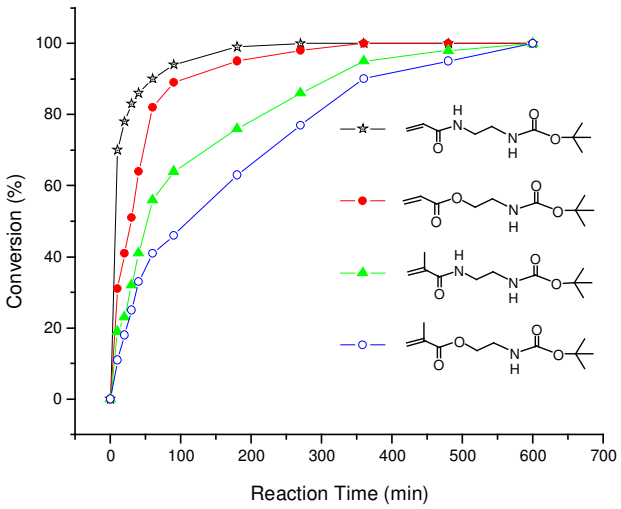
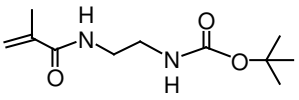
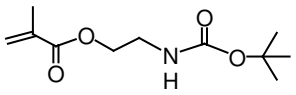


Figure 3.3.2. Kinetics of the polymerization of various monomers with AIBN in DMF at 70°C ([M]/[I] = 40:1, [M]/Solvent = 0.1 g/ml).

As concerns the conversion values, generally, an optimized free radical polymerization mechanism makes it possible to reach 100% when the reaction is performed for a reasonably long time. From the comparison experiments one may draw the conclusion that acryl derivatives are more active than methacryl derivatives, and the reactivity of (meth)acrylamide is higher than that of (meth)acrylates.

Certain polymers from different reaction conversions (i.e. different reaction time) were selected for GPC measurement for the investigation of the influence of the conversion on the molar masses and molar mass distribution of the polymers. The GPC results of polymers synthesized by conventional free radical polymerization are shown in Table 3.3.2. All polymers have quite broad molar mass distributions, even broader (PD > 2) than that of **P12a**. The molar masses of the polymers **R5** and **R6** decreased with increasing conversion of the monomers and the molar mass distribution of the polymers increased slightly with the conversion. The decrease of the molar mass and the increase of molar mass distribution with conversion could arise from a cleavage of the Boc protective groups in the polymer side chain. These results indicate that it is not possible to achieve a controlled radical polymerization initiated by AIBN.

Table 3.3.2. GPC results of polymers synthesized by conventional free radical polymerization ([M]/[AIBN] = 40:1).

No.	M	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,GPC}$ (g/mol)	$M_{w,GPC}$ (g/mol)	PD M_w/M_n
R5		70	0.1	1.5	64	16500	35200	2.13
		70	0.1	3	76	10900	25900	2.47
		70	0.1	6	95	8200	23200	2.83
R6		70	0.1	1,5	46	15700	35400	2.25
		70	0.1	3	63	13700	33200	2.42
		70	0.1	6	91	11000	30800	2.80

3.3.2. Controlled Radical Polymerization by NMP

The ability to control accurately macromolecular architecture is becoming an increasingly important aspect of polymer chemistry. For a controlled radical polymerization in general three methods are applied, the Nitroxide-Mediated radical Polymerization (NMP), the Atom Transfer Radical Polymerization (ATRP) and the Reversible Addition-Fragmentation chain Transfer (RAFT) procedures. All these methods were used to polymerize the multifunctional acryl- and methacryl derivatives.

NMP attracts much interest because it is based on potentially simpler systems than ATRP or RAFT and it does not require the addition of a metal complex. This leads to greater functional group tolerance and easier purification (no metal ion contamination). Therefore, the nitroxide-mediated polymerization was investigated first. The activity of different initiators and their influence on the control of polymerization were proved. Initiators **I1a**, **I1b** and **I1c** are termed Hawker Adduct I, while initiators **I2a** and **I2b** are termed Hawker Adduct II.

3.3.2.1. Polymerization of various monomers initiated by Hawker Adduct I (I1a, I1b, I1c)

Nitroxide-mediated radical polymerization procedures can be carried out in two different ways, i.e. “bimolecular system” or “unimolecular system”. To compare the molecular weight control of unimolecular initiators with that obtained with the corresponding bimolecular system, these two methods were both applied to polymerize styrene at 125°C. Because styrene is a suitable and often used monomer for “living”/controlled radical polymerization,[20-24] we used these optimized polymerization conditions for the further investigation of acryl- and methacryl derivatives.

In a bimolecular polymerization system a conventional free radical initiator, such as dibenzoyl peroxide (BPO) and a terminator (TEMPO or HTEMPO) were employed in a molar ratio of 1:1.3, as reported by Sogah.[228] The monomer was used in 100 fold excess. In the unimolecular system, the modified TEMPO-based Hawker Adduct I compounds (**I1a**, **I1b** and **I1c**) were used as unimolecular initiators for the polymerization, with the same 100 fold ratio of monomer to initiator. The reaction conditions and the results are summarized in Table 3.3.3.

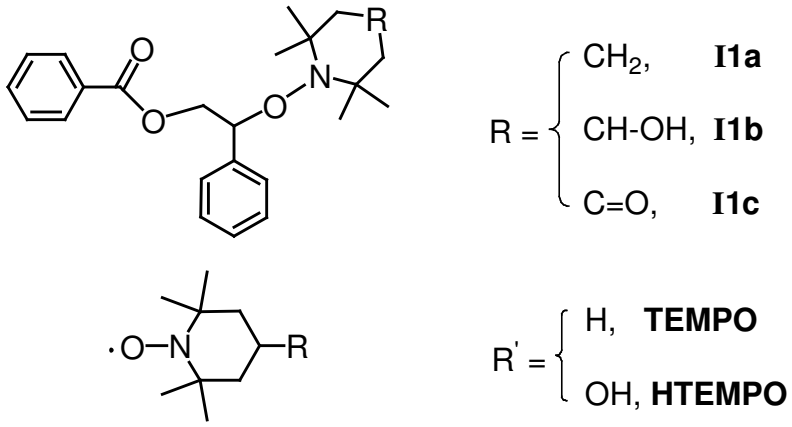


Figure 3.3.3. Structures of Hawker Adduct I.

Table 3.3.3. Results of the controlled radical polymerization of styrene using different initiators (M:I = 100:1).

No.	M	I	T (°C)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R7	styrene	**I1a**	125	13	84	8748	9048	1.28
R8		**I1b**	125	13	82	8539	8574	1.29
R9		**I1c**	125	13	78	8123	8129	1.29
R10		BPO/TEMPO	125	46	76	7915	9749	1.32
R11		BPO/HTEMPO	125	46	74	7706	9775	1.28

One can see that all the styrene polymerization results using unimolecular initiators **I1a**, **I1b**, **I1c** under the selected conditions are almost identical (**R7**, **R8**, **R9**), including the reaction yield, the molar mass and the molar mass distribution of polystyrene. The experimental molecular weights of the polymers ($M_{n\ GPC}$) are close to the theoretical molecular weights ($M_{n,theor}$) calculated from the molar ratio of styrene to initiator and with a conversion, determined by NMR. All the polydispersities remain low.

These results indicate that the substituent at the 4 position of TEMPO derivatives (**I1a**, **I1b**, **I1c**) does not influence radical polymerization, which is in agreement with earlier results.[229] The same situation is also observed in the bimolecular system. There is no difference in the use of TEMPO or HTEMPO as terminator or scavenger. The time to polymerize styrene in the bimolecular system is much longer. Sogah[228] has reported that the polymerization is extremely

slow and requires several days at higher [NO•]/[BPO] ratio and the ratio of 1.3:1 is the best ratio to obtain a lower polydispersity of polystyrene, but not the best ratio for the polymerization rate. They found that a lower [NO•]/[BPO] gave a faster polymerization, but a broader molar mass distribution. The calculation of the theoretical molecular weight is complicated by the actual number of initiating species that are generated from a 1:1.3 mixture of BPO/TEMPO, and therefore a comparison with the theoretical molecular weight is not possible in the bimolecular system. If the initial active radicals from BPO are calculated as the actual initiating species, the deviations of the experimental molecular weights from the theoretical molecular weights are extremely large (**R10**, **R11**), which can be clearly observed in Figure 3.3.4.

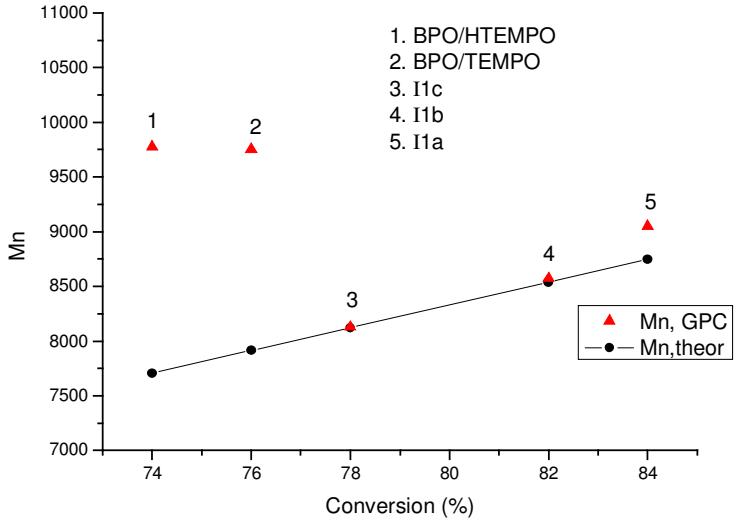
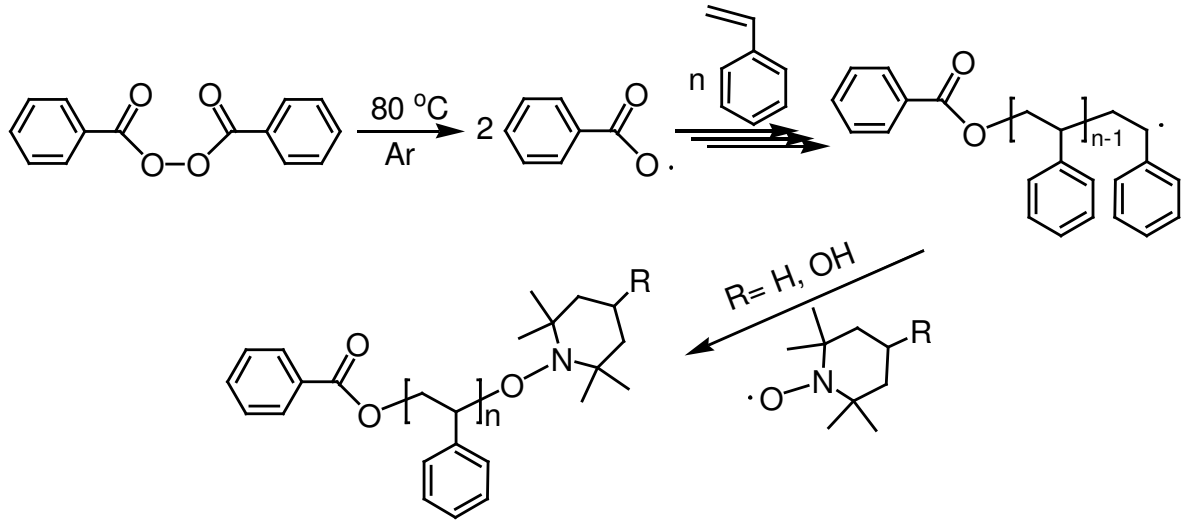


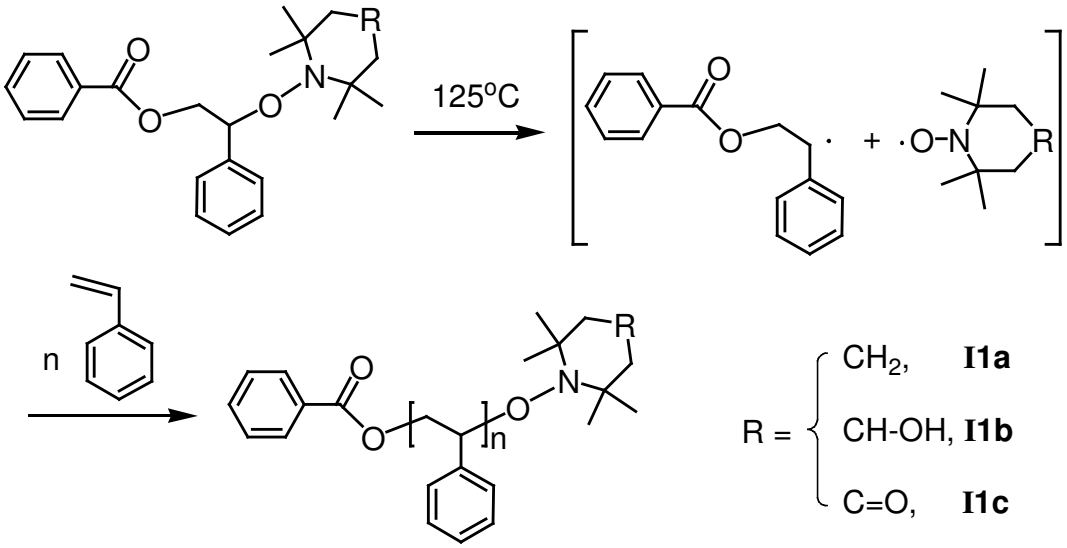
Figure 3.3.4. Deviation of experimental molecular weights ($M_{n\ GPC}$) from the theoretical molecular weights ($M_{n,theor}$) for the polymerization of styrene at 125°C using bimolecular and unimolecular initiators.

From these results it can be concluded that unimolecular initiators allow the preparation of macromolecules with better control over molecular weight and polydispersity than the corresponding bimolecular systems. This general behavior can be rationalized by an examination of the initial steps in both processes. For the bimolecular systems, such as BPO/TEMPO, the initial step is the decomposition of the benzoyl peroxide followed by the reaction of the radical with a styrene monomer and subsequent trapping of this species with TEMPO. Moad has shown that this series of reactions is complicated by a variety of side reactions,[53] which lead to a loss of initiator efficiency and the generation of unwanted side products. This results in slightly higher polydispersities and a lower degree of control over

molecular weights. In contrast, this inefficient initiating step does not occur with unimolecular initiators since the TEMPO adducts are preformed and actually resemble the unimers, which occur with a higher efficient initiator and a lower amount of undesirable side products, giving rise to accurate control over molecular weights and lower polydispersities. The mechanism of bimolecular and unimolecular initiators in the polymerization of styrene are shown in Scheme 3.3.2 and Scheme 3.3.3.



Scheme 3.3.2. Mechanism of bimolecular initiator for polymerization of styrene.



Scheme 3.3.3. Mechanism of unimolecular initiator for polymerization of styrene.

- **Temperature dependence of nitroxide-controlled styrene polymerization**

In order to investigate the behavior of living radical polymerization within a wide temperature profile, the reactions were performed in the range of 80-160°C. The polydispersities of

polystyrene were examined and compared using the selected initiator **I1c**. The results are summarized in Table 3.3.4. The PD of polystyrene versus reaction temperature is shown in Figure 3.3.5. One can observe that the PD decreased to a minimum limit at 125°C and then increased with rising temperature. At 160°C the PD exceeds the theoretical limit of 1.5 for conventional radical polymerization of styrene. Fukuda *et al.* discussed the decomposition of PS-TEMPO (Scheme 3.3.4), leading to dead-end polymers **43** and hydroxylamine **42**.[230] Alongside the desired reversible dissociation of PS-TEMPO, upon *β*-proton abstraction the resulting radicals decompose. In conclusion, the relatively high degree of polymerization control is limited to a specific temperature range of 100 to 140°C when using initiator **I1c**.

Table 3.3.4. Polymerization of styrene with initiator **I1c** at different temperatures.

No.	M	I	T (°C)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R12	styrene	**I1c**	80	188	65	6769	6897	1.93
R13		**I1c**	90	168	68	7081	6928	1.46
R14		**I1c**	100	96	66	6873	6607	1.38
R15		**I1c**	125	13	78	8123	8129	1.29
R16		**I1c**	140	5	78	8123	8966	1.32
R17		**I1c**	160	2	80	8331	9322	1.54

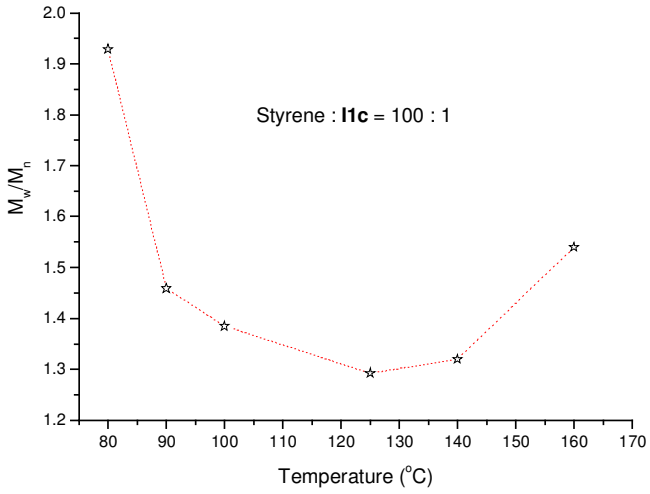
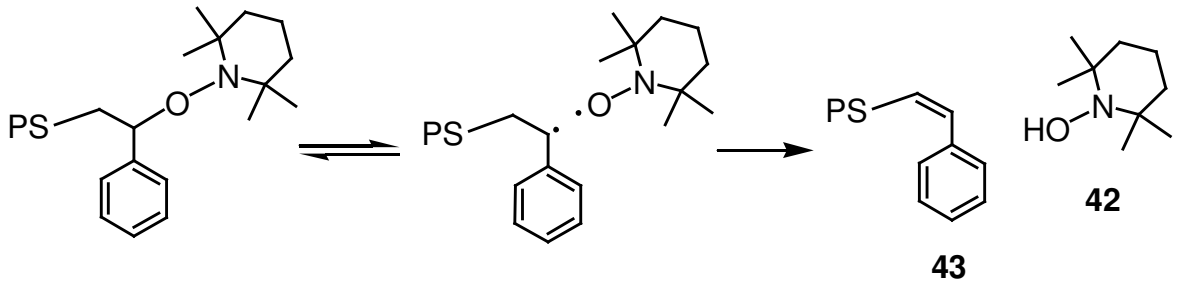


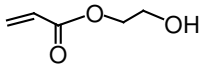
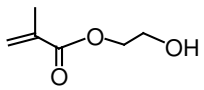
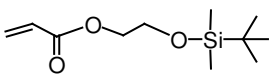
Figure 3.3.5. Polydispersities of polystyrene vs reaction temperature: styrene with initiator **I1c** (100:1 mol/mol, 70% conversion).

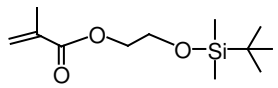
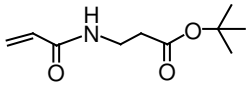
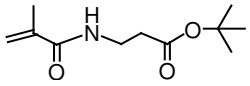
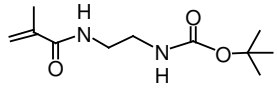


Scheme 3.3.4. Decomposition of PS-TEMPO leading to dead-end polymers **43** and hydroxylamine **42**.

For the investigation of the controlled radical polymerization of acryl- and methacryl derivative monomers, **I1c** was used as unimolecular initiator for this family of monomers. The similar monomer without any functional groups, such as *n*-butyl acrylate, was polymerized as well. Table 3.3.5 shows the results of heating **I1c** with a predetermined amount of monomer at 125°C under argon. In general, all the polymerizations took a very long time. With methacrylamide the conversions are especially very low (10% and 20%), even after 66 h of polymerization. The polydispersities of the poly(methacryl derivative) are higher than the corresponding polydispersities of the poly(acryl derivative). With the exception of **R18**, **R19**, **R20** and **R21** the molecular weights were significantly different from the theoretical molecular weights. All the polydispersities were higher than 1.50. In comparison with styrene, the polymerization of multifunctional acryl and methacryl derivatives with **I1c** did not follow a controlled radical polymerization.

Table 3.3.5. Polymerization of multifunctional acryl- and methacryl derivatives with initiator **I1c** at 125°C.

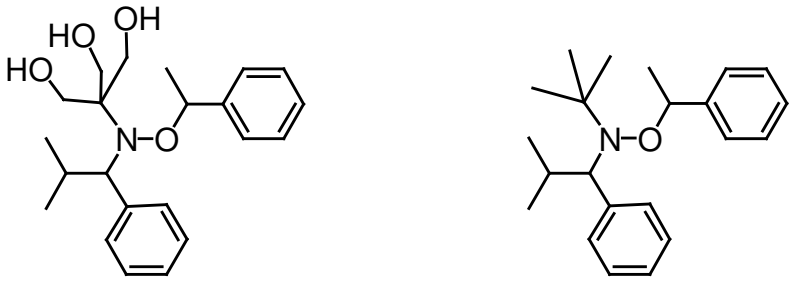
No.	M M:I=100:1	I	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R18	*n*-butyl acrylate	**I1c**	125	bulk	144	90	11535	9428	1.52
R19		**I1c**	125	0.5	70	68	7895	8912	1.86
R20		**I1c**	125	0.5	70	62	8068	9700	2.52
R21		**I1c**	125	bulk	144	92	18891	15510	1.70

R22		**I1c**	125	bulk	144	90	21997	48100	2.68
R23		**I1c**	125	0.5	66	100	19925	8796	1.51
R24		**I1c**	125	0.5	66	20	4266	6363	1.53
R25		**I1c**	125	0.5	66	10	2283	1200	4.58

In conclusion, it can be stated that the unimolecular initiators based on the TEMPO system are ineffective for the controlled radical polymerization of multifunctional acryl- and methacryl derivatives. To overcome this difficulty, new initiators should be synthesized and examined.

3.3.2.2. Polymerization of various monomers initiated by Hawker Adduct II (I2a, I2b[§])

Besides the TEMPO-based unimolecular initiator, Hawker and co-workers developed a variety of new unimolecular initiators for NMP and synthesized a large number of new polymer structures with a high degree of molecular weight control and a low polydispersity. With a hydrogen in the α position to the nitrogen atom nitroxides **I2a** and **I2b** were able to control the polymerization of a wide variety of monomer families, especially for acrylates without a functional group, such as *n*-butyl acrylate or methyl acrylate.[26, 63, 64, 77,78] A goal of our work was to evaluate the ability of a controlled radical polymerization of styrene and multifunctional acryl- and methacryl derivatives initiated by the newer Hawker Adduct II, (**I2a**, **I2b**, Figure 3.3.6).



I2a **I2b**

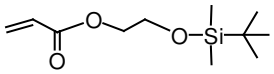
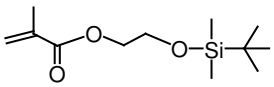
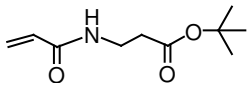
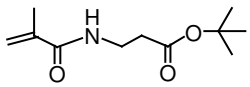
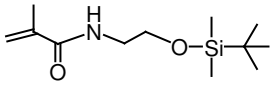
Figure 3.3.6. Structures of Hawker Adduct II (**I2a** and **I2b**).

[§] Initiator **I2b** was synthesized by Martin Messerschmidt (IPF, Dresden)

3.3.2.2.1. Polymerization of various monomers initiated by initiator I2b

The polymerization of multifunctional acryl- and methacryl derivatives initiated by **I2b** was carried out at 120°C (Table 3.3.6). Obviously the PD of polystyrene **R26** and the polyacrylate **R27** were quite low, 1.18 and 1.19 respectively. However, with the exception of styrene, the experimental molecular weights of the derived polymers were lower than the theoretical values, and the polymerization rates of methacrylamides (**R30**, **R31**) were still very low. In comparison with TEMPO, the presence of a hydrogen atom on the α-carbon bound to the nitrogen atom in Hawker Adduct II decreases the stability of the nitroxide. This destabilization results in extensive decomposition of the nitroxide during the polymerization, especially at elevated temperatures and as a result the concentration of surviving nitroxide is insufficient to mediate the polymerization. Nevertheless, the living character of the acrylate polymerization, as in **R27**, was enhanced when compared to TEMPO.

Table 3.3.6. Polymerization of various monomers initiated by initiator **I2b** at 120°C.

No.	M M:I=100:1	I	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R26	styrene	**I2b**	120	0	14	72	7499	7100	1.18
R27		**I2b**	120	1	14	98	22346	7673	1.19
R28		**I2b**	120	1	14	63	15153	8609	2.41
R29		**I2b**	120	1	14	68	13549	6988	1.79
R30		**I2b**	120	1	80	33	7038	4910	1.79
R31		**I2b**	120	1	80	37	9006	6141	2.19

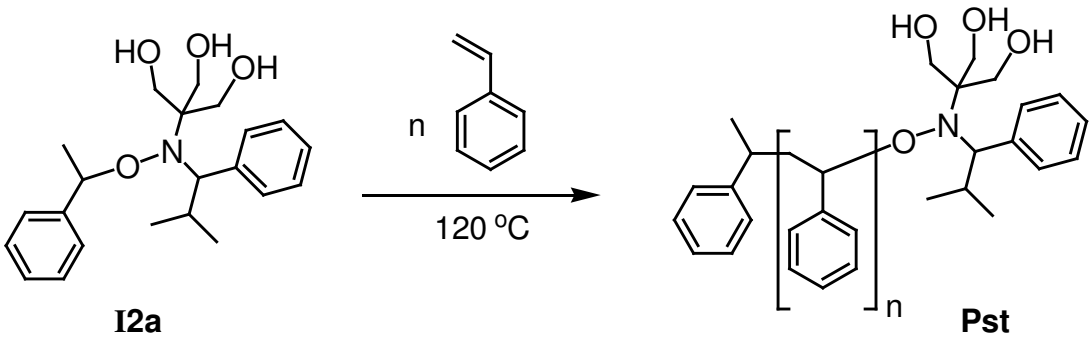
3.3.2.2.2. Polymerization of styrene initiated with initiator I2a[#]

The effectiveness of **I2a** for the living free radical polymerization of styrene was proved under bulk conditions at 120°C. Special attention should be paid to molecular weight and polydispersity control.

Since the two diastereomers of initiator **I2a** could be isolated by flash chromatography the influence of each diastereomer on initiating ability was investigated. The bulk polymerizations of styrene with different diastereomers of **I2a**, with a molar ratio of 100:1, were performed at 120°C. The results are given in Table 3.3.7. The conversion, molecular weight, and the polydispersity of polystyrene initiated by diastereomer I (**R32**), diastereomer II (**R33**) and the mixtures of diastereomer I and II (**R34**) are very close to each other after the same polymerization time (4 h), indicating that there is no influence of the different diastereomers of initiator **I2a** on the controlled initiating abilities. All the subsequent polymerizations were, thus, carried out with the obtained mixture of diastereomers. The polymerization of styrene with initiator **I2a** is shown in Scheme 3.3.5.

Table 3.3.7. Homopolymerization of styrene with diastereomer I, diastereomer II and the mixture of diastereomers I and II of initiator **I2a**. (M:I = 100:1 mol/mol).

No.	M	T (°C)	I	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R32	styrene	120	*Dia I*	4	69	7186	7200	1.18
R33	styrene	120	*Dia II*	4	67	6977	7000	1.16
R34	styrene	120	*DiaI+DiaII*	4	68	7081	7000	1.16



Scheme 3.3.5. Homopolymerization of styrene with the initiator **I2a**.

- **The influence of the reaction temperature**

All the data of polystyrene polymerized by **I2a** in bulk at different temperatures are given in Table 3.3.8. The observed reaction time, based on a fixed conversion of about around 70% as examined by ^{1}H-NMR spectroscopy, decreased with increasing temperature. At 110°C the reaction time decreased to 6 h and the conversion was rather high (72%, **R39**), indicating that polymerization occurred fairly rapidly. By comparison with initiators **I2b** (**R26**: 120°C, 14 h) and **I1(a,b,c)** (**R7**, **R8**, **R9**: 125°C, 13 h), the polymerization with initiator **I2a** is very fast (**R34**: 4 hours at 120°C).

Table 3.3.8. Styrene polymerized by **I2a** in bulk at different temperatures (M:**I2a** = 100:1 (mol/mol)).

No.	M	I	T (°C)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R35	styrene	**I2a**	80	96	64	6664	6676	1.37
R36		**I2a**	85	66	68	7081	8100	1.26
R37		**I2a**	90	40	68	7081	7004	1.25
R38		**I2a**	100	20	68	7081	7171	1.25
R39		**I2a**	110	6	72	7498	7546	1.22
R34		**I2a**	120	4	68	7081	7000	1.16

It is also clear that the polymerization of styrene initiated by **I2a** occurs in a controlled fashion. All the data of the experimental molecular weights ($M_{n,\ GPC}$) are close to the theoretical molecular weights ($M_{n,theor}$). At the same time the molar mass distribution is quite low. Even at the lowest temperature (80°C) the molar mass distribution of 1.37 is less than the limitation of 1.5. When the same polymerizations were performed at higher temperatures, the products were formed with much lower polydispersities (PD $\leq$ 1.26). Finally, the best results were obtained at 120°C, with the lowest polydispersity of PD = 1.16. The evolution of the reaction time and polydispersity with reaction temperature is shown in Figure 3.3.7.

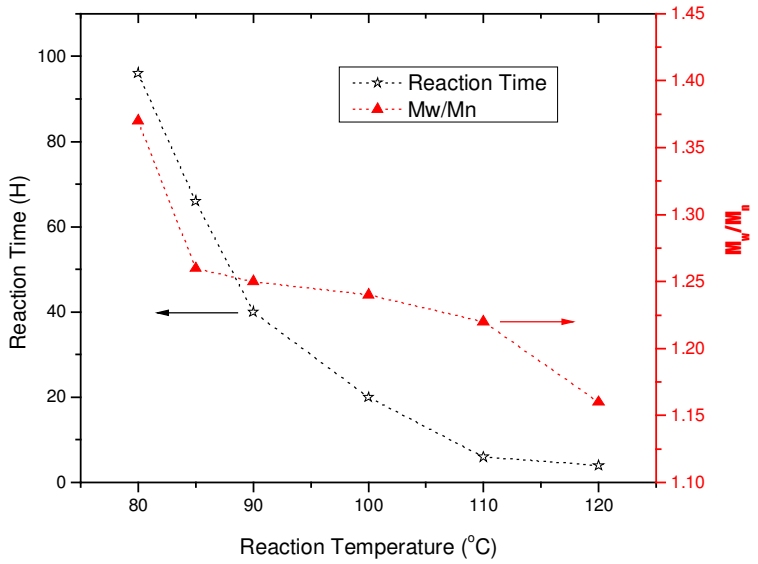


Figure 3.3.7. Evolution of reaction time and polydispersity with reaction temperature during the polymerization of styrene with initiator **I2a** ([styrene]/[**I2a**] =100:1 (mol/mol).

- **The influence of additive**

Although the polymerization of styrene was quite rapid when initiated by **I2a** at 120°C, at lower temperatures, such as 80°C and 90°C, it took rather long (96 h and 66 h respectively). From literature it is known that an additive like acetic anhydride accelerates the polymerization rate.[66, 67]

To reduce the reaction time at low temperature Ac_2O was added to the polymeric system. It is apparent that the additive led to the acceleration of the polymerization reaction. All the polymerizations performed with additive (**R43**, **R44**, **R45**) faster than those without additive (**R40**, **R41**, **R42**) respectively, while the conversions are the same or higher (Table 3.3.9 and Figure 3.3.8.). However, an enlargement of the molar mass distribution of the polymers was observed when reaction time was reduced to 38 h from 96 h and the PD rose to 1.63 from 1.37. One possible reason is that the addition of Ac_2O reacted with the hydroxyl groups in nitroxide **37**, limiting the formation of the intramolecular hydrogen bonds in nitroxide **37**, which would lead to changes in the equilibrium between the activation and deactivation reactions, which are crucial for a controlled radical polymerization.

Table 3.3.9. Reaction time, reaction temperature, conversion, molecular weight and polydispersity data for homopolymerization of styrene (M:I=100:1) in the presence of Ac_2O (5% of **I2a**).

No.	M	I	T (°C)	Ac_2O (%)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R40	styrene	**I2a**	80	-	96	64	6664	6676	1.37
R41		**I2a**	90	-	40	68	7081	7004	1.25
R42		**I2a**	100	-	20	68	7081	7171	1.25
R43		**I2a**	80	5	38	71	7394	8800	1.63
R44		**I2a**	90	5	25	68	7081	8100	1.54
R45		**I2a**	100	5	18	93	9685	10500	1.67

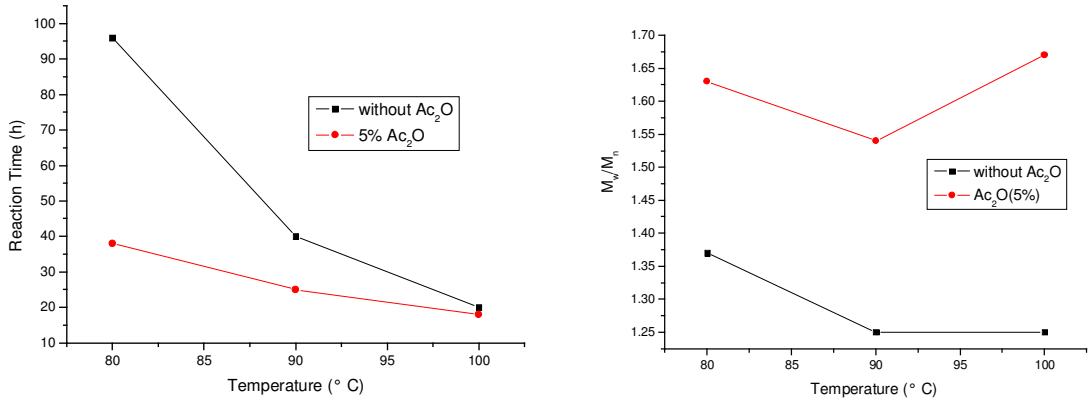


Figure 3.3.8. Influence of Ac_2O on the reaction time and polydispersity of polystyrene.

- **Kinetics of the polymerization of styrene initiated by I2a**

In order to examine the kinetics of polymerization and to prove the living character of the nitroxide-mediated polymerization initiated by alkoxyamine **I2a** as a unimolecular initiator, styrene was selected as monomer. The general kinetics mechanism of the nitroxide-mediated radical polymerization is shown in Scheme 3.2.14.

The reaction kinetics for a "living" radical polymerization can be derived by consideration of certain assumptions:

- $k_a >> k_p$, i.e. initiation occurs completely before the growth reaction occurs;

- $k_t \approx 0$, i.e. chain termination by combination and disproportionation or chain transfer reaction hardly occur and can be neglected;
- k_p is the equivalent constant value for different chain lengths;

Since the rate constants, including those of the primary radicals, do not depend on chain length, there is a rate equation that can be established from Scheme 3.2.14.

$$-\frac{d[M]}{dt} = k_p[M]\,[P_n^{\bullet}] \qquad \text{Equation 3.3.1}$$

During the polymerization, the termination is negligible ($k_t \approx 0$) and the concentration of the active chain radicals [P_n•] can be regarded as constant. So one can integrate Equation 3.3.1 to

$[M] = [M]_0 e^{-k_p[P_n^{\bullet}]t}$ and transform it to $\ln\frac{[M]_0}{[M]} = k_p[P_n^{\bullet}]t$ Equation 3.3.2

The conversion (C) of the reaction is given by

$$C = \frac{[M]_0 - [M]}{[M]_0} = 1 - \frac{[M]}{[M]_0} \qquad \text{Equation 3.3.3}$$

Equation 3.3.2 and 3.3.3 lead to Equation 3.3.4

$$\ln\frac{[M]_0}{[M]} = \ln\left(\frac{1}{1-C}\right) = k_p[P_n^{\bullet}]t = k' t \qquad \text{Equation 3.3.4}$$

Equation 3.3.4 means that the slope of $\ln[M]_0/[M]$ vs time must be a constant for an ideal living radical polymerization, which is applied to prove the criterion for a living polymerization.

Styrene was polymerized in dioxane at 120°C and the conversion was calculated by the ratio of monomer to polymer in the reaction mixture, as measured by NMR at regular time intervals. Further, the evolution of $\ln([M]_0/[M])$ vs time, calculated from conversion by Equation 3.3.4, is also represented in Figure 3.3.9. The plot of $\ln([M]_0/[M])$ versus time is linear, indicating pseudo-first-order kinetics; hence, the number of active species is constant throughout the course of the reaction (i.e. k_p [P_n•] = constant) in this investigated case.

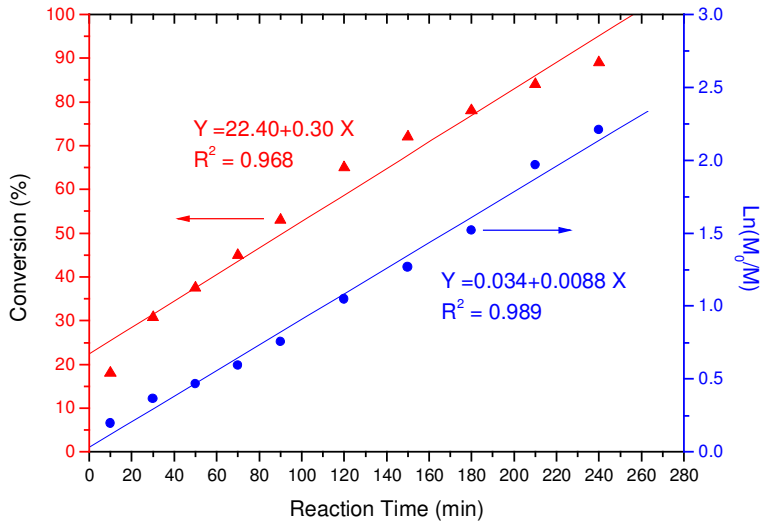


Figure 3.3.9. Conversion and ln([M]$_0$/[M]) plots vs time for the polymerization of styrene (5 M) in dioxane with the initiator **I2a** (0.05 M) at 120°C.

The typical evolution of the molecular weight and the polydispersity as a function of monomer conversion is presented in Figure 3.3.10. As presupposed for a "living"/controlled polymerization process the number average molecular weight $M_{n,GPC}$ increases almost linearly with conversion. This observation, together with the kinetics plot of ln([M]$_0$/[M]) vs time, confirms that the polymerization process is controlled/"living" and that the contribution of chain breaking, transfer, and termination reactions during the course of the polymerization is negligible.

Simultaneously the molar mass distribution (PD) decreased with conversion and remained quite low even at conversions higher than 50%, ranging from 1.25 to 1.16. The polydispersities (PD = 1.41 and 1.34) were a little higher at the beginning of the polymerization (at conversions of 18% and 30%). The loss and the chain transfer reactions of the C-radicals at the beginning of the reaction are responsible for the higher polydispersities, resulting in the rise of the persistent nitroxide **37** concentration in the polymerization medium. As the polymerization continues, the active chain radicals [P_n•] can disappear by their self-termination (eq.**4**, Scheme 3.2.14) and by cross-reaction to form the dormant species (eq. **2**, Scheme 3.2.14), whereas by definition the persistent nitroxide **37** should not self-terminate but disappear only by the cross-reaction. Since every self-termination event of [P_n•] causes an excess of nitroxide **37**, this excess continues as time goes on. Hence, the dormant species becomes the main product and the concentration of active chain radicals [P_n•] stays low to

minimize the termination reaction. Therefore, a dynamic equilibrium is reached where the reaction is controlled and the polydispersities remain low.

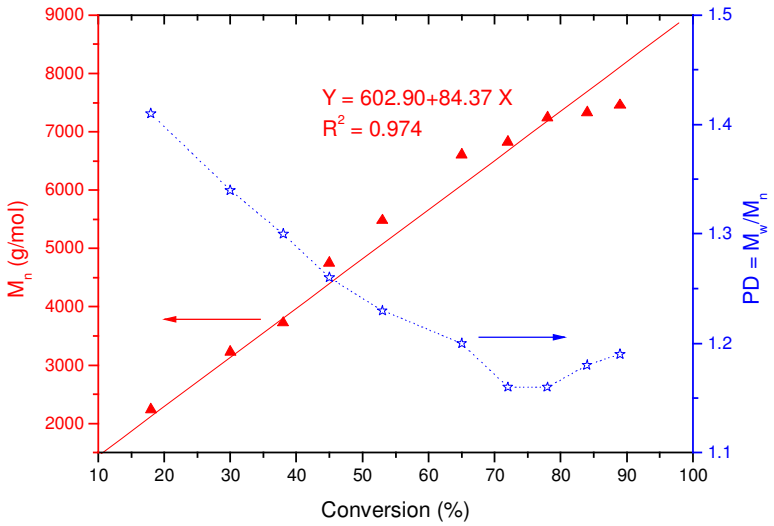


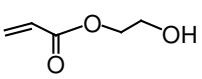
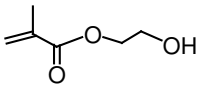
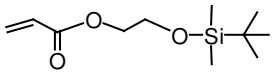
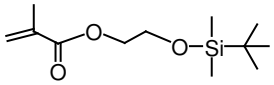
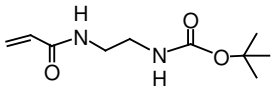
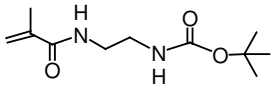
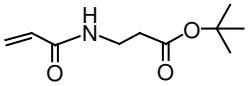
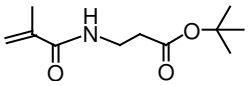
Figure 3.3.10. Evolution of M_n and PD = M_w/M_n vs conversion for the polymerization of poly(styrene) in dioxane at 120°C, [styrene] = 5 M, [**I2a**] = 0.05 M.

By comparison with TEMPO-based initiators the **I2a**-initiated polymerization of styrene has several advantages, such as lower polymerization temperature (120°C), shorter polymerization time (4 h), lower polydispersities (PD of 1.29 reduced to 1.16), and an excellent agreement of theoretical and experimental molecular weight.

3.3.2.2.3. Polymerizations of acryl- and methacryl derivatives initiated by initiator I2a

The high degree of control afforded by **I2a** in the polymerization of styrene prompted a thorough investigation into the polymerization of other monomers, such as acryl and methacryl derivatives. For evaluating this alkoxyamine the initial screening procedure involved the polymerization of 100 equiv. of monomer in the presence of 1.0 equiv. of the initiator. A complete list of multifunctional acryl and methacryl derivatives polymerized by initiator **I2a** in this way is given in Table 3.3.10.

Table 3.3.10. Polymerization of various monomers initiated by initiator **I2a** at 100 and 120°C.

No.	M M:I=100:1	I	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R46		**I2a**	100	0.5	4	80	9289	19900	2.36
R47			120	0.5	2.5	96	11147	23800	2.79
R48		**I2a**	100	0.5	4	43	5597	16900	2.04
R49			120	0.5	2.5	50	6500	40300	1.86
R50		**I2a**	100	2	6	85	19582	46501	1.71
R51			120	2	2.5	96	22116	22905	1.56
R52		**I2a**	100	2	6	73	17842	33034	1.74
R53			120	2	2.5	70	17109	28701	1.58
R54		**I2a**	120	1	9	99	21213	15200	2.17
R55		**I2a**	120	1	36	24	5479	8100	3.48
R56		**I2a**	120	1	9	97	19327	12697	1.56
R57		**I2a**	120	1	36	39	7681	5699	1.85

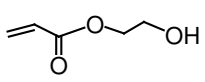
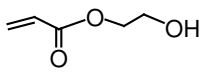
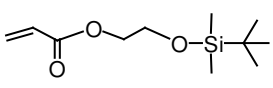
In general, the overall rates of polymerization increased with use of initiator **I2a**, compared to the use of **I2b** (Table 3.3.6). For instance, the polymerization rate of acrylate **M13b** initiated by **I2a** reaches 96% conversion after only 2.5 h at 120°C (**R51**), in direct contrast to **I2b** for which a conversion of 98% is obtained after 14 h (**R27**). A similar increase of conversion can be seen in the polymerization of methacrylate **M13a** (70% conversion after 2.5 h, **R53**) initiated by **I2a**, compared with the use of **I2b** (63% conversion after 14 h, **R28**).

This improvement now permits acrylate and methacrylate monomers to be polymerized by **I2a** with high conversion in only 2-3 h, compared to 14 h for **I2b**. Attempts to perform the polymerization of acrylate monomers at lower temperatures were also successful with moderate conversion (ca. 40-85%) being obtained after heating at 100°C for 4-6 h (**R46**, **R48**, **R50**, **R52**).

Interestingly, an increase in the rate of polymerization was again observed when the comparing polymerizations of acrylamides and methacrylamides initiated by **I2a** and **I2b**, though this was not as dramatic an increase as in the polymerization rate of acrylates. These findings suggested that the increased efficiency of **I2a** is monomer dependent. As with the use of **I2b** the polymerizations rates of acryl derivatives are higher than the corresponding methacryl derivatives. Unfortunately, all polydispersities of the polymers are rather high. With the exception of **R51**, the experimental molecular weights of the derived polymers are quite different from the theoretical values calculated.

The high rate of polymerization, coupled with the increased polydispersity, suggests that the presence of an additional nitroxide-mediating agent may be required to give a true living character, a concept similar to that previously reported[63] for the homopolymerization of acrylate monomers. A small excess (5 mol%) of free nitroxide **37** was therefore added to the reaction mixture (**R63**, **R64**). As can be seen in Table 3.3.11, the polydispersities are still high, even with use of a lower concentration of the monomer (**R61**, **R62**). Therefore, the effort to use **I2a** for controlled radical polymerization of multifunctional acryl- and methacryl derivatives failed.

Table 3.3.11. Polymerization of acrylates initiated by initiator **I2a** at 120°C.

No.	M M:I=100:1	I	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R58		**I2a**	120	bulk	0.33	93	10798	20200	3.14
R59			120	2	2.5	94	10914	16700	3.35
R60			120	1	2.5	91	10566	23000	3.23
R61			120	0.5	2.5	96	11147	23800	2.79
R62			120	0.3	3.5	88	10218	12600	2.36
R63		**I2a** +NO·(**37**)	120	2	2	78	9057	17500	2.46
R64		**I2a** + NO·(**37**)	120	2	2.5	93	21425	26630	1.62

3.3.2.2.4. Polymerization of *n*-butyl acrylate initiated with initiator I2a

The initial effort of controlled radical polymerization of multifunctional acryl- and methacryl derivatives initiated by **I2a** come from the study of Hawker's report.[64] They reported that the polymerization of *n*-butyl acrylate, initiated by **I2a** in the presence of 5 mol% of the corresponding nitroxide **37**, reaches 80% conversion after 2 h at 120°C, accompanied by narrow polydispersities (in the region of 1.1) and controlled molecular weight. Due to the previous failure of the controlled radical polymerizations of multifunctional acryl- and methacryl derivatives, the same polymerizations were repeated to check for reproducibility.

In our original screening process, a polydispersity of 1.33 was obtained after only 1 h (**R73**) when nitroxide **37** was used as a capping agent at 120°C. A polydispersity of 1.33 is higher than Hawker's value of 1.1. Therefore, as seen in Table 3.3.12, different amounts of solvent were used for further polymerization of *n*-butyl acrylate to optimize the reaction conditions. The results show that all polydispersities achieved are around 1.31-1.46, with exception of the protected nitroxide **33** as scavenger (**R69**), when the PD of 1.61.

When the concentration of monomer in DMF was increased the difference of experimental molecular weights of the derived polymers with the theoretical values decreased (**R65, R66, R67** at 100°C**; R70, R71, R72** at 120°C). At a temperature of 120°C, the agreement between experimental and calculated M_n values was excellent when the lowest concentration of monomer was used (**R72**).

Table 3.3.12. Polymerization of *n*-butyl acrylate with initiator **I2a** at 100°C and 120°C in DMF ([M]/[**I2a**] = 200:1 or [M]/[**I2a**]/[**37**] = 200:1:0.05).

No.	I	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R65	**I2a**	100	bulk	1	90	23071	84740	1.43
R66		100	2	1	87	22302	42257	1.41
R67		100	1	3.5	96	24609	37360	1.40
R68	**I2a**+NO· (**37**)	100	bulk	0.5	77	19738	43860	1.42
R69	**I2a**+NO· (**33**)	100	bulk	0.5	82	20763	69821	1.61
R70	**I2a**	120	bulk	1	92	23583	33540	1.46
R71		120	2	1	95	24352	30000	1.31

R72		120	1	3.5	99	25378	25830	1.39
R73	**I2a**+NO· (**37**)	120	bulk	1	90	23071	22074	1.33
R74	**I2a+**NO· (**33**)	120	bulk	0.5	84	21533	44278	1.38

When the polymerization of *n*-butyl acrylate was performed at lower temperature, the polydispersities are still around 1.3-1.4 (Table 3.3.13). However the difference of the experimental and calculated M_n values increased with a decrease in the temperature.

Table 3.3.13. Polymerization of *n*-butyl acrylate with initiator **I2a** at different temperature in DMF ([M]/[**I2a**] = 200:1).

No.	I	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R75	**I2a**	70	2	23	84	21533	100100	1.42
R76	**I2a**	80	2	8	96	24609	64810	1.33
R77	**I2a**	100	2	1	87	22302	42257	1.41
R78	**I2a**	120	2	1	95	24352	30000	1.31

The polymerizations of *n*-butyl acrylate with initiator **I2a** at 120°C were carried out with different ratios of monomer to initiator (Table 3.3.14). Remarkably, the experimental molecular weights of the derived polymers are close to the theoretical values, and the polydispersities are 1.39-1.42 (**R79**, **R80**, **R81**).

Table 3.3.14. Polymerization of *n*-butyl acrylate initiated by initiator **I2a** with a different ratio of monomer to initiator at 120°C in DMF.

No.	M : **I2a** (mol/mol)	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R79	M:I (200:1)	120	1	3.5	99	25378	25830	1.39
R80	M:I(100:1)	120	1	3.5	99	12689	14160	1.42
R81	M:I(75:1)	120	1	3.5	99	9517	11230	1.40

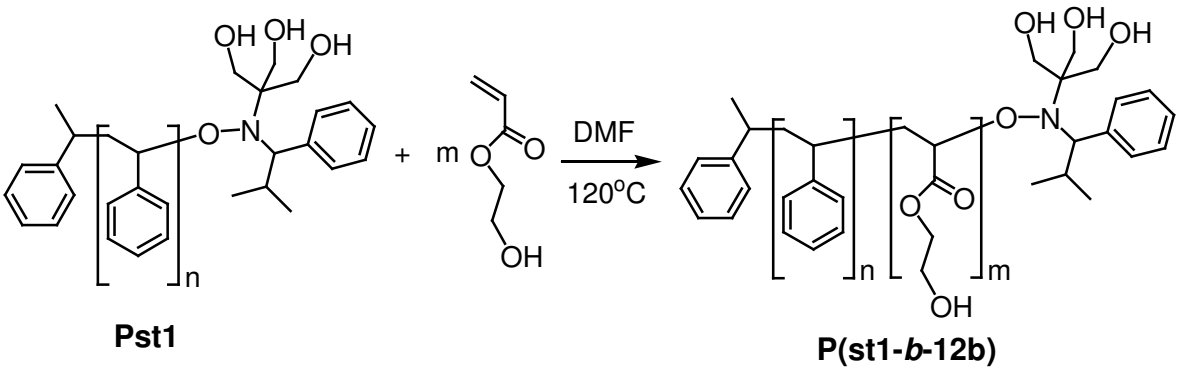
All the results above are consistent with the previous work of Hawker, i.e. the use of **I2a** as the mediating nitroxide leads to a faster rate of polymerization when compared to the use of **I2b**.[64] However, the low polydispersity of 1.1 from Hawker's report[64] was not reproducible. Another advantage of initiator **I2a** is that the nitroxide and alkoxyamine have reactive hydroxyl functionalities, which can be used to prepare telechelic polymers and further modified systems such as chromophore-labeled materials.[231, 232]

3.3.2.3. Block copolymerization

One of the primary driving forces behind the recent interest in living radical procedures is the ability to prepare block copolymers. The alkoxyamine-terminated polymer achieved by nitroxide-mediated homopolymerization can be used as a macroinitiator to prepare block copolymers. The right choice of the first block is thus crucial for efficient synthesis of block copolymers. To carry out the copolymerization the alkoxyamine-terminated polystyrene **Pst1** made by NMP of styrene initiated by **I2a** (Table 3.3.15) was selected as a macroinitiator to initiate the polymerization of second monomers. An example of such block copolymerization is shown in Scheme 3.3.6.

Table 3.3.15. Homopolymerization of styrene (M:I=100:1).

No.	M	I	T (°C)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD
Pst1	styrene	**I2a**	120	5	72	7498	7309	1.10



Scheme 3.3.6. Synthesized block copolymer **P(st1-*b*-12b)** starting from polystyrene.

The functional end group in alkoxyamine-terminated polystyrene **Pst1** could be clearly observed from ^{1}H-NMR spectra (**A**), shown in Figure 3.3.11. Comparing the proton spectra (**A**) of homopolymer polystyrene and the proton spectra (**B**) of block copolymer **P(st1-*b*-12b)** shown in Figure 3.3.11, it s possible to see new signals at 4.75 ppm (-OH), 4.01 and 3.56 (-CH_2-). These peaks are generated from the monomer **M12b** units present in the chain. All the block copolymer samples have been characterized by NMR and GPC.

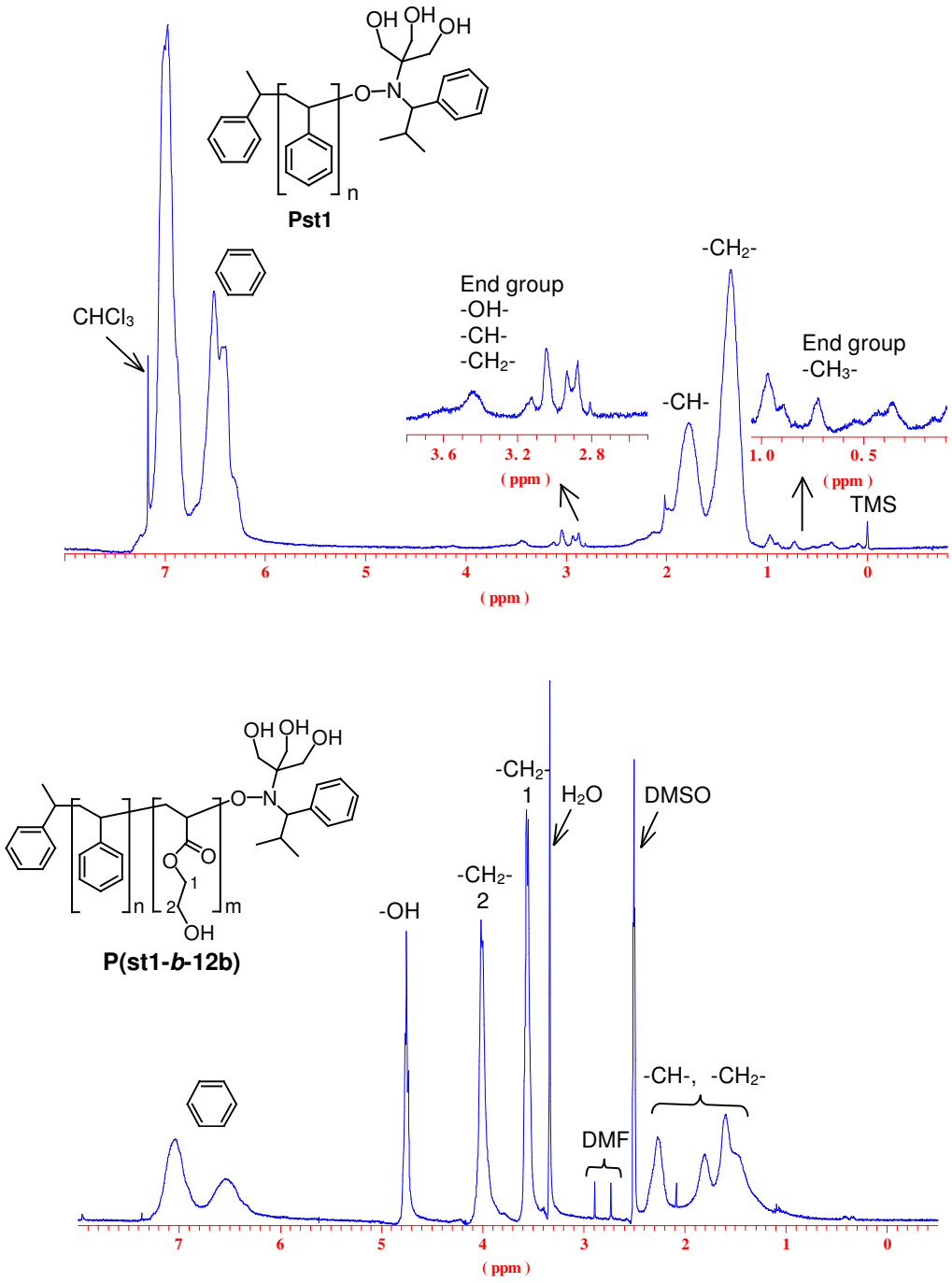
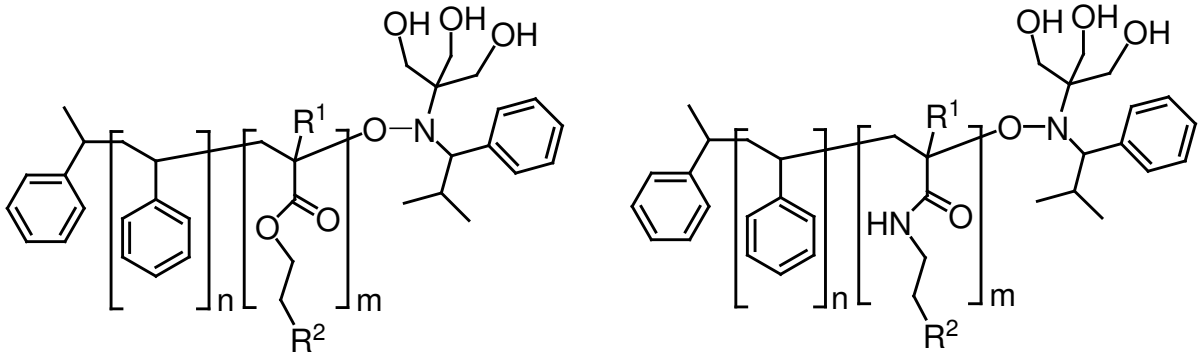


Figure 3.3.11. ^{1}H-NMR spectra of alkoxyamine-terminated polystyrene **Pst1** (**A**) and block copolymer **P(st1-*b*-12b)** (**B**) by NMP.

The polymerization data of different block-copolymers are summarized in Figure 3.3.12 and Table 3.3.16. The copolymerization rates of acryl derivatives are faster than those of methacryl derivatives. For acrylates, conversions of 86% **P(st1-*b*-12b)** and 95% **P(st1-*b*-13b)** were obtained after only 1 hour. The rates of acrylates and methacrylates are higher than those of acrylamides and methacrylamides.

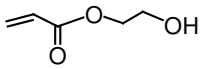
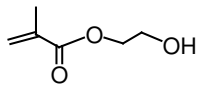
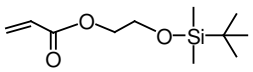
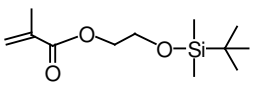
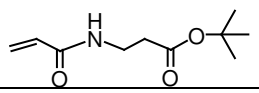
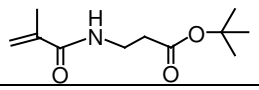


R^1 = H , R^2 = OH: **P(st1-*b*-12b)**
R^1 = CH_3, R^2 = OH: **P(st1-*b*-12a)**
R^1 = H, R^2 = OTBDMS: **P(st1-*b*-13b)**
R^1 = CH_3, R^2 = OTBDMS: **P(st1-*b*-13a)**

R^1 = H, R^2 = COOTB: **P(st1-*b*-9b)**
R^1 = CH_3, R^2 = COOTB: **P(st1-*b*-9a)**

Figure 3.3.12. Block copolymers by NMP.

Table 3.3.16. Block co-polymerization of acryl- and methacryl derivatives starting from alkoxyamine-terminated polystyrene.

No.	M M:I=200:1	macroI	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
P(st1-*b*-12b)		**Pst1**	120	0.5	1	86	26971	11800	1.28
P(st1-*b*-12a)		**Pst1**	120	0.5	1	36	16370	8900	1.27
P(st1-*b*-13b)		**Pst1**	120	1	1	95	50772	14160	1.43
P(st1-*b*-13a)		**Pst1**	120	0.5	1	44	28508	17450	1.72
P(st1-*b*-9b)		**Pst1**	120	0.5	128	98	46053	12584	1.27
P(st1-*b*-9a)		**Pst1**	120	0.5	128	20	15531	13425	1.46

The GPC results show that almost all block-copolymers contain higher molecular weight and higher molar mass distributions as compared to the polystyrene (**Pst1**) macroinitiator. Examples of the GPC curves are given in Figure 3.3.13.

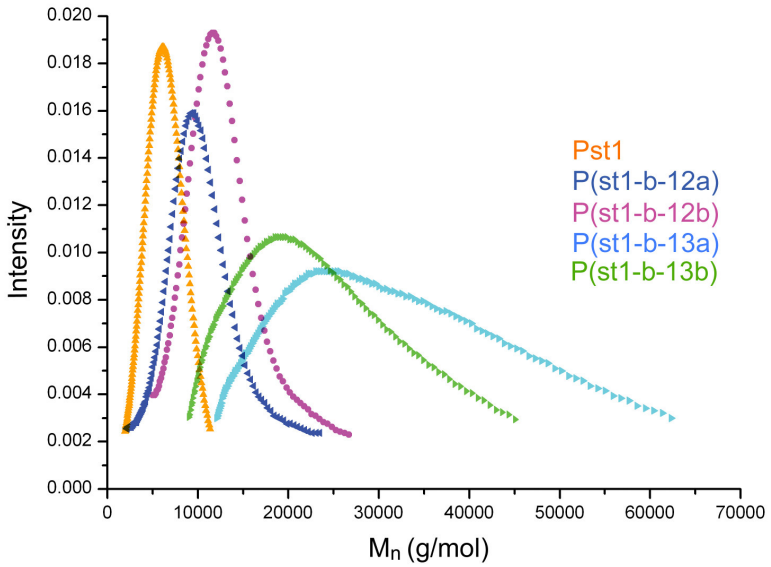


Figure 3.3.13. The GPC curves of block-copolymers.

In comparison with the corresponding homopolymers initiated by **I2a**, all the block co-copolymers have lower polydispersities. The PD of most block-copolymers are lower than 1.5. The polydispersities of block-copoly(acryl derivatives) are lower than those of block-copoly(methacryl derivatives), with the exception of **P(st1-*b*-12b)** and **P(st1-*b*-12a)** (almost equal PD=1.28 and 1.27). However, the experimental molecular weights of the derived block-copolymers are lower than the theoretical values.

Nevertheless, amphiphilic block copolymers with narrow molar mass distribution, which contain a hydrophobic and a hydrophilic block, could be synthesized. It was proved that the macroinitiator **Pst1** with an alkoxyamine functional end group is able to initiate the polymerization of a second monomer species to achieve block-copolymers.

- **Conclusion**

In comparison with TEMPO-based initiators **I1c** (Hawker Adduct I), **I2a** and **I2b** (Hawker Adduct II), especially **I2a** gives a much faster polymerization rate of a range of monomers such as styrene, acrylates, methacrylates, and acrylamides. However, the homopolymerization of multifunctional acryl- and methacryl derivatives initiated by **I1c**, and **I2a** and **I2b** afforded

homopolymers with rather higher polydispersities, which indicates that it was failed to polymerize multifunctional acryl- and methacryl derivatives in a controlled way.
The polymerization of styrene initiated by **I1a**, **I1b**, **I1c** (Hawker Adduct I) and **I2a**, **I2b** (Hawker Adduct II) gave polystyrenes with low polydispersity. With the use of **I2a** the polymerization of styrene proceeded very fast and in a controlled way. The alkoxyamine-terminated polystyrene is also able to initiate the polymerization of multifunctional acryl- and methacryl derivatives to afford various block copolymers with narrow molar mass distribution.

3.3.3. Controlled Radical Polymerization by ATRP

A large amount of monomers have been polymerized by atom transfer radical polymerization (ATRP).[91, 233-236] Important parameters of ATRP are: the catalyst system, the reaction temperature, and the ratios between the components of the entire reaction system. In addition, the concentration of the monomer in the reaction solution and the reaction time have to be tailored to obtain the desired products. For this reason it was important to find optimized conditions for the controlled radical polymerization of the selected acryl- and methacryl derivatives, in order to generate the corresponding polymers with a low polydispersity and a reasonably high polymerization rate.

3.3.3.1. ATRP of (meth)acrylates

To optimize the reaction conditions and to investigate the influence of different factors like ligand, initiator, and solvent, the simple commercially available *n*-butyl acrylate was used as a model monomer.

- **ATRP of *n*-butyl acrylate**

A. Selection of the transition metal/halide system

Atom transfer radical polymerization with copper and nitrogen ligands as catalysts is one of the most investigated systems, probably due to its low cost and versatility in terms of polymerizable monomers. One important structural parameter in the ATRP process is the transferred atom (or group), represented by a halogen in this work. The use of different transferred atoms changes the rate of polymerization as well as the level of control over the polymerization.[8] ATRP with Cl-based systems is usually slower and less controlled than those

with Br-based systems.[23, 237] The reason is that the rate constant of the activation step is smaller in Cl-based systems than in Br-based systems. The overall equilibrium is dominated by the differences in the activation rate constants, resulting in slower rates of polymerization for Cl-based system. At the same time, the slower deactivation rate in the Cl-based system leads to higher polydispersities.[23, 237] Therefore in our work copper bromide (CuBr) has been chosen as transition metal/halide system.

B. Effect of ligands

The ligand tunes the electronic, steric, and solubility properties of ATRP catalysts.[8] Thus, the determination of the right ligand is very important. 2,2'-bipyridine (bipy) is one of the "first generation" ligands,[16] unfortunately, 2,2'-bipyridine leads to heterogeneous systems and is a relatively expensive compound. For these reasons, alkyl chains were introduced on the 4,4'-positions, such as 4,4'-di-*tert*-butyl-2,2'-bipyridine (DTB-bipy), increasing the solubility and improving the product properties.[88, 125] Actually, both of them are weak ligands for copper. We decided to test them together with two more strongly binding ligands: *N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine (PMDETA)[238, 239] and tris[2-(dimethylamino)-ethyl]amine (Me_6TREN)[91, 240] (see Fig. 3.3.14). These four representative ligands have been used in the effort of understanding which level of control can be achieved, what the effect on the distribution of the molar masses is and what the effect of the ligands on the rate of ATRP is.

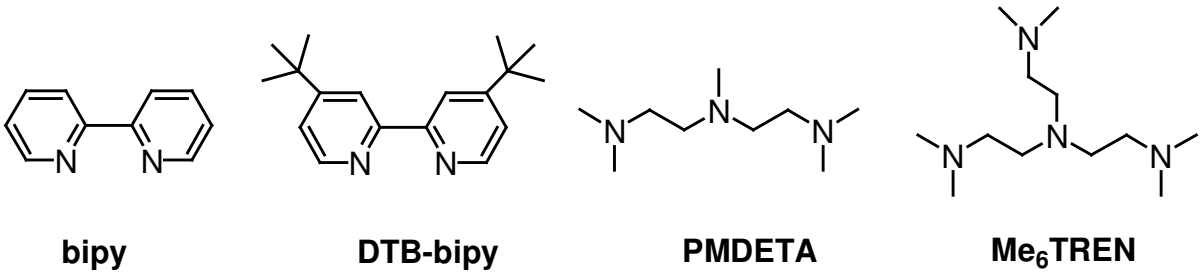


Figure. 3.3.14. Multidentate nitrogen-based ligands.

Another main feature in the optimization of the reaction conditions is the ratio between the various components. Considering the solubility and the relatively smooth polymerization, the ratios between the components of the ATRP reaction system are fixed at [Monomer] : [Initiator] : [CuBr] : [Ligand] equal to 100:1:1:2 (molar ratio). When a solvent was used, the concentration of the monomer in solvent is, in general, 0.5-1 g/ml (monomer/solvent).

The effect of ligands on the polymerization was investigated. As can be seen in Table 3.3.17, the data obtained here for four ligands clearly indicate that the rates of the ATRP of *n*-butyl acrylate can be adjusted by using different ligands. For example, a very fast polymerization was observed when *n*-butyl acrylate was polymerized in bulk using Me_6TREN or PMDETA as ligand, methyl 2-bromopropionate (MBrP) as an initiator and copper bromide (CuBr) as the catalyst. Under conditions of M : I : CuBr : L = 100:1:1:2, use of Me_6TREN (**R82**) or PMDETA (**R83**) gives monomer conversions of 82% and 70% after 20 min or 1.5 h at 90°C, respectively. Under the same conditions, however, a weaker binding ligand such as DTB-bipy- and bipy-based catalytic systems (**R84**, **R85**) gave slower polymerization rates. Only 57% and 64% monomer conversion were reached after 8 and 9.5 hours.

During the polymerization one could observe that the color of copper changed (light green for Me_6TREN; mint green for PMDETA; dark orange for DTB-bipy; and brown for bipy), and the homogeneous solutions became viscous as the reaction time increased. All the polymer solutions were purified by passing through alumina columns before characterization by gel permeation chromatography (GPC). The polymer solutions were almost colorless after being passed through the alumina columns, indicating the strong coordination between copper and the ligand and the separation by alumina.

Table 3.3.17. Effect of the ligand on the rate of polymerization of *n*-butyl acrylate using MBrP and EBrP as initiator ([M]:[I]:[Cat]:[L] = 100:1:1:2).

No.	I	Cat	L	T (°C)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R82	MBrP	CuBr	Me_6TREN	90	20 min	82	10510	9845	1.18
R83			PMDETA	90	1.5	70	8972	8812	1.11
R84			DTB-bipy	90	8	57	7306	7259	1.20
R85			bipy	90	9.5	64	8203	14250	1.37
R86	EBrP	CuBr	Me_6TREN	90	0.5	98	12560	14140	1.27
R87			PMDETA	90	2.25	85	10894	9700	1.19
R88			DTB-bipy	90	17	80	10254	12940	1.22
R89			bipy	90	20	82	10510	13420	1.32

The GPC results in Table. 3.3.17 show that Me_6TREN, PMDETA, and DTB-bipy were clearly suitable ligands for the polymerization of *n*-butyl acrylate using MBrP as initiator. The agreement between the experimental and theoretical molecular weight are excellent and the distributions are quite narrow (PD = 1.11-1.20), confirming that the reactions undergo a controlled mechanism. Compared to the other ligands, bipy gives a remarkably higher experimental molecular weight of the product than those predicted by the ratio of monomer to initiator and a relatively broad distribution (PD = 1.37). The weak bonding ability of the amine and the worse solubility of the CuBr in bipy, which leads to a heterogeneous system could be responsible for this behavior.

C. Effect of initiator

The ATRP of *n*-butyl acrylate was carried out under the same reaction conditions as described previously, but ethyl 2-bromopropionate (EBrP) was used as an initiator instead of MBrP. All the polymerization data are also given in Table 3.3.17. While the polymerization time is prolonged, all the monomer conversions are higher than when MBrP is used as an initiator (**R86**, **R87**, **R88**, **R89**). In general, no significant difference is observed in the rate of polymerization using the different initiators. Differences in the polymerization rate are observed again when using different ligands. The experimental molecular weights of the products are in agreement with the theoretical molecular weight and the distributions are relative narrow (PD = 1.19-1.32).

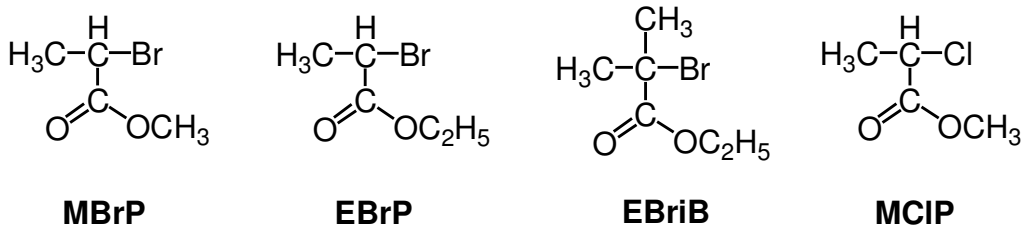


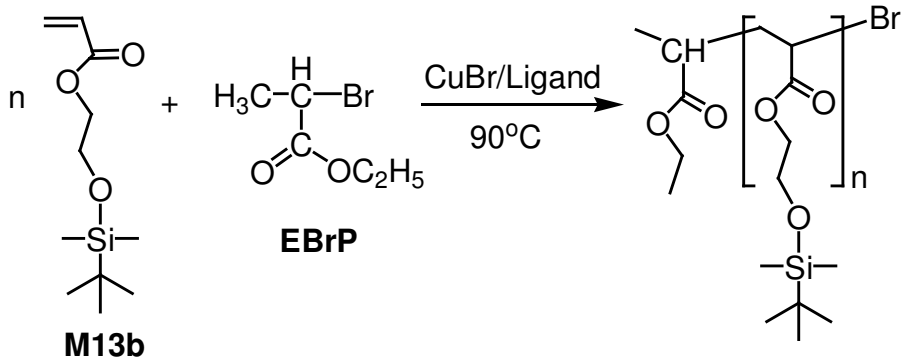
Figure 3.3.15. Initiators used in ATRP.

Hence, the choice of initiators did not significantly influence either the rate of the ATRP of *n*-butyl acrylate or the degree of control of the polymerization. The structures of initiators, which were used, are summarized in Figure 3.3.15. The polymerizations using MBrP and EBrP as initiator both showed that the rate of polymerization of *n*-butyl acrylate decreases in the order of Me_6TREN >> PMDETA > DTB-bipy > bipy, which is consistent with the order of the rates in the copper-catalyzed ATRP of methyl acrylate.[241] On the basis of this result the first three

ligands have been selected for the further investigation of ATRP polymerization of (meth)acrylate derivatives **M13a**, **M13b**, **M15a** and **M15b** for considerable short reaction time and narrow distribution of polymer.

- **ATRP of 2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl acrylate (M13b)**

ATRP of 2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl acrylate was carried out, in bulk, under the same conditions as the previous described ATRP of *n*-butyl acrylate (Scheme 3.3.7). The reaction conditions and the results are summarized in Table 3.3.18.



Scheme 3.3.7. Homopolymerization of **M13b** by ATRP.

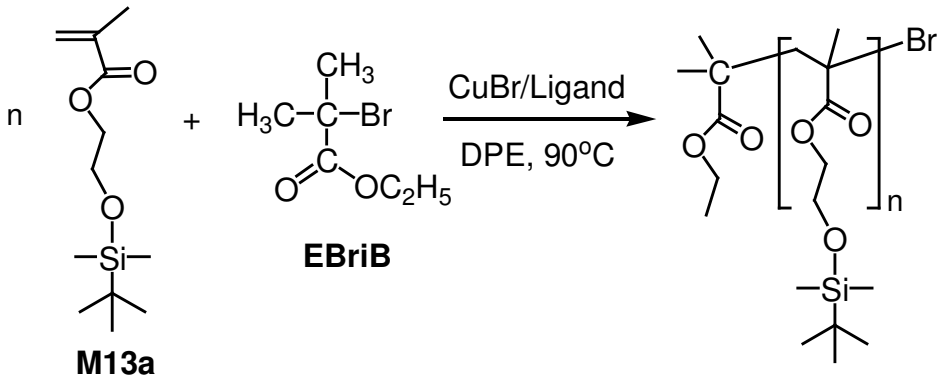
One can see that the ATRP system using Me_6TREN (**R90**) as a ligand showed very fast polymerization rates; a conversion of 90% was achieved only after 10 min. The ligands Me_6TREN (**R90**) and PMDETA (**R91**) afforded polymers with narrow weight distribution (PD = 1.24 and 1.18), and a satisfactory agreement of experimental and the theoretical molecular weights. As similarly observed for *n*-butyl acrylate, the polymerization of **M13b** in the presence of DTB-bipy as ligand (**R92**) went slowly, only 67% monomer conversion was reached after 11 hours. The resulting polymer showed a number average molecular weight (M_n) of 18066 and a polydispersity of 1.43. The polydispersity value rises significantly (PD = 1.43) in comparison to those produced with the ligands Me_6TREN and PMDETA, but are still lower than 1.5.

Table 3.3.18. ATRP of 2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl acrylate (**M13b**) (M:I:Cat:L=100:1:1:2).

No.	I	Cat	L	T (°C)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R90	EBrP	CuBr	Me_6TREN	90	10 min	90	20734	17090	1.24
R91	EBrP	CuBr	PMDETA	90	2.5 h	93	21425	17707	1.18
R92	EBrP	CuBr	DTB-bipy	90	11 h	67	15435	18066	1.43

- **ATRP of 2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl 2-methylacrylate (M13a)**

The alkyl halide ethyl 2-bromoisobutyrate (EBriB) was used as initiator for ATRP of 2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl 2-methylacrylate (**M13a**). The atom transfer radical polymerization of **M13a** was carried out in diphenyl ether (DPE) under the same reaction condition as the previous ATRP of **M13b** (Scheme 3.3.8).



Scheme 3.3.8. Homopolymerization of **M13a** by ATRP.

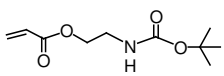
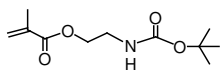
The results of ATRP of **M13a** are summarized in Table 3.3.19 and show no significant difference in the rate of polymerization and the polydispersities from the ATRP of **M13b**. Similar to the ATRP of **M13b**, the lowest polydispersity (PD = 1.22) comes from the PMDETA (**R94**) ligand system.

Table 3.3.19. ATRP of 2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl 2-methylacrylate (**M13a**) in DPE (1 g/ml) (M:I:Cat:L=100:1:1:2).

No.	I	Cat	L	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R93	EBriB	CuBr	Me_6TREN	90	1	2	88	21508	18576	1.32
R94	EBriB	CuBr	PMDETA	90	1	4	96	23110	21000	1.22
R95	EBriB	CuBr	DTB-bipy	90	1	8	98	23952	28026	1.44

Two other monomers, methacrylate **M15a** and acrylate **M15b**, were polymerized under the same reaction conditions using PMDETA as ligand. The results are shown in Table 3.3.20. The distributions are both narrow (PD = 1.21 for **R96**, PD = 1.26 for **R97**), confirming that PMDETA is an effective ligand for the ATRP of acrylates and methacrylates.

Table 3.3.20. ATRP of 2-[(*tert*-butoxycarbonyl)amino]ethyl 2-methylacrylate (**M15a**) and 2-[(*tert*-butoxycarbonyl)amino]ethyl acrylate (**M15b**) in DMF (0.5 g/ml) (M:I:Cat:L=100:1:1:2) using PMDETA as ligand.

No.	M	I	Cat	L	T (°C)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R96		EBriB	CuBr	PMDETA	90	2.5	50	10763	9122	1.21
R97		EBriB	CuBr	PMDETA	90	1.5	93	21323	20440	1.26

The results received lead to the conclusion that the ligand has an important influence on the rate of polymerization of (meth)acrylates, as well as on the degree of control of the polymerization. ATRP of acrylates and methacrylates were rather rapid using Me_6TREN as ligand. A high conversion is often achieved in a few minutes, giving polymers with a narrow distribution. Systems using PMDETA as a ligand show reasonably high polymerization rates in the space of 2-4 hours and afford polymers in high yield with quite narrow distributions. In comparison with the stronger ligands Me_6TREN and PMDETA, polymerization with DTB-bipy proceeded slowly and gave polymers with a relatively high polydispersity. PMDETA is

the most effective ligand for the ATRP of acrylates and methacrylates when considering the rate of polymerization and the polydispersity.

- **Living character**

To see if the polymerization could be controlled, the relationship between time-conversion and molecular weight-conversion was studied. In principle, the characteristics of a controlled process are revealed through (1) a first-order kinetic plot of molecular weight and conversion, and (2) a low polydispersity.

The living character was investigated by ATRP of 2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl acrylate **(M13b)** with molar ratio of **M13b** : EBrP : CuBr : PMDETA = 100:1:1:2. As shown in Figure 3.3.16, although the linear relationship between conversion and reaction time is not perfect (R^2 = 0.918), an excellent linear relationship is seen between $\ln([M]_0/[M])$ and reaction time, obeying first-order kinetics (R^2 = 0.995), and indicating that the number of propagating species remained constant.

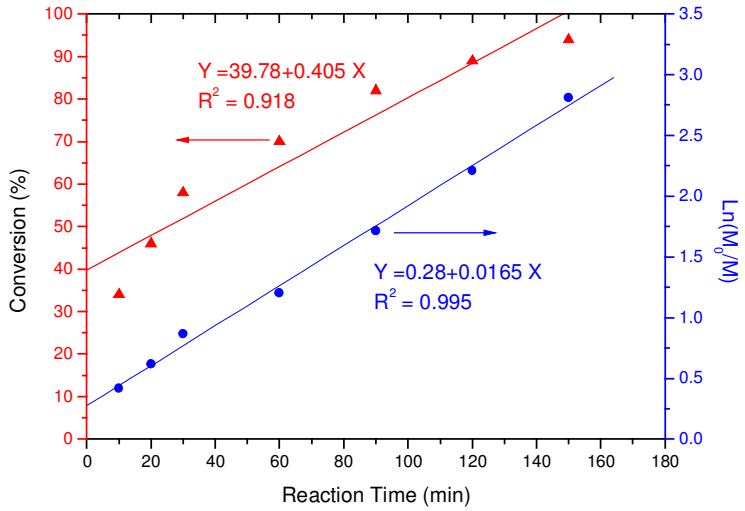


Figure 3.3.16. Kinetics plot of the ATRP of **M13b** using PMDETA as ligand (Molar ratios **M13b** : EBrP : CuBr: PMDETA = 100:1:1:2, 90°C).

Further, one can observe from Figure 3.3.17 that the molecular weights increase linearly with conversion, and the polydispersities decrease to 1.18 from 1.30 over the same period. However, the molecular weights measured by GPC are lower than the theoretical values, especially at the higher conversion. It seems possible that the polymer chain might partly broke with increasing polymerization time. The break of polymer chains during ATRP has been reported in the literature.[109]

Nevertheless, the linear kinetic plot and low polydispersity confirmed that the ATRP of **M13b** proceeded in a living fashion when PMDETA was used as a ligand.

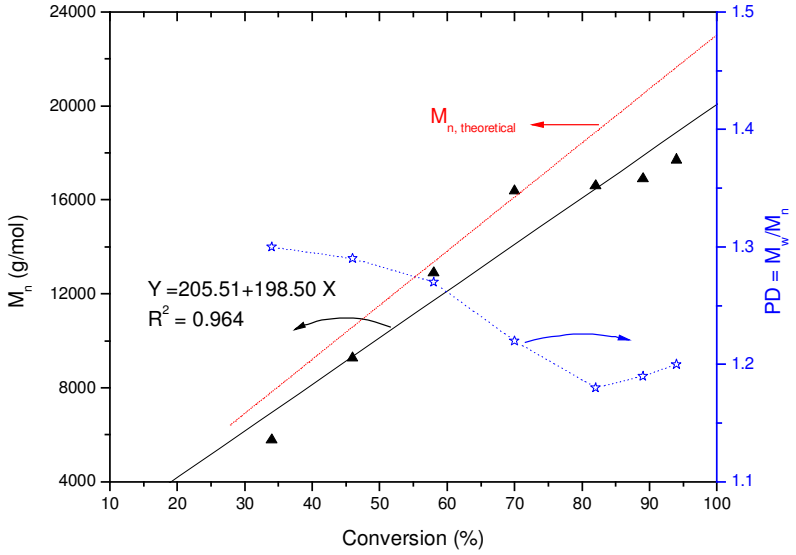


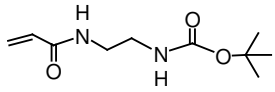
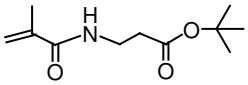
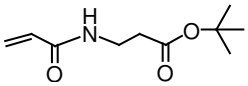
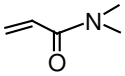
Figure 3.3.17. Effect of conversion during the ATRP of **M13b** on the PD and molecular weight using PMDETA as ligand.

3.3.3.2. ATRP of (meth)acrylamides

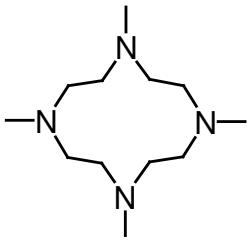
Various initiators, copper halides and ligand systems have been used in the ATRP of (meth)acrylamides. As can be seen in Table 3.3.21 in Me_6TREN- and PMDETA-based catalytic systems (**R98**, **R99**, **R100**, **R101**) no polymers were obtained after a reaction time of 30 days at room temperature, although these ligands were successfully used in the ATRP of styrene, methyl methacrylate and other monomers.[76] In general, an increase in temperature can increase the rate of an ATRP process. However the increase of temperature to 50°C and 90°C did not significantly improve the reaction rate of the systems (**R102**, **R103**, **R104**, **R105**). Only traces of polymer were found in the systems after 20 days at 90°C.

In addition, the ATRP of the common monomer *N*,*N*-dimethylacrylamide (DMAA) using methyl 2-chloropropionate (MClP)/CuCl/Me_6TREN as the initiating/catalyst system in toluene solution, at room temperature, did not lead to a polymer after 5 days (**R106**, **R107**). This is in contrast to Neugebauer and Matyjaszewski's reports.[242] They prepared homopolymers of DMAA with narrow molecular weight distribution (M_w/M_n = 1.05-1.06) in 70-79% yield under the same reaction condition after 2-4 hours.

Table 3.3.21. ATRP of (methyl)acrylamides DMF/toluene = 1:1 v/v (M:I:Cat:L=100:1:1:2); DMAA performed in toluene (M:I:Cat:L=100:1:2:2).

No.	M	I	Cat	L	T (°C)	Con. (g/ml)	t (day)	Y (%)
R98		MClP	CuCl	Me_6TREN	25	0.5	30	0
R99		MBrP	CuBr	Me_6TREN	25	0.5	30	0
R100		MBrP	CuBr	Me_6TREN	25	0.5	30	0
R101		MClP	CuCl	Me_6TREN	25	0.5	30	0
R102		MClP	CuCl	Me_6TREN	50	0.5	20	0
R103		MClP	CuCl	Me_6TREN	90	0.5	20	5
R104		MBrP	CuBr	Me_6TREN	90	0.5	20	6
R105		MBrP	CuBr	PMDETA	90	0.5	20	6
R106	 DMAA	MClP	CuCl	Me_6TREN	25	0.5	5	0
R107		MClP	CuCl	Me_6TREN	25	1	5	0

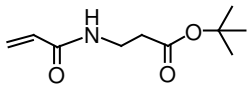
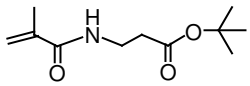
When 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4Cyclam) was used as a ligand, (methyl)acrylamides could be polymerized rapidly at 25°C. With reaction conditions of [Monomer] : [Initiator]: [CuCl]: [Me_4Cylam] equal to 100:1:1:1 (molar ratio), the methacrylamide reaction mixture in DMF became increasingly viscous as the reaction time increased, and the conversion reached 36% after 40 minutes (**R109**). For acrylamide the polymerization proceeded faster, the monomer conversion achieved 98% after only 12 min (**R108,** Table 3.3.22). The stronger complex formation between copper ions and Me_4Cyclam, compared to that with PMDETA or Me_6TREN, might explain the high rate of polymerization of (meth)acrylamide. The results are comparable with those in the literature.[109, 243] Although the ATRP of (meth)acrylamide using Me_4Cyclam as a ligand proceeded very quickly the obtained polymers had a broad distribution (PD = 2.11 and 3.30), indicating that the ATRP proceeded in an uncontrolled fashion.



Me_4Cyclam

Figure 3.3.18. Structure of Me_4Cyclam.

Table 3.3.22. ATRP of (methyl)acrylamides in DMF (0.5 g/ml) (M:I:Cat:L=100:1:1:1).

No.	M	I	Cat	L	T (°C)	t (min)	Y (%)	$M_{n,\ theor}$ (g/ml)	$M_{n,GPC}$ (g/ml)	PD M_w/M_n
R108		MBrP	CuBr	Me_4Cyclam	25	12	98	19527	24170	2.11
R109		MBrP	CuBr	Me_4Cyclam	25	40	36	7678	6917	3.30

Although PMDETA or Me_6TREN were successfully used in ATRP of (meth)acrylates, they did not work for ATRP of (meth)acrylamides. When Me_4Cyclam was used as a ligand, the ATRP proceeded quite rapidly, however, the obtained polymers had rather high polydispersities, indicating an uncontrolled polymerization.

3.3.3.3. ATRP of styrene

ATRP of styrene has been investigated extensively.[22, 236, 244] In contrast to the acryl- and methacryl derivatives, our work with styrene was done in bulk, ATRP conditions, using two kinds of ligands (PMDETA and DTB-bipy). The results are shown in Table 3.3.23.

Table 3.3.23. Styrene polymerized by ATRP (M:I:Cat:L=100:1:2:2).

No.	I	Cat	L	T (°C)	t (h)	Y (%)	$M_{n,theor}$ (g/ml)	$M_{n,GPC}$ (g/ml)	PD M_w/M_n
R110	MBrP	CuBr	PMDETA	90	2	82	8540	17000	1.29
R111	MBrP	CuBr	DTB-bipy	90	24	68	7082	5936	1.19

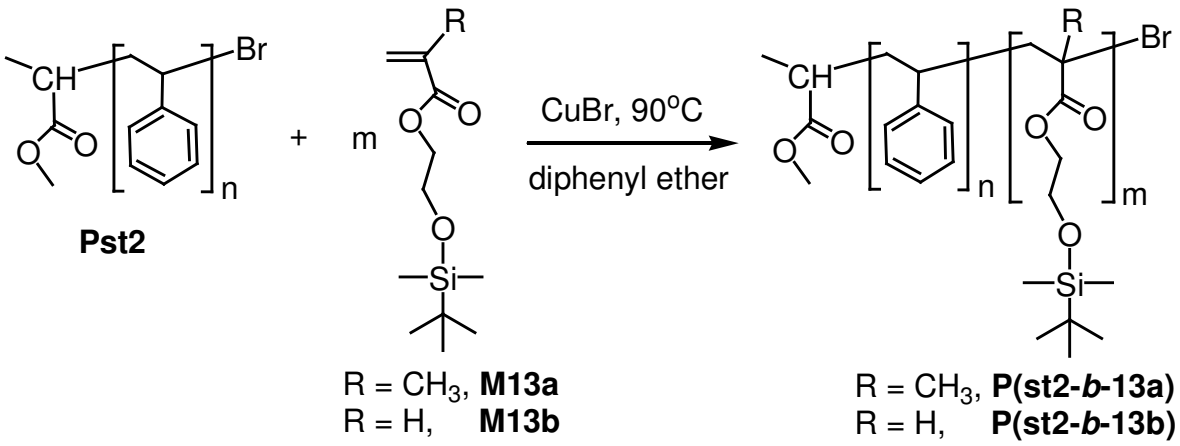
Similar to the ATRP of *n*-butyl acrylate, use of PMDETA as a ligand gave a faster polymerization rate. A conversion of 82% was obtained after 2 hours at 90°C (**R110**). Under the same reaction conditions, a conversion of 68% was reached after 24 hours using DTB-bipy as a ligand (**R111**). Although it takes a longer reaction time using DTB-bipy as a ligand, the values obtained for the polystyrene are excellent. The measured molecular weight is close to the theoretical molecular weight, and the molecular weight distribution is quite narrow (PD = 1.19, **R111**). However, the GPC data for **R110** shows a molecular weight is 50% higher than that predicted by the ratio of consumed monomer to initially injected initiator. The fact that PMDETA is a multi dentate amine could be responsible for this behavior. Compared to aromatic amines, alkyl amines have a more flexible structure that could help them build strong complexes with the growing chain. The decreased concentration of active catalyst in the reaction solution would explain the higher molecular weight. The relatively low polydispersity in both cases suggests that termination reactions were insignificant. Hence, it is relatively easy to get polystyrene with a narrow molecular weight distribution by ATRP.

3.3.3.4. Block-copolymerization by ATRP

The atom transfer radical polymerization was also used to prepare block copolymers, since this method has been successful for different monomers.[22, 236, 244-246] Preliminary investigations have shown that the halogen-terminated polystyrene **Pst2** (M_n = 5936, M_w/M_n =1.19) can be successfully used as macroinitiator for the synthesis of block copolymers **P(st2-*b*-13a)**, **P(st2-*b*-13b)** (Table 3.3.24 and Scheme 3.3.9).

Table 3.3.24. Block copolymerization of **M13a** and **M13b** by ATRP using polystyrene as macroinitiator (M:I:Cat:L=100:1:1:2).

No.	MacroI	Cat	L	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
P(st2-*b*-13a)	**Pst2** M_n=5936 PD=1.19	CuBr	PMDETA	90	0.5	3	54	19134	12040	1.32
P(st2-*b*-13b)		CuBr	PMDETA	90	0.5	2	25	11695	8288	1.40

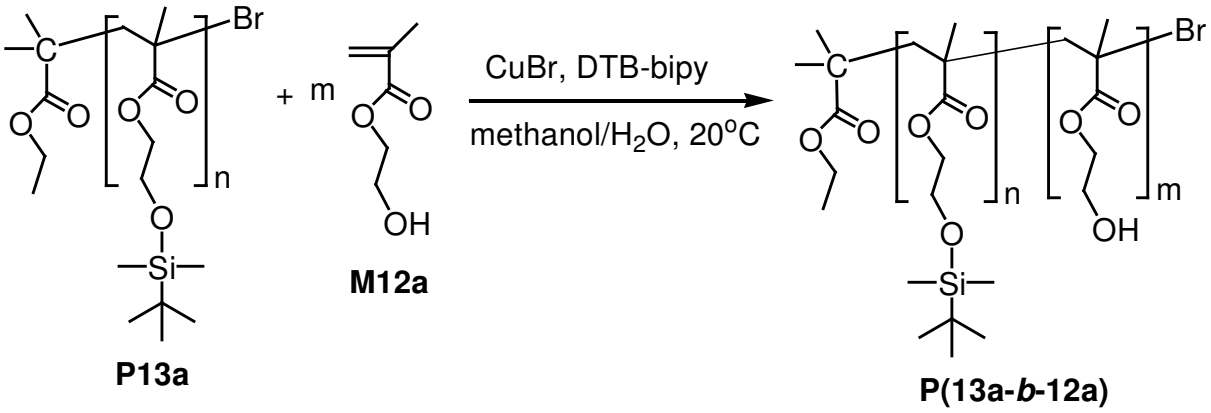


Scheme 3.3.9. Synthesized block copolymers **P(st2-*b*-13a)**, **P(st2-*b*-13b)** starting from **Pst2**.

Robinson has reported that a well-defined homopolymer, poly(HEMA), could be prepared by using a mixed solvent system (50/50 mixture of methanol and water) at ambient temperature.[247] Therefore, the similar reaction conditions were used for the block copolymerization of HEMA initiated by macroinitiator **P13a**. The amphiphilic block copolymer **P(13a-*b*-12a)** could be generated from halogen-terminated poly(2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl methacrylate) **P13a** initiating the polymerization of 2-hydroxyethyl 2-methylacrylate (**M12a**, HEMA) (Table 3.3.25, Scheme 3.3.10). An amphiphilic block copolymer **P(13a-*b*-12a)** with relatively narrow polydispersity (PD = 1.36) was synthesized and the molecular weight measured by GPC is slightly higher than that predicted by the ratio of consumed monomer to initiate macroinitiator.

Table 3.3.25. Block copolymerization of **M12a** by ATRP using **P13a** as macroinitiator (M:I:Cat:L=100:1:1:2).

No.	macroI	Cat	L	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
P(13a-*b*-12a)	**P13a** M_n=21000 PD=1.22	CuBr	DTB-bipy	20	0.5	3	33	25295	27800	1.36



Scheme 3.3.10. Amphiphilic block copolymer **P(13a-*b*-12a)** synthesized by ATRP.

Unfortunately, the methyl and methylene groups of the initiator (i.e. end groups) are overlapped in the broad signals of -CH_3 and -CH_2- groups of the repetition units in the proton NMR spectra. Nevertheless, the different peaks of different regions in the block copolymers are clearly observed in the proton NMR spectra. One example of proton NMR spectra of block copolymer **P(st2-*b*-13a)** is shown in Figure 3.3.19.

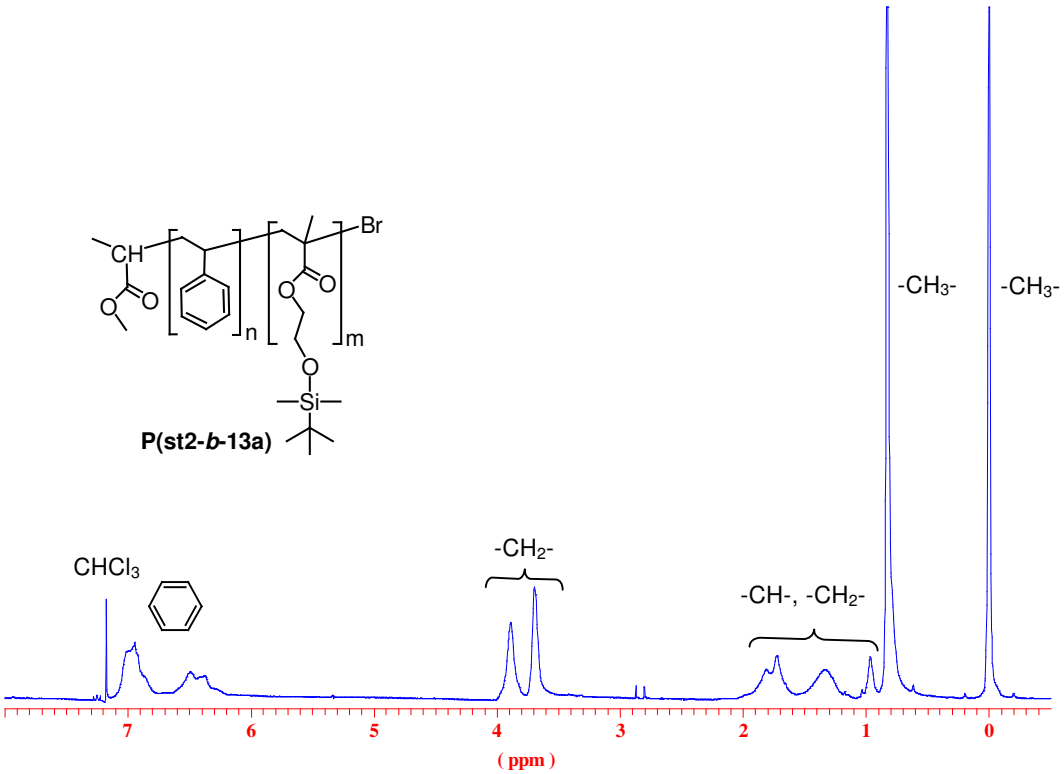


Figure 3.3.19. ^{1}H-NMR spectra of block copolymer **P(st2-*b*-13a)** synthesized by ATRP.

- **Conclusions**

The ATRP of acrylates and methacrylates have been successfully performed under various conditions (Table 3.3.17-3.3.20). The type of ligand has an important influence on the polymerization rate and polydispersity. A relatively low polydispersity of the corresponding polymers and reasonably high rates of polymerization could be achieved when Me_6TREN and PMDETA were used as ligands. Further kinetic studies confirmed that the ATRP of 2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl acrylate **M13b** proceed in a living fashion when PMDETA was used as a ligand.

In systems using Me_4Cyclam as ligand, high polymerization rates of acrylamide and methacrylamide were observed at a low reaction temperature (25°C). However, the ATRP of acrylamide and methacrylamide using Me_4Cyclam as a ligand is an uncontrolled process, as evidenced by the polydispersities of the obtained polymers being rather high ($M_w/M_n \approx$ 2-3). The broad molecular weight distribution may be attributed to termination and transfer reactions in Me_4Cyclam based-systems.

The ATRP of styrene has been successfully performed to achieve a polymer with a narrow distribution.

The halogen-terminated polystyrene **Pst2** (M_n= 5936, M_w/M_n =1.19) and halogen-terminated poly(2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl methacrylate) **P13a** could be used as macroinitiators for the synthesis of block copolymers **P(st2-*b*-13a)**, **P(st2-*b*-13b)** and **P(13a-*b*-12a)**.

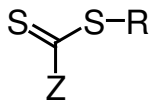
3.3.4. Reversible Addition-Fragmentation Chain Transfer Polymerization

3.3.4.1. General background

So far, the controlled radical polymerization (CRP) of (meth)acrylamide has proven to be challenging using techniques such as atom transfer radical polymerization or nitroxide mediated radical polymerization. Li and Brittain reported the polymerization of as *N*,*N*-dimethylacrylamide (DMAA) by NMP using TEMPO, but the process was shown to be uncontrolled.[248] Subsequently, with the development of more universal nitroxides, Benoit *et al.* demonstrated the ability to polymerize DMAA via NMP.[63] Teodorescu and Matyjaszewski reported the ATRP of several (meth)acrylamides.[102] However, McCormick concluded that

these systems were not "living".[249] This was subsequently confirmed by Rademacher *et al.*[109] Senoo *et al.* reported the ATRP synthesis of PDMAA, employing the $RuCl_2(PPh_3)_3$-based initiating systems, although resulting polydispersities were typically >1.60.[110] With the discovery of reversible addition fragmentation chain transfer (RAFT) polymerization, a wider range of monomers are now amenable to CRP. Significantly, the CRP of DMAA[250-252] and *N*-isopropylacrylamide[253] via RAFT in *organic* media have already been demonstrated. Recently, McCormick reported the synthesis of homopolymers and block copolymers with several acrylamides in aqueous media via RAFT.[249]

The RAFT process, illustrated in Scheme 2.8, involves the conventional free radical polymerization in the presence of a chain transfer agent (CTA) such as a dithioester. The degenerative transfer between the growing radicals and the dithiocarbonyl group provides a "living" or controlled chain growth. The mechanism has been already reviewed in the theoretical part. The key to controlled RAFT polymerizations is the choice of the CTA. The general structure of CTA is given in Figure 3.3.20. A wide range of structurally diverse CTAs have been reported including dithioesters,[17] trithiocarbonates,[18] dithiocarbamates,[51, 151] xanthates,[254, 255] and phosphoryl-/(thiophosphoryl)dithioformates.[24]

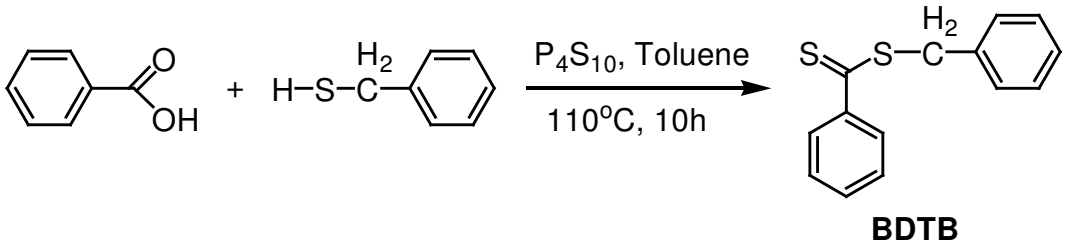


Z = aryl, alkyl, NR'_2, OR', SR'
R = homolytic leaving group

Figure 3.3.20. General structure of CTA.

- **Selection of CTA**

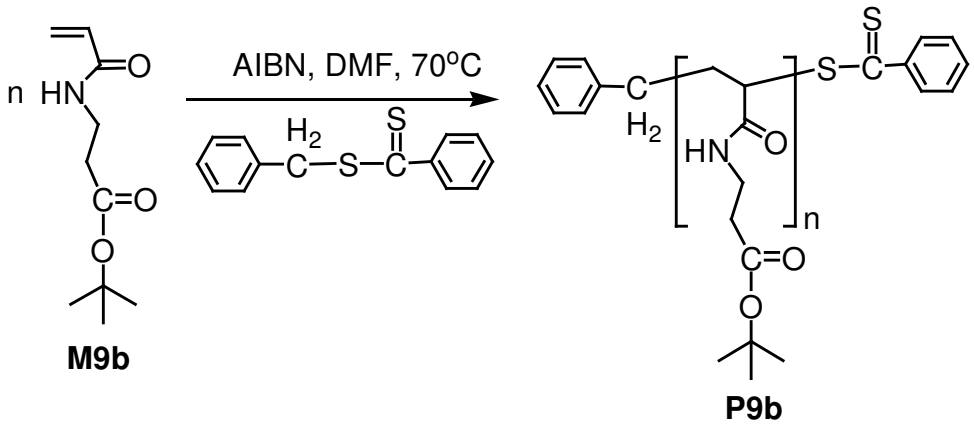
The electronic nature of the Z group (Figure 3.3.20.) influences the relative rates of formation and scission of the radical intermediates. We chose phenyl as the Z group for our studies based on the success of previous authors in the RAFT polymerization of DMAA[44, 143] and other acrylamido-based monomers.[139, 255] The benzyl group was selected as the R group because the leaving radical R• has a sufficient potential energy to reinitiate the polymerization. Benzyl dithiobenzoate (BDTB) is available by synthesis according to literature procedures[256] (Scheme 3.3.11) and was employed as a CTA for the envisaged controlled radical polymerization of multifunctional acryl- and methacryl derivatives.



Scheme 3.3.11. Synthesis of benzyl dithiobenzoate (BDTB).

3.3.4.2. RAFT-process of acrylamides and methacrylamides

The synthesized methacrylamides and acrylamides as well as the common acrylamide DMAA and styrene were used as model monomers for polymerization by the RAFT process, using BDTB as a CTA and AIBN as a conventional radical initiator at CTA:I ratios of 5:1. For solubility reasons, DMF and toluene were used as solvents. An example polymerization of **M9b** is shown in Scheme 3.3.12.



Scheme 3.3.12. RAFT of acrylamide **M9b**.

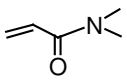
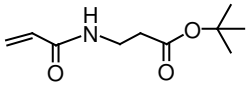
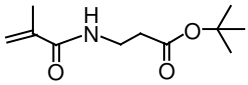
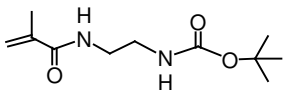
The data from the RAFT process and the theoretical molecular weights ($M_{n,theor}$) for the polymerizations are listed in Table 3.3.26. The $M_{n,theor}$ values, which were determined using Equation 3.3.10, show good correlation with the experimentally determined molecular weights ($M_{n,GPC}$), with the exception of **R116** (methacrylamide). The $M_{n,GPC}$ of **R116** is two times higher than $M_{n,theor}$.

$$M_{n,theor} = \frac{[M]\ x\ MW_{mon}}{[CTA]}\ x\ conversion\% \qquad \textbf{Equation 3.3.10}$$

It can be clearly seen that all the RAFT processes investigated proceeded rather slowly. The

reaction conversion just reached approximately 50% after 42 to 80 h, even by the RAFT polymerization of styrene in bulk. When comparing four polymerizations (**R113**, **R114**, **R115**, **R116**) at specific reaction times (42 h), the polymerizations of methacrylamides (**R115**, **R116**) proceeded slightly faster than those of acrylamides (**R113**, **R114**). A conversion of 50% and 67% respectively was reached for methacrylamides (**R115**, **R116**); but a lower conversion of 40% and 42% was obtained for acrylamides (**R113**, **R114**). Despite the lower polymerization rate, RAFT polymerization of acrylamide **M9b** and DMA afforded polymers with quite low polydispersity (1.19 and 1.22). In the same way, a PD of 1.13 was obtained when styrene (**R112**) was polymerized in bulk. These results indicated that the polymerization rates of acrylamide and styrene are very slow by the RAFT-process using BDTB as a CTA. Thankfully, the molecular weight and the molecular weight distribution of the polymers are controlled. However, the broader PD of 2.17 (**R116**) and 1.46 (**R115**) indicate that CRP of methacrylamide by RAFT polymerization utilizing BDTB as a CTA is still a problem. Though 1.46 is lower than the theoretical limitation of 1.5 for CRP, it is hard to say whether it is controlled or not.

Table 3.3.26. RAFT polymerization of various monomers with BDTB (CTA:I Ratio of 5:1 in DMF at 70°C, styrene was in bulk and DMAA in toluene).

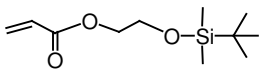
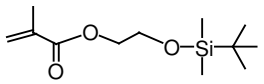
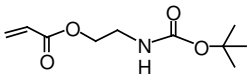
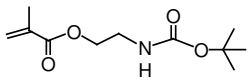
No.	M	M:CTA:I	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R112	styrene	2000:5:1	70	bulk	80	58	24162	20320	1.13
R113		2000:5:1	70	0.5	42	42	16640	17441	1.22
R114		500:5:1	70	0.5	42	40	7970	7100	1.19
R115		500:5:1	70	0.5	42	67	14296	13890	1.46
R116		500:5:1	70	0.5	42	50	11415	22700	2.17

3.3.4.3. RAFT-process of acrylates and methacrylates

For comparison, the RAFT-processes were also carried out with acrylates and methacrylates as monomers. The polymerization results are given in Table 3.3.27. As previously observed, the polymerization rates of methacrylates (**R118**, **R120**) are faster than those of the corresponding acrylates (**R117**, **R119**). This is in contrast to the conventional radical polymerization as reported in Part 3.3.1. That means the polymerization mechanisms in the presence of BDTB (RAFT-process) or in absence of BDTB (conventional radical polymerization) as chain transfer agent are absolutely different. The reason could be explained as following.

For conventional radical polymerization, the polymerization rate depends on the reactivity of the propagation radical. The reactivities of acrylates and acrylamides are higher than those of the corresponding methacrylates and methacrylamides.

Table 3.3.27. RAFT polymerization of acrylates and methacrylates (M:CTA:I Ratio of 1000:5:1 in DMF at 70°C).

No.	M	M:CTA:I	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R117		1000:5:1	70	1	17	60	27646	21304	1.18
R118		1000:5:1	70	1	17	98	47904	64000	2.31
R119		1000:5:1	70	0.5	40	44	9472	7773	1.24
R120		1000:5:1	70	0.5	15	99	22698	91700	2.65

For RAFT-polymerization, as depicted in Scheme 2.8, step IV, the transfer of the RAFT dithioester group between dormant and active chains gives rise to polymer molecules with predominantly dithioester end groups. These polymer molecules are essentially macromolecular chain transfer agents, with the polymer chain P_n now becoming the RAFT leaving group R. In general, the leaving ability decreases in the following order: methacryl > styryl > acryl.[257] As time goes on, the better leaving ability of the macromolecular group will exhibit a faster polymerization process to consistently produce polymer materials with longer

chains. Therefore, the knowledge of the leaving ability of the macromolecular group is needed to explain the abnormal appearance of the polymerization rate during the RAFT process.
The data from Table 3.3.25 show that the polydispersities of poly(methacrylates) (**R118**, **R120**) are quite high, even higher than 2. The differences between $M_{n,theor}$ and $M_{n,GPC}$ are also dramatically larger, indicating uncontrolled processes. On the other hand, the polydispersities of poly(acrylates) (**R117**, **R119**) are quite low (PD = 1.18, 1.24). The differences between $M_{n,theor}$ and $M_{n,GPC}$ are rather small, indicating the successful control of RAFT polymerization of acrylates.

- **Living character**

The aim of the present work was to find and confirm a suitable method to polymerize acrylamide and methacrylamide in a "living" way. Because *tert*-butyl *N*-acryloyl-*β*-alaninate (**M9b**) has shown the lowest PD of 1.19 resulted from RAFT-polymerization of an acrylamide, the living character of RAFT-polymerization was investigated using acrylamide **M9b** as a monomer.
The kinetic plots for RAFT-polymerizations of **M9b** with BDTB are shown in Figure 3.3.21. It can be clearly seen that the RAFT-polymerizations of **M9b** exhibit a first-order relationship between monomer conversion and polymerization time, however, this first order relationship is maintained up to approximately 51% conversion, after that the polymerization rates decrease. The breakdown in "livingness" of this polymerization, like other controlled free radical processes, is indicative of bimolecular termination events (step V, Scheme 2.8). At extended times the conversion rates decrease dramatically due to a reduction in the number of active chains and the low concentration of monomer. These events can be sufficiently suppressed by increasing the CTA:I ratio as previously discussed.[250]

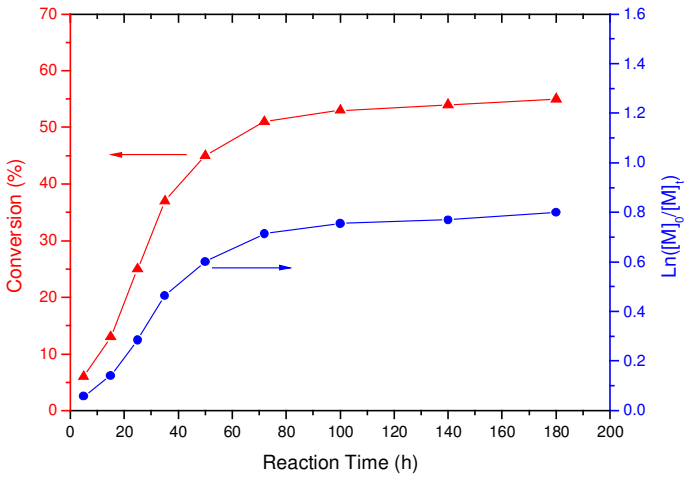
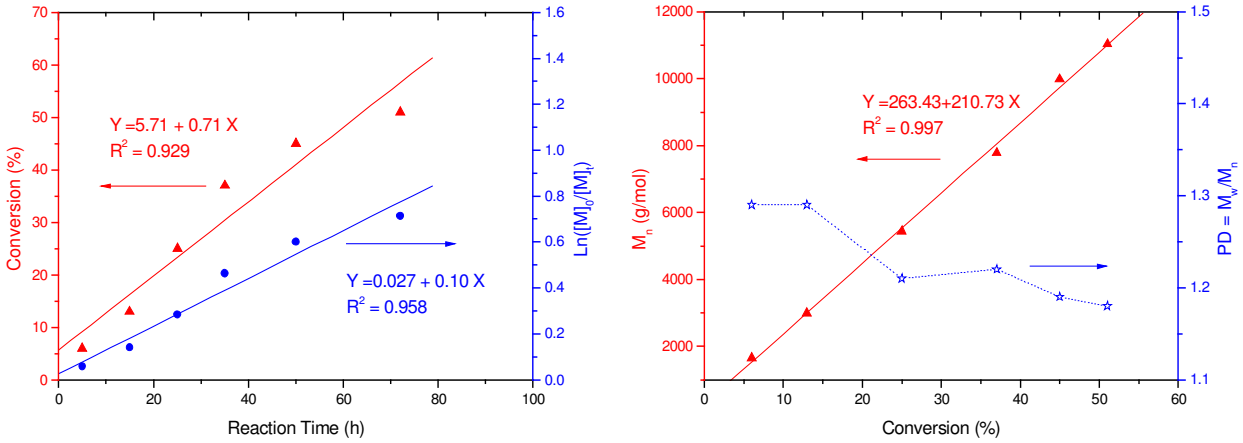


Figure 3.3.21. Plots of conversion and ln([M_0]/[M_t]) vs time for **M9b** polymerization using BDTB as a CTA, 5:1 ratio of CTA:I (70°C).

In the case of **M9b** the conversion is limited to less than 51%, the evolution of conversion (less than 51%) and ln([M_0]/[M_t]) vs polymerization time show excellent first-order behavior, and the number-average molecular weight increases in a linear fashion with reaction conversion, implying a constant number of radicals (Figure 3.3.22).



A B

Figure 3.3.22. (A) Evolution of conversion (less than 51%) and ln([M_0]/[M_t]) with polymerization time. (B) Evolution of number-average molecular weight ($M_{n,GPC}$) and polydispersity (PD = M_w/M_n) with conversion.

The results received demonstrate that an excellent degree of control is achievable with the RAFT process of acrylamide **M9b** in the presence of BDTB at 70°C, with a limit of

conversion less than 51%. The dithioester terminated homopolymer **P9b** was characterized by ^{1}H-NMR spectra and is shown in Figure 3.3.23.

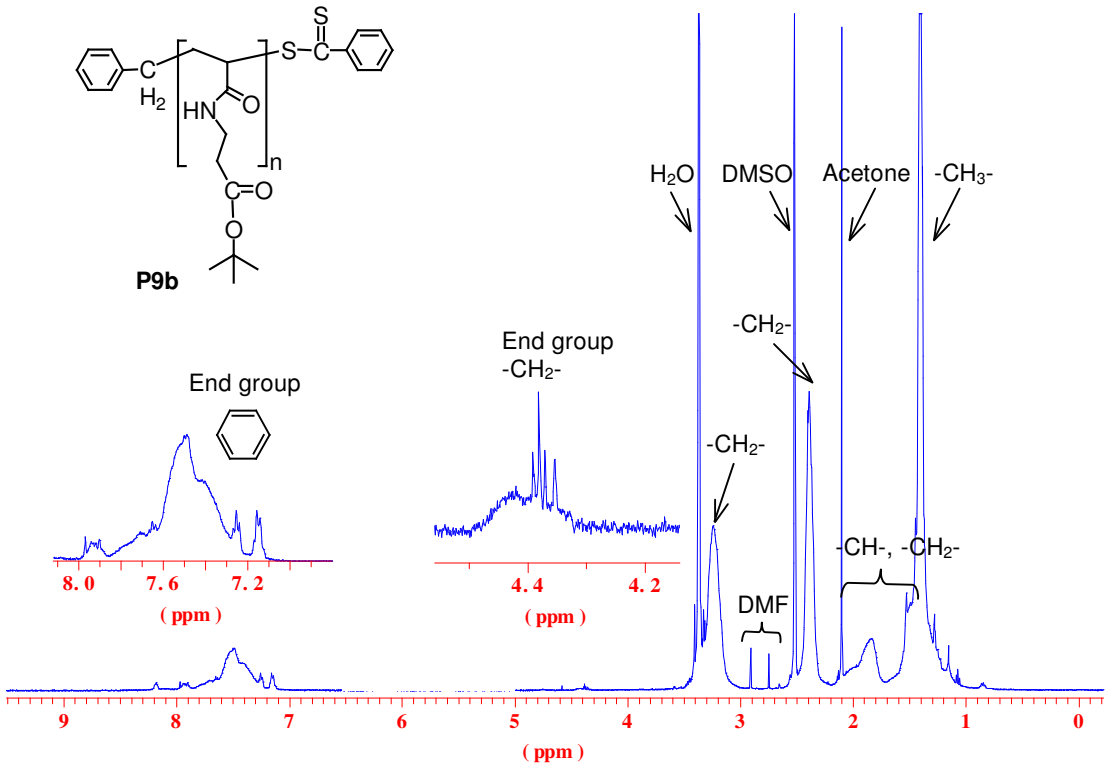


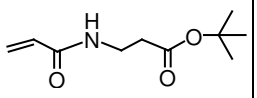
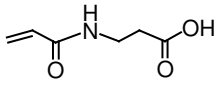
Figure 3.3.23. ^{1}H-NMR spectra of dithioester terminated homopolymer **P9b**.

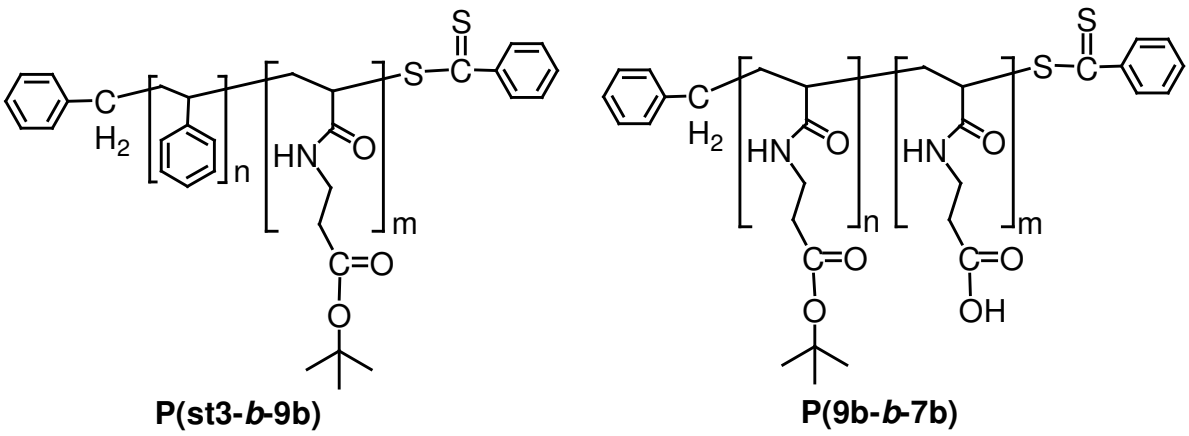
3.3.4.4. Block copolymerization

RAFT, like any other living polymerization process, can also be used to produce block copolymers. Because the RAFT agent terminates the growing polymer chain by transferring the functional moiety, the terminated polymer will serve as a macromolecular chain transfer agent itself. The polymer chain now becomes the RAFT leaving group R. It is then possible to access the living nature of this end group and such end group functionalized polymers can be isolated and employed as a macromolecular chain transfer agent in a second polymerization reaction, using a different monomer to obtain block copolymers.[143] Good control of polymerization of the first block is essential for the synthesis of block copolymers. In general, to minimize the increasing risk of incomplete end group functionalization of the first block, the polymerization of the first block was stopped at moderate conversion.[258] Therefore, polymers with narrow polydispersities and low conversion were selected first, such as **Pst3**

and **P9b**. The block copolymerization with a second monomer is outlined in Table 3.3.28 and the structures of block copolymers are given in Scheme 3.3.24.

Table 3.3.28. Block copolymerization of **M7b** and **M9b** using **P9b** and **Pst3** as macroCTA (molar ratio of M:macroCTA:I = 500:5:1, in DMF at 70°C).

No.	M	MacroCTA	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD
Pst3-*b*-P9b		**Pst3** M_n=20320 PD=1.13	70	0.25	18	45	29286	25760	1.20
P9b-*b*-P7b		**P9b** M_n=7100 PD=1.19	70	0.25	18	70	17120	10700	1.44



Scheme 3.3.24. Structures of block copolymers by RAFT.

The block copolymers were synthesized in DMF. The solution became turbid after 18 h of polymerization, but no precipitate was observed during the reaction. The isolation and purification of the block copolymers was complicated. To separate the block copolymers, the products were repeatedly precipitated from different solvents, such as methanol, water and ether; sometimes mixtures of the solvents need to be tested. Finally we have successfully prepared block copolymers having narrow molecular weight distributions, such as styrene-*b*-*tert*-butyl *N*-acryloyl-β-alaninate (**Pst3-*b*-P9b**), and block copolymers with one free and one protected carboxyl function, such as *tert*-butyl *N*-acryloyl-β-alaninate-*b*-*N*-acryloyl-β-alanine (**P9b-*b*-P7b**). ^{1}H-NMR spectra of block copolymer **P(st3-*b*-9b)** is shown in Figure 3.3.25.

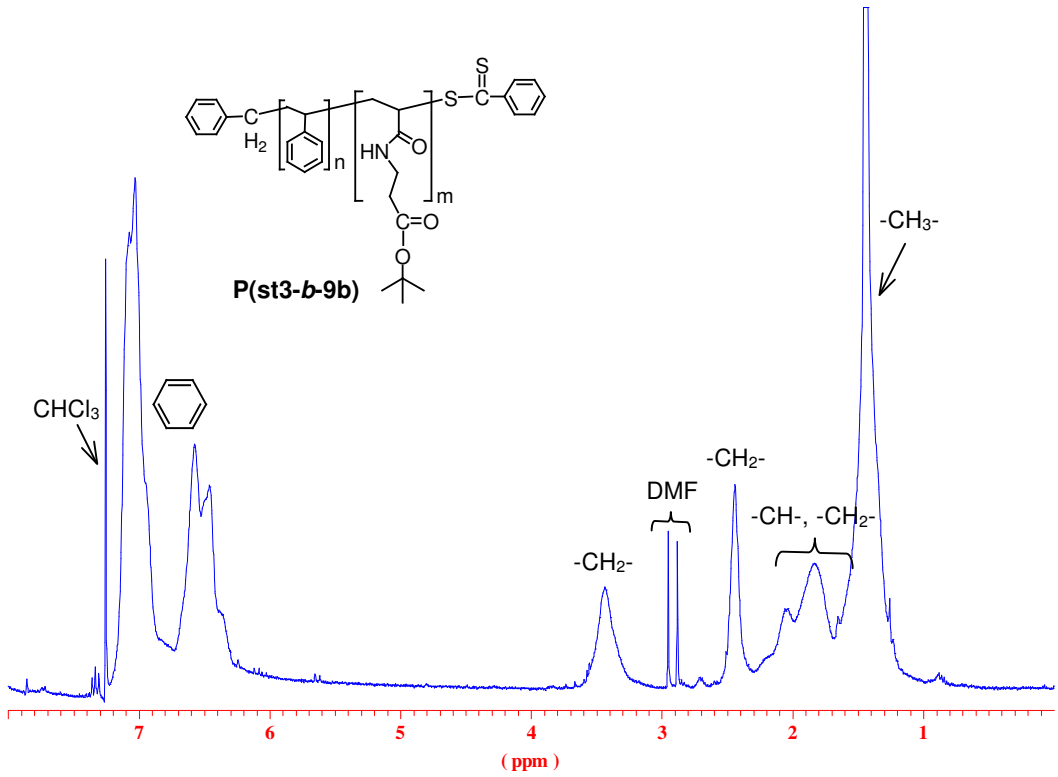


Figure 3.3.25. ^{1}H-NMR spectra of block copolymer **P(st3-*b*-9b)**.

Homopolymer **Pst3** and **P9b** can be used to prepare block copolymers. The ability to extend the chain with different monomers demonstrates the living character of the polymerization and indicates that the product is predominantly composed of dithioester terminated polymer chains, which can be reactivated when required.

- **Conclusion**

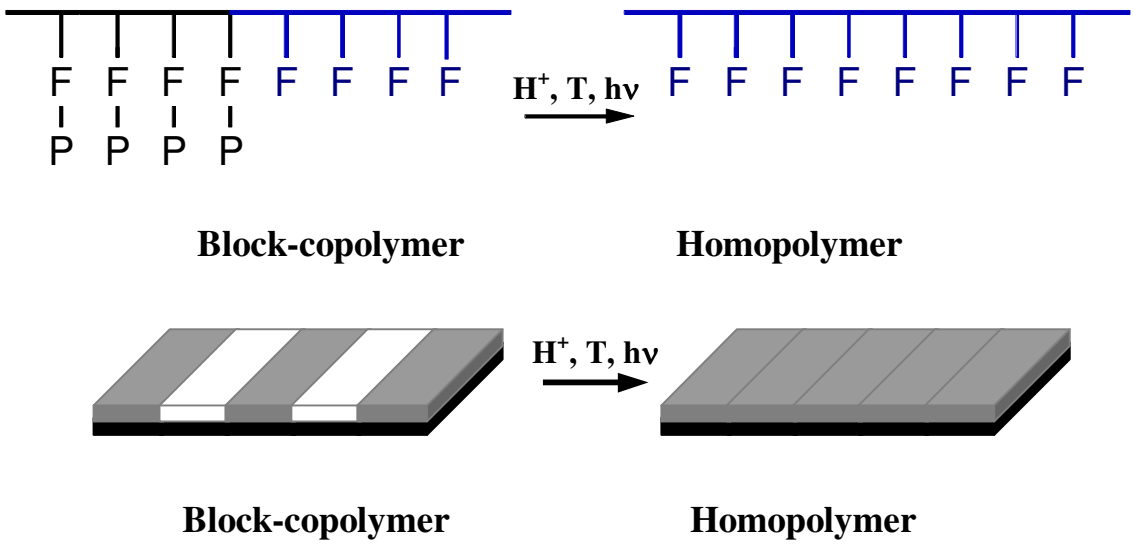
In conclusion, BDTB is clearly shown to be a good CTA for the polymerization of styrene, acrylamides and acrylates using AIBN as an initiator. Even if the achieved molecular weight is not extremely high, the distribution is narrow, confirming that the reaction undergoes a controlled mechanism. The kinetic investigation showed that the RAFT process of acrylamide **M9b** proceeded in a living way, with a limit of conversion less than 51%.

This cannot be asserted of methacrylates and methacrylamides. Under the same reaction conditions, the molecular weights of the products are remarkably higher and their distributions are much broader. In short, the studies demonstrated that BDTB does not control the reaction of methacrylic monomers, in agreement with the reports of Rizzardo *et al.*[143]

The homopolymers **Pst3** and **P9b** with a dithioester group can be used as macroCTA for the further block copolymerization of acrylamides **M9b** and **M7b**, the resulting block copolymers **Pst3-*b*-P9b** and **P9b-*b*-P7b** having low polydispersities, indicating that the acrylamide **M9b** is successfully homopolymerized and block copolymerized by the RAFT process.

3.4. Phase behavior of block copolymers

After the synthesis of well-defined homopolymers and block copolymers by controlled radical polymerization, one of the important topics of our work has been the evaluation of the bulk and surface behavior of block-copolymers. For well-defined block-copolymers with free (F) and protected (P) functional groups, the phase behavior of each block should be different, i.e. two-phase separation should be observed. After the removal of the protective group the surface phase behavior of the former block-copolymer should be now the same as the corresponding homopolymer, because the former block-copolymer produces a homopolymer having only free functional groups. The transformation of the block copolymer to the homopolymer is shown in Scheme 3.4.1.



Scheme 3.4.1. Transformation of the block-copolymer to homopolymer by removal of the protective group.

- **Differential Scanning Calorimetry (DSC)**

The thermal properties of the different homopolymers and block copolymers synthesized have been investigated by differential scanning calorimetry (DSC). To investigate the range of glass transition temperatures (T_g) of different types of homopolymers, the DSC curves of different homopolymers were measured. It is noticed that T_g values of one type of homopolymer slightly increase with the increase of the molecular weight of polymer. An example of the evolution of T_g with molecular weight of polystyrene is shown in Figure. 3.4.1. Although the variations in the temperature values for T_g are not very big, and deviations have to be taken into account during these measurements, nevertheless, the existence of such a tendency cannot be denied.

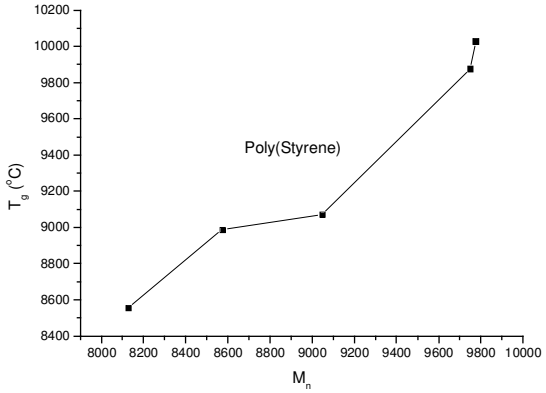
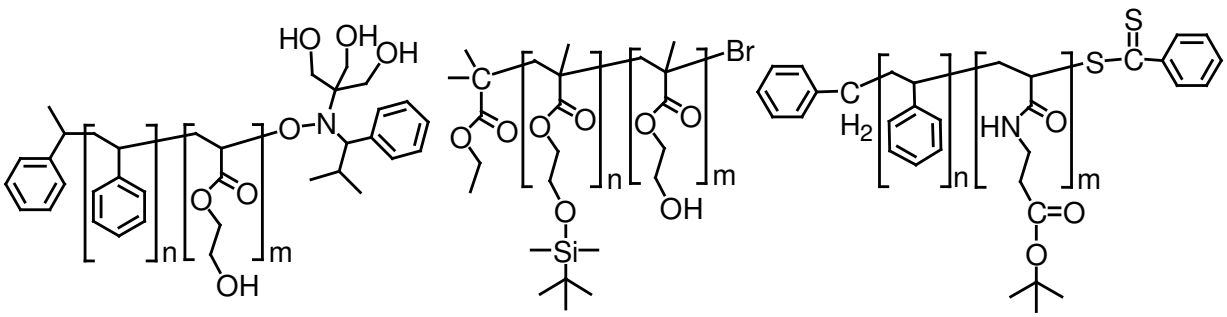


Figure 3.4.1. T_g value of polystyrene with different M_n.

Generally, the T_g of polystyrene synthesized in this work is in the range of 80-100°C, -40-20°C for polyacrylates, and 40-80°C for polyacrylamides.

The phase behavior of the synthesized block copolymers was examined by means of DSC. The structures of the measured block copolymers, which obtained from NMP, RAFT and ATRP, are given in Figure 3.4.2. As shown in Figure 3.4.3, two glass transitions that can be clearly observed in the endothermic curves.



P(st1-*b*-12b)
M_n=11800, PD=1.28
by NMP

P(13a-*b*-12a)
M_n=27800, PD=1.36
by ATRP

P(st3-*b*-9b)
M_n=25760, PD=1.20
by RAFT

Figure 3.4.2. Structures of the block copolymers.

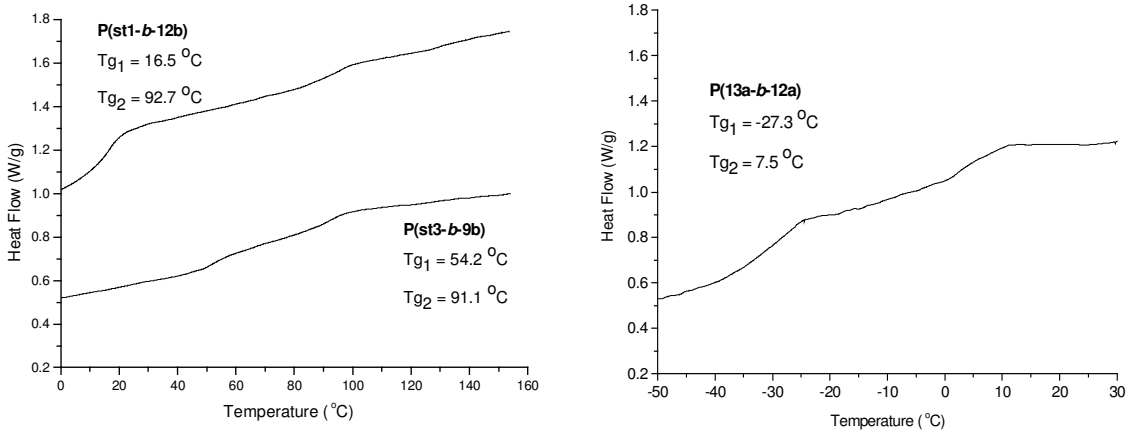


Figure 3.4.3. DSC curves of block copolymers.

- **Morphology by AFM**

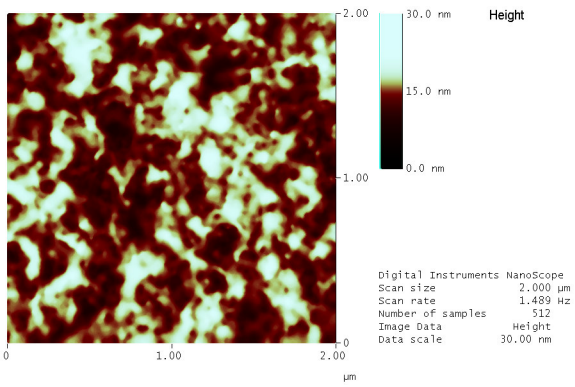
The observed two phase transitions by the DSC measurements of the block copolymers hints that there is obviously a phase separation. Further investigation of phase separation in thin films prepared on silica wafers by spin coating was examined with atomic force microscopy (AFM).

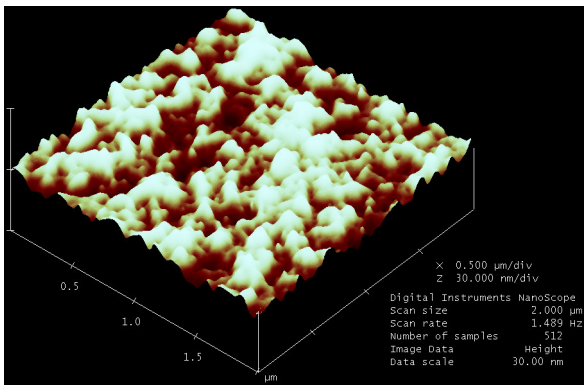
The influence of the wafer surface on the adhesion of the spin-coated solution is a very important feature during the preparation and characterization of thin films. Untreated wafers with native oxide layer, for example, have proved to be unsuitable substrates for all the prepared solutions, since no continuous film could be achieved. Treating the wafers with CH_2Cl_2 in an ultrasonic bath for 20 min and with a solution obtained by mixing

$NH_3/H_2O_2/H_2O$ in ratio 1:1:1 for 1 hour at 60°C and drying them under a nitrogen stream before spin coating the solutions generally leads to continuous films. Examining the surface by optical microscopy, one could notices that the films were very smooth and the layer was unbroken.

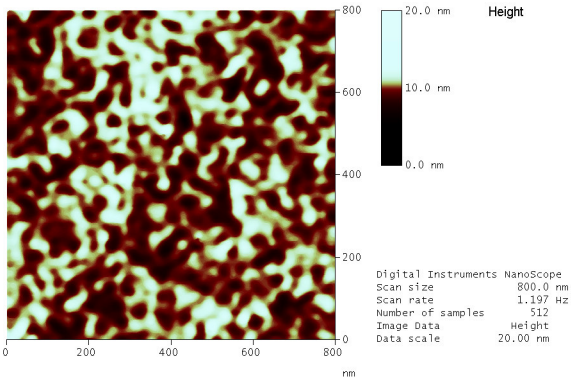
The concentration of the spin-coated solutions is also a very important parameter to consider during the investigation of thin films. Spin coating solutions of different concentration leads to films with varying thickness. Our experiments have been performed with films obtained from 0.5wt% and 3wt% solutions of the block copolymer in THF. The lower concentration (0.5wt%) gave thinner layers and obvious phase separation. The AFM phase image and AFM topographical 3D image of the selected block copolymers are shown in Figure 3.4.4. The thickness of the film is approx. 20-40 nm.

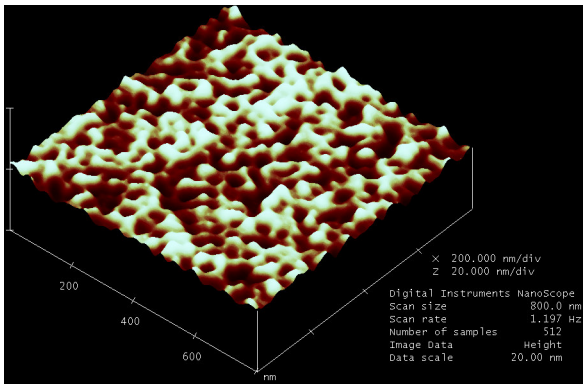
Among the AFM images, the film obtained from block copolymers **P(13a-*b*-12a)** and **P(st3-*b*-9b)** showed regular and well-distributed phase separation.



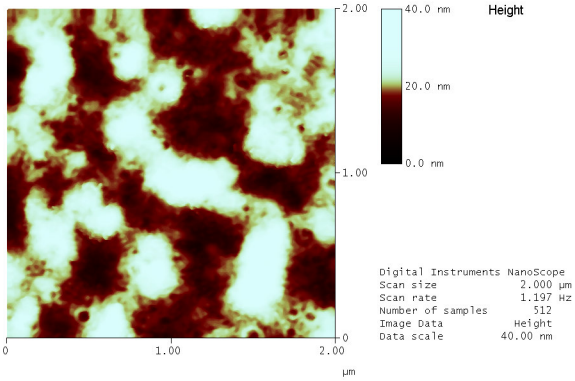


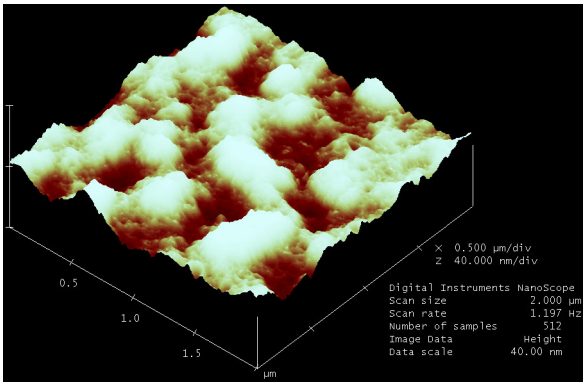
P(st1-*b*-12b) A **B**





P(13a-*b*-12a) A **B**

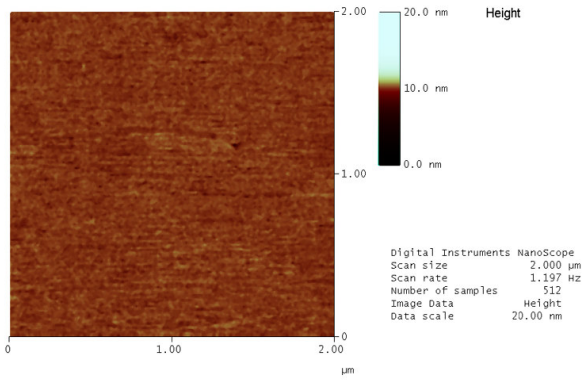


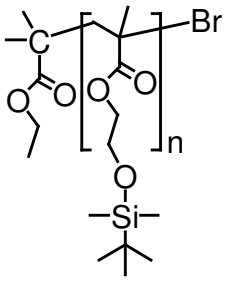


P(st3-*b*-9b) A **B**

Figure 3.4.4. AFM images of films obtained by spin coating (0.5 wt% block copolymers in THF on silica wafers). A) AFM phase image and B) AFM topographical 3D image.

For comparison, the AFM phase image of homopolymer **P13a** film (Figure 3.4.5) shows a smooth surface, indicating only one phase.





P13a
M_n=21000, PD=1.22
by ATRP

Figure 3.4.5. AFM phase image of homopolymer **P13a** film on silica wafer obtained by spin coating (0.5 wt% in THF).

To conclude, one can say that the block copolymers of acryl and methacryl derivatives with styrene, such as **P(st1-*b*-12b)** and **P(st3-*b*-9b)** and the block copolymer of functional methacrylate, with and without protective group like **P(13a-*b*-12a),** exhibit two glass transitions by DSC, and reveal obvious phase separation in thin films as shown by AFM. Therefore, the changing of the phase behavior in thin layers by removal of the protective group, which would result in the change of the surface properties (wetting, mechanics) arising from changes of the surface morphology, are directions for the future work.

4. SUMMARY

Aim of this work was the synthesis of multifunctional acryl- and methacryl derivatives with a free and a protected functional group (-NH_2, -OH and -COOH), and their polymerization as well as their copolymerization with styrene by nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP) and reversible addition-fragmentation chain transfer polymerization (RAFT). The influence of the different methods of controlled radical homo-polymerization of the multifunctional monomers was throughout investigated and compared. In this context, various initiators had to be synthesized and examined for their efficiency in the polymerization and copolymerization of acryl- and methacryl derivatives.

4.1. Synthesis of multifunctional monomers

The reaction of acryloyl and methacryloyl chloride with diamines, dialcohols or aminoalcohols was used for the synthesis of different acryl- and methacryl derivatives containing additional functional groups (-NH_2, -OH and -COOH) and their protected species. The general structures of the multifunctional monomers are given in Figure 4.1. During the synthesis of multifunctional monomers, the *tert*-butyloxycarbonyl (Boc) group was used as a protective group for the -NH_2 function; trimethylsilyl (TMS), *tert*-butyldimethylsilyl (TBDMS) and 2,2,2-trichloroacetyl (TCA) were employed to protect –OH functional groups; TBDMS, *tert*-butyl (TB), *o*-nitrobenzyl (ONB) and (7-methoxy-2-oxo-2*H*-chromen-4-yl)methyl (MCM) groups were selected as protective groups for the -COOH function.

I

R = CH_3 or H
X = O, NH
Y = OH, NH_2, COOH

II

R = CH_3 or H
X = O, NH
Y = O, NH, COO
PG: protective group

Figure 4.1. General structure of the monomers.

Of these protective groups, the Boc, TMS, TBDMS and TB groups were removed by acidic media, such as CF_3COOH or HCl solution; the TCA group was removed by basic media ($EtOH/NH_4OH$); ONB and MCM groups were removed by UV light. Investigation of the photoremovable groups proved that the MCM group was a more effective protective group than the ONB group. The MCM group could be completely removed during one hour of irradiation. Boc, TBDMS and TB groups were suitable and effective protective groups for the corresponding $-NH_2$, -OH and -COOH functions and their protected monomers were selected for further investigation of controlled radical polymerization. The structures of monomers selected for further investigation are summarized in Figure 4.2.

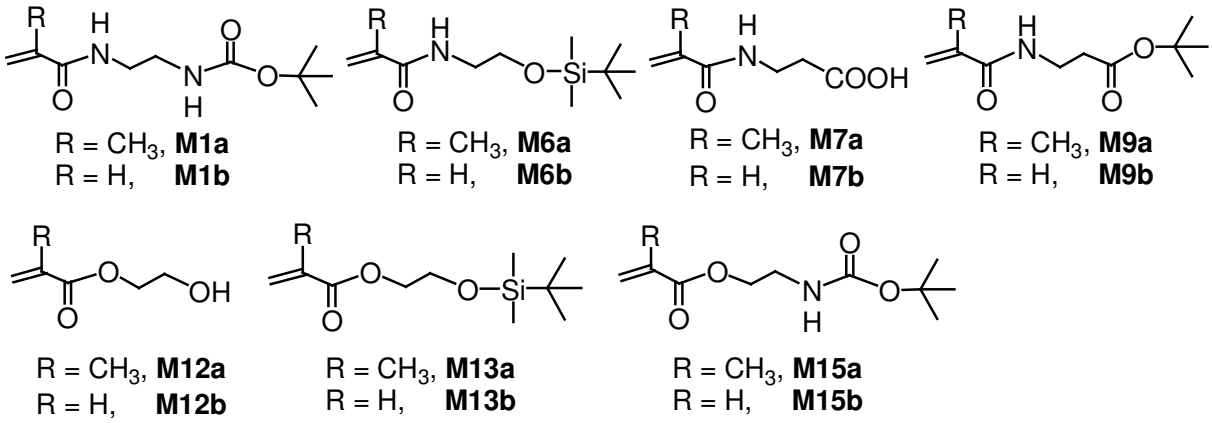


Figure 4.2. The selected monomers for controlled radical polymerization.

4.2. NMP of multifunctional acryl- and methacryl derivatives

Suitable initiators **I1a**, **I1b**, **I1c, I2a** and **I2b** for the NMP of selected monomers have been prepared and characterized (Figure 4.3), and the reaction conditions have been optimized.

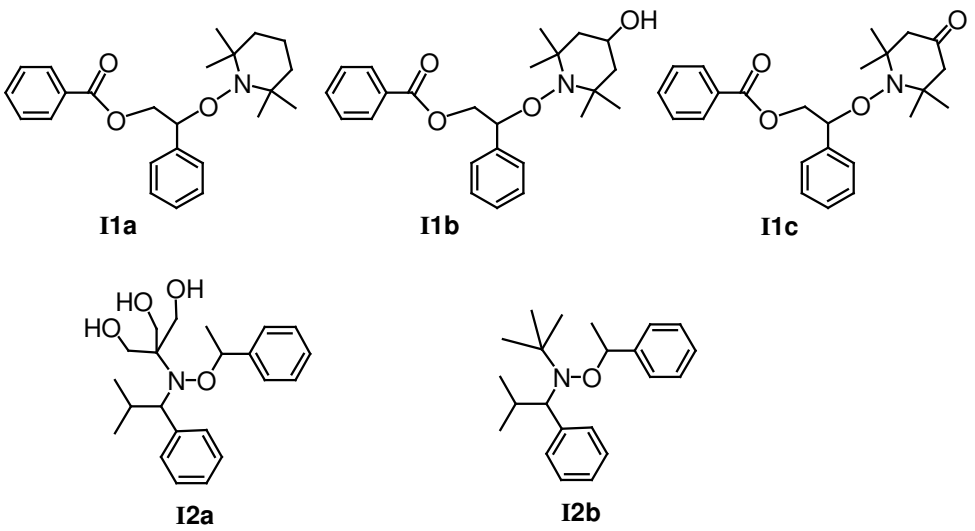


Figure 4.3. Structures of alkoxyamines **I1a**, **I1b**, **I1c**, **I2a** and **I2b**.

To verify the efficacy of the synthesized initiators, styrene and *n*-butyl acrylate were selected as model monomers for the NMP investigation.

The reaction conditions and results of the NMP of styrene are given in Table 4.1. The experimental molecular weights of polystyrene ($M_{n,GPC}$) were close to the theoretical molecular weights ($M_{n,theor}$) and the molar mass distributions of polystyrene were quite low. In particular the polymerization performed very fast by use of initiator **I2a** (5 hours at 120°C) and the obtained polymer with lowest polydispersity. Further kinetic study showed that with the use of initiator **I2a** the polymerization of styrene proceeded quite fast and in a living way.

Table 4.1. Results of the controlled radical polymerization of styrene using different initiators (M:I = 100:1).

No.	M	I	T (°C)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R7	Styrene	**I1a**	125	13	84	8748	9048	1.28
R8		**I1b**	125	13	82	8539	8574	1.29
R9		**I1c**	125	13	78	8123	8129	1.29
R34		**I2a**	120	5	72	7499	7309	1.10
R26		**I2b**	120	14	72	7499	7100	1.18

Alkoxyamines **I1c** and **I2a** were selected as initiators for the further polymerization of *n*-butyl acrylate. The NMP of *n*-butyl acrylate with initiator **I1c** afforded the polymers with higher polydispersities and the polymerization rate was very slow, 90% conversion was obtained after 144 hours (**R18**, Table 4.2). With the use of newly developed initiator **I2a** all the polymerizations proceeded very fast (1-3.5 h) and the polydispersities of poly(*n*-butyl acrylate) obtained were around 1.31-1.42. Under the optimized reaction conditions, the experimental molecular weights of the derived polymers were close to the theoretical values, while the polydispersities were still higher than 1.30 (**R72**, **R80**, **R81**, **R73**), which are higher than that value reported in the literature.[64]

All the initiators mentioned above proved to be effective for the controlled radical polymerization of styrene. Initiator **I2a** was only of moderate efficiency for the NMP of *n*-butyl acrylate.

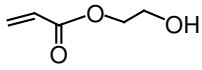
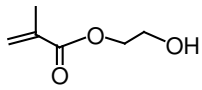
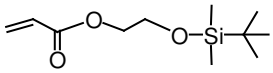
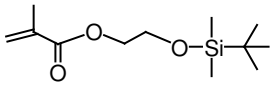
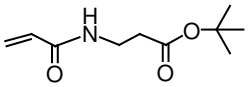
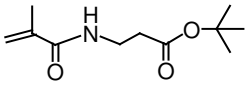
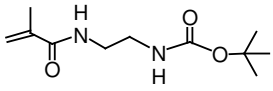
Table 4.2. Polymerization of *n*-butyl acrylate with initiator **I1c** and **I2a** in DMF, ([M]:[**I2a**] = 200:1 or [M]:[**I2a**]:[**37**] = 200:1:0.05).

No.	M : I (mol/mol)	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R18	M:**I1c**=100:1	125	0	144	90	11535	9428	1.52
R71	M:**I2a** (200:1)	120	2	1	95	24352	30000	1.31
R72	M:**I2a** (200:1)	120	1	3.5	99	25378	25830	1.39
R80	M:**I2a**(100:1)	120	1	3.5	99	12689	14160	1.42
R81	M:**I2a**(75:1)	120	1	3.5	99	9517	11230	1.40
R73	**I2a**+NO· (**37**)	120	bulk	1	90	23071	22074	1.33
R74	**I2a+**NO· (**33**)	120	bulk	0.5	84	21533	44278	1.38

For the investigation of the homopolymerization of multifunctional acryl- and methacryl derivatives, the alkoxyamines **I1c** and **I2a** were again used as unimolecular initiators for this family of monomers. In general, all the polymerizations with initiator **I1c** took a very long time, this was especially true for methacrylamides (**R24**, **R25**), with 20% and 10% conversions obtained after 66 h of polymerization. The polydispersities of the poly(methacryl derivative) are higher than the corresponding polydispersities of the poly(acryl derivative), and

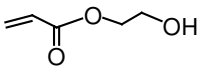
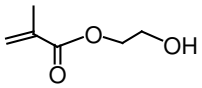
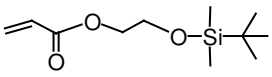
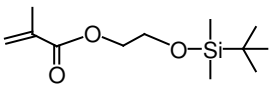
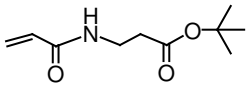
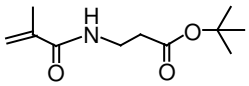
the molecular weights were significantly different from the theoretical molecular weights (Table 4.3).

Table 4.3. Polymerization of multifunctional acryl- and methacryl derivatives with initiator **I1c** at 125°C (M:I=100:1).

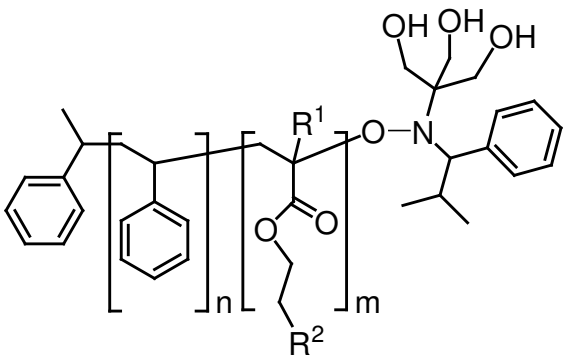
No.	M	I	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R19		**I1c**	125	0.5	70	56	6502	8912	1.86
R20		**I1c**	125	0.5	70	62	8068	9700	2.52
R21		**I1c**	125	0	144	92	18891	15510	1.70
R22		**I1c**	125	0	144	90	21997	48100	2.68
R23		**I1c**	125	0.5	66	100	19925	8796	1.51
R24		**I1c**	125	0.5	66	20	4266	6363	1.53
R25		**I1c**	125	0.5	66	10	2283	1200	4.58

It has been shown that by use of initiator **I2a**, the overall rates of polymerization of multifunctional acryl- and methacryl derivatives are increased (Table 4.4) compared to the application of initiator **I1c** (Table 4.3). The polymerization rates of acryl derivatives (**R47**, **R51**, **R56**) are higher than those of the corresponding methacryl derivatives (**R49**, **R53**, **R57**), and all the polydispersities of the polymers are rather high (PD > 1.5). With the exception of **R51**, the experimental molecular weights of the derived polymers are quite different from the theoretical values, indicating that it has failed to polymerize multifunctional acryl- and methacryl derivatives in a controlled way.

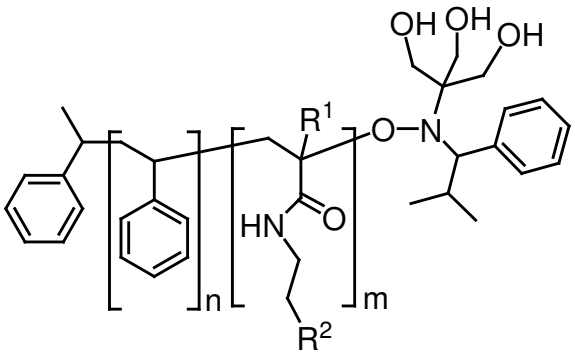
Table 4.4. Polymerization of various monomers initiated by initiator **I2a** at 120°C (M:I=100:1).

No.	M	I	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R47		**I2a**	120	0.5	2.5	96	11147	23800	2.79
R49		**I2a**	120	0.5	2.5	50	6500	40300	1.86
R51		**I2a**	120	2	2.5	96	22116	22905	1.56
R53		**I2a**	120	2	2.5	70	17109	28701	1.58
R56		**I2a**	120	1	9	97	19327	12697	1.56
R57		**I2a**	120	1	36	39	7681	5699	1.85

Further block copolymerization of multifunctional acryl- and methacryl derivatives with the alkoxyamine-terminated polystyrene, however, resulted in various block copolymers with narrow molar mass distribution (with exception of **P(st1-*b*-13a)**, PD = 1.72). The structures of few block copolymers are shown in Figure 4.4. The reaction conditions and polymer data are summarized in Table 4.5. In comparison with the corresponding homopolymers initiated by **I2a**, all the block co-copolymers show narrow distributions, and the PD of most block-copolymers are lower than 1.5. The PD of block-copoly(acryl derivatives) are lower than those of block-copoly(methacryl derivatives), which is in agreement with the homopolymers. It has be shown that the macroinitiator **Pst1** with an alkoxyamine-dormant end group is able to initiate a second monomer species to achieve block-copolymers with a relatively narrow molecular weight distribution at 120°C.



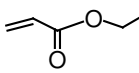
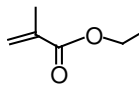
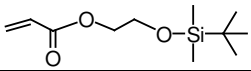
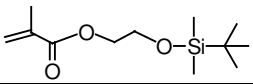
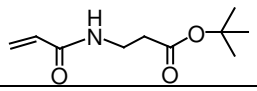
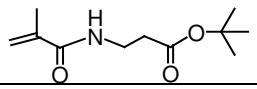
R^1 = H , R^2 = OH: **P(st1-*b*-12b)**
R^1 = CH_3, R^2 = OH: **P(st1-*b*-12a)**
R^1 = H, R^2 = OTBDMS: **P(st1-*b*-13b)**
R^1 = CH_3, R^2 = OTBDMS: **P(st1-*b*-13a)**



R^1 = H, R^2 = COOTB: **P(st1-*b*-9b)**
R^1 = CH_3, R^2 = COOTB: **P(st1-*b*-9a)**

Figure 4.4. Block copolymers by NMP.

Table 4.5. Block co-polymerization of acryl- and methacryl derivatives starting from alkoxyamine-terminated polystyrene (M:I=200:1).

	M	macroI	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
P(st1-*b*-12b)		**Pst1**	120	0.5	1	86	26971	11800	1.28
P(st1-*b*-12a)		**Pst1**	120	0.5	1	36	16370	8900	1.27
P(st1-*b*-13b)		**Pst1**	120	1	1	95	50772	14160	1.43
P(st1-*b*-13a)		**Pst1**	120	0.5	1	44	28508	17450	1.72
P(st1-*b*-9b)		**Pst1**	120	0.5	128	98	46053	12584	1.27
P(st1-*b*-9a)		**Pst1**	120	0.5	128	20	15531	13425	1.46

Homopolymer **Pst1** and block copolymer samples have been characterized by NMR and GPC measurements. GPC curves of block-copolymers and the first block (homopolymer **Pst1**) are shown in Figure 4.5. In comparison with the corresponding homopolymers initiated by **I2a**, the block co-copolymers have lower polydispersities. The experimental molecular weights of the derived block-copolymers are higher than that of the first block (homopolymer **Pst1**).

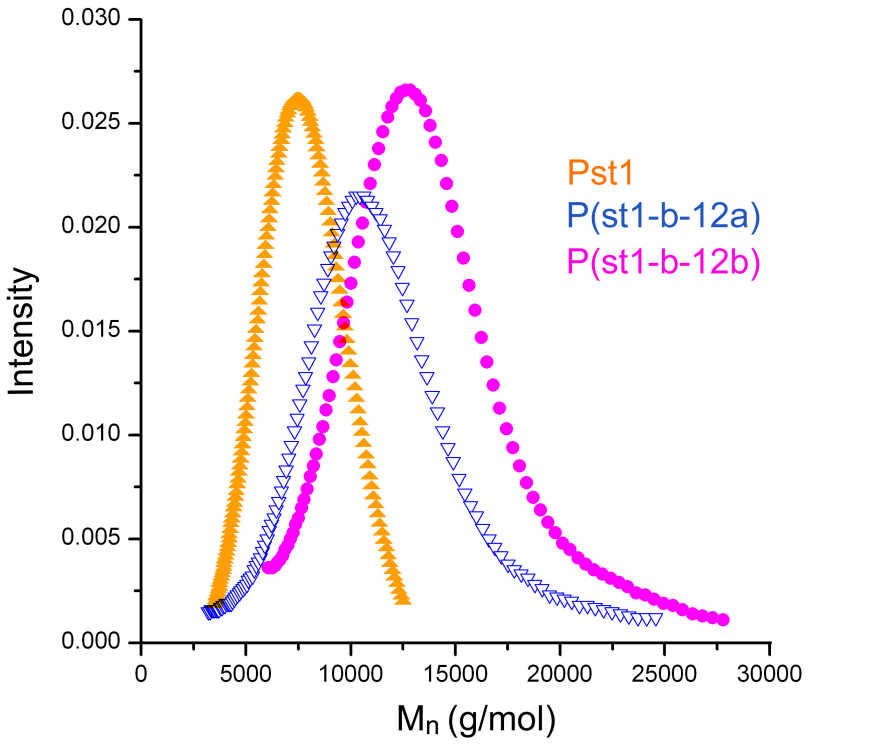


Figure 4.5. The GPC curves of block-copolymers.

In conclusion, efforts to use initiator **I1c** and **I2a** for controlled radical polymerization of multifunctional acryl- and methacryl derivatives failed. It can be stated that NMP was not suitable method for use with multifunctional acryl- and methacryl derivatives to achieve well-defined homopolymers, although it was successful for the control of the polymerization of styrene and the block copolymerization of multifunctional acryl- and methacryl derivatives with alkoxyamine terminated polystyrene.

4.3. ATRP of multifunctional acryl- and methacryl derivatives

The ATRP method was employed to find a controlled polymerization of multifunctional acryl- and methacryl derivatives. Copper has been chosen as transition metal and bromine as the halogen. The initiators included methyl 2-bromopropionate (MBrP), ethyl 2-bromopropionate (EBrP) and ethyl 2-bromoisobutyrate (EBriB), and the ligands were composed of 2,2'-bipyridine (bipy), 4,4'-di-*tert*-butyl-2,2'-bipyridine (DTB-bipy), *N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine (PMDETA) and tris[2-(dimethylamino)-ethyl]amine (Me_6TREN).

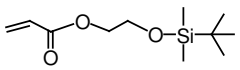
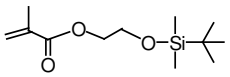
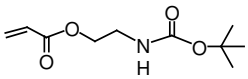
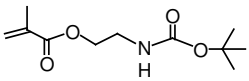
The ATRP of *n*-butyl acrylate showed that the type of ligand has an important influence on the polymerization rate and polydispersity (see Table 4.6). Polymerizations of *n*-butyl acrylate using MBrP or EBrP as an initiator both showed that their rates decrease in the order of Me_6TREN >> PMDETA > DTB-bipy > bipy. One can also see that the choice of initiators did not significantly influence the polymerization rates or the polydispersities of the polymers. In general, all the ligands used were effective for ATRP of *n*-butyl acrylate. The PD values are between 1.11-1.32 and the experimental molecular weights were close to the theoretical molecular weights.

Table 4.6. Effect of ligand on the rate of polymerization of *n*-butyl acrylate using MBrP and EBrP as initiator (M:I:Cat:L=100:1:1:2).

No.	I	Cat	L	T (°C)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R82	MBrP	CuBr	Me_6TREN	90	20 min	82	10510	9845	1.18
R83			PMDETA	90	1.5	70	8972	8812	1.11
R84			DTB-bipy	90	8	57	7306	7259	1.20
R85			bipy	90	9.5	64	8203	14250	1.37
R86	EBrP	CuBr	Me_6TREN	90	30 min	98	12560	14140	1.27
R87			PMDETA	90	2.25	85	10894	9700	1.19
R88			DTB-bipy	90	17	80	10254	12940	1.22
R89			bipy	90	20	82	10510	13420	1.32

The investigation of ATRP of multifunctional acrylates and methacrylates showed that Me_6TREN and PMDETA were suitable ligands for the ATRP of acrylates (**R90**, **R91**, **R96**) and methacrylates (**R93**, **R94**, **R97**, Table 4.7). A relatively low polydispersity of the corresponding polymers and reasonably high rates of polymerization could be achieved. The "living" character of the ATRP of 2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl acrylate **M13b** was confirmed by a kinetic study and the reinitiation ability for production of block copolymers was characterized.

Table 4.7. ATRP of acrylates **M13b**, **M15b** and methacrylates **M13a**, **M15a** (Cat: CuBr, M:I:Cat:L=100:1:1:2).

No.	M	I	L	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R90	 **M13b**	EBrP	Me_6TREN	90	0	0.2	90	20734	17090	1.24
R91		EBrP	PMDETA	90	0	2.5	93	21425	17707	1.18
R93	 **M13a**	EBriB	Me_6TREN	90	1	2	88	21508	18576	1.32
R94		EBriB	PMDETA	90	1	4	96	23110	21000	1.22
R96	 **M15b**	EBriB	PMDETA	90	0.5	2.5	50	10763	9122	1.21
R97	 **M15a**	EBriB	PMDETA	90	0.5	1.5	93	21323	20440	1.26

The ATRP of styrene has been successfully performed using PMDETA or DTB-bipy to achieve a polymer with a narrow distribution (Table 4.8).

Table 4.8. Styrene polymerized by ATRP (M:I:Cat:L=100:1:2:2).

No.	I	Cat	L	T (°C)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
R110	MBrP	CuBr	PMDETA	90	2	82	8540	17000	1.29
R111	MBrP	CuBr	DTB-bipy	90	24	68	7082	5936	1.19

In comparison to acrylates, methacrylates and styrene, however, the ATRP of acrylamide and methacrylamide using Me_6TREN and PMDETA as ligands failed; no polymer was obtained at all. When 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4Cyclam) was used as ligand the ATRP of acrylamide and methacrylamide afforded the corresponding polymers with rather high polydispersities, indicating an uncontrolled polymerization.

The halogen-terminated polystyrene **Pst2** (M_n= 5936, M_w/M_n =1.19) and halogen-terminated poly(2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl methacrylate) **P13a** (M_n=21000, PD=1.22) were successfully used as macroinitiators for the further synthesis of block copolymers **P(st2-*b*-13a)**,

P(st2-*b*-13b) and **P(13a-*b*-12a)** (Table 4.9). The experimental molecular weights of the block copolymer ($M_{n,GPC}$) are higher than those of the first block, and were close to the theoretical molecular weights ($M_{n,theor}$). The polydispersities of block copolymers increased compared to those of the first block, but were still low (PD = 1.32-1.40). This indicates that the atom transfer radical polymerization of styrene, acrylate and methacrylate using these macroinitiators follows a controlled radical polymerization mechanism. The structures of block copolymers are shown in Figure 4.6.

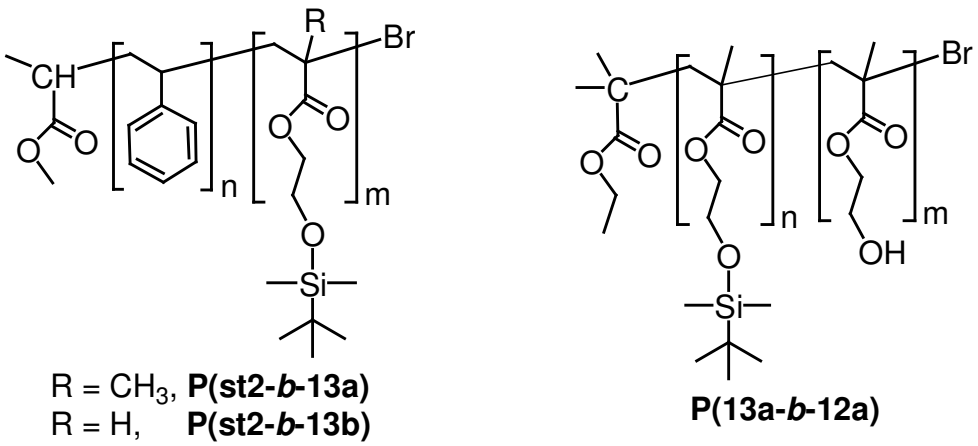


Figure 4.6. Block copolymers by ATRP.

Table 4.9. Block copolymerization of **M13a**, **M13b** and **M12a** by ATRP using **Pst2** and **P13a** as macroinitiators (M:I:Cat:L=100:1:1:2).

No.	macroI	Cat	L	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD M_w/M_n
P(st2-*b*-13a)	**Pst2** M_n=5936 PD=1.19	CuBr	PMDETA	90	0.5	3	54	19134	12040	1.32
P(st2-*b*-13b)		CuBr	PMDETA	90	0.5	2	25	11695	8288	1.40
P(13a-*b*-12a)	**P13a** M_n=21000 PD=1.22	CuBr	DTB-bipy	20	0.5	3	33	25295	27800	1.36

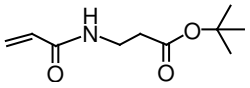
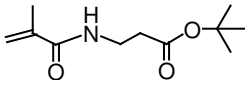
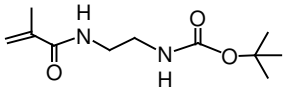
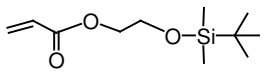
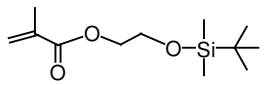
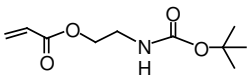
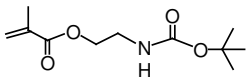
In conclusion, the ATRP of functional acrylates and methacrylates have been successfully performed, as well as the block copolymerization of functional acrylates and methacrylates. Relatively low polydispersities of the corresponding polymers and reasonably high rates of polymerization could be achieved when Me_6TREN and PMDETA were used as ligands. However, the ATRP of functional acrylamide and methacrylamide failed.

4.4. RAFT of multifunctional acryl- and methacryl derivatives

The synthesized multifunctional monomers were also polymerized by RAFT. Benzyl dithiobenzoate (BDTB) was used as chain transfer agent and AIBN as an initiator.

The homopolymerization of multifunctional acryl- and methacryl derivatives showed that BDTB was an efficient chain transfer agent (CTA) for the polymerization of styrene, acrylamide and acrylate. The polydispersities of the resulting polymers were relatively low (PD = 1.18-1.24), and the differences between $M_{n,theor}$ and $M_{n,GPC}$ are rather small (see Table 4.10). The kinetic investigation showed that the RAFT process of acrylamide **M9b** undergoes a controlled mechanism, with the conversion limited to less than 51%.

Table 4.10. Data from the RAFT polymerization of various monomers with BDTB in DMF at 70°C (styrene is in bulk and DMAA is in toluene).

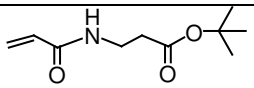
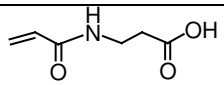
No.	M	M:CTA:I	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD
R112	styrene	2000:5:1	70	bulk	80	58	24162	20320	1.13
R114		500:5:1	70	0.5	42	40	7970	7100	1.19
R115		500:5:1	70	0.5	42	67	14296	13890	1.46
R116		500:5:1	70	0.5	42	50	11415	22700	2.17
R117		1000:5:1	70	1	17	60	27646	21304	1.18
R118		1000:5:1	70	1	17	98	47904	64000	2.31
R119		1000:5:1	70	0.5	40	44	9472	7773	1.24
R120		1000:5:1	70	0.5	15	99	22698	91700	2.65

The polymerizations of methacryl derivatives performed faster than those of the corresponding acryl derivatives (Table 4.10). BDTB was not a suitable CTA for the polymerization of

methacrylamide (**R116**) and methacrylates (**R118**, **R120**). The distributions of the obtained polymers were quite broad, even higher than 2 (with exception of **R115**, PD = 1.46), and the differences between $M_{n,theor}$ and $M_{n,GPC}$ are dramatically higher.

A homopolymer with a dithioester terminated end group can be used as a macroCTA for the further block copolymerization and the resulting block copolymers have a narrow molecular weight distribution (see Table 4.11 and Figure 4.7), indicating that the acrylamide **M9b** has been successfully homopolymerized and block copolymerized by the RAFT process. NMR measurements proved the existence of dithioester terminated end groups.

Table 4.11. Block copolymerization of **M7b** and **M9b** using **P9b** and **Pst3** as macroCTA in DMF at 70°C (molar ratio of M/macroCTA/I = 500/5/1).

No.	M	macroCTA	T (°C)	Con. (g/ml)	t (h)	Y (%)	$M_{n,theor}$ (g/mol)	$M_{n,GPC}$ (g/mol)	PD
Pst3-*b*-P9b		**Pst3** M_n=20320 PD=1.13	70	0.25	18	45	29286	25760	1.20
P9b-*b*-P7b		**P9b** M_n=7100 PD=1.19	70	0.25	18	70	17120	10700	1.44

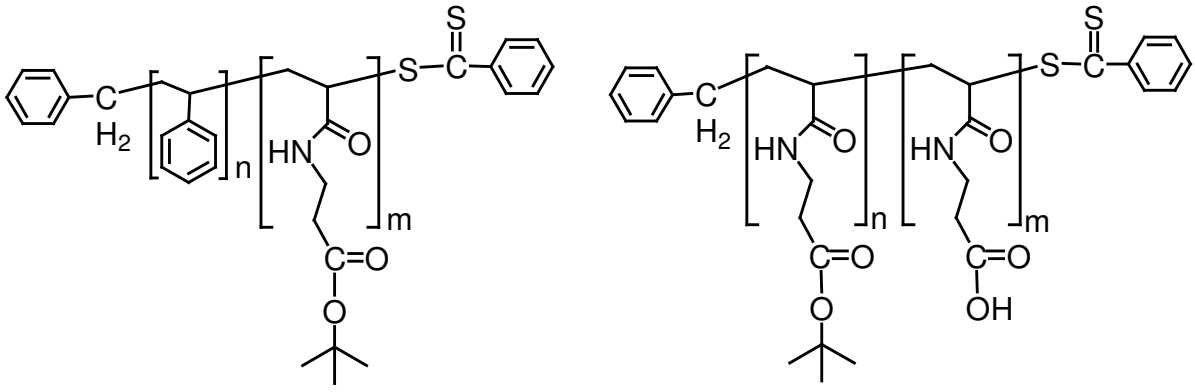


Figure 4.7. Structures of block copolymers by RAFT.

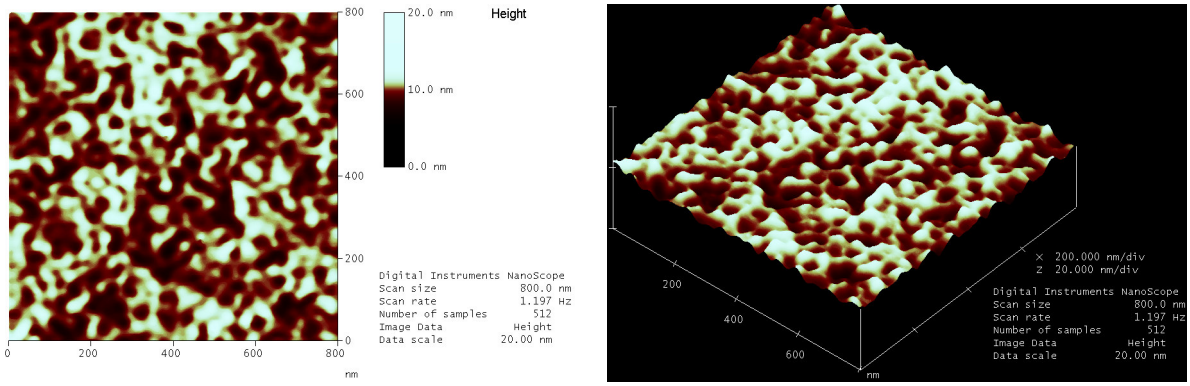
In conclusion, the polymerization of styrene, acrylamide and acrylate using BDTB as a CTA and AIBN as an initiator afforded polymers with narrow molecular weight distributions. A kinetic investigation and the further synthesis of block copolymers using dithioester-

terminated homopolymers as macroCTAs showed that the RAFT polymerization of acrylamide **M9b** proceeded in a living manner.

However, BDTB does not control the reaction of methacrylic monomers, such as methacrylates and methacrylamides.

4.5. Bulk phase behavior and surface morphology of block copolymers

After the synthesis, the bulk phase behaviors of the block copolymers were examined by means of DSC and the surface behaviors of block copolymers as thin layers were examined with AFM. Two-phase transitions in the block copolymers were clearly observed by DSC, indicating that a phase separation occurs, which was confirmed by the AFM image. One example of an AFM image is shown in Figure 4.8.



P(13a-*b*-12a) **A** **B**

Figure 4.8. AFM images of **P(13a-*b*-12a)** films obtained by spin coating. A) AFM phase image and B) AFM topographical 3D image.

4.6. Conclusion

In conclusion, multifunctional acryl- and methacryl derivatives failed to achieve well-defined homopolymers by NMP, however, this method was successful for block copolymerization of multifunctional acryl- and methacryl derivatives with alkoxyamine terminated polystyrene.

Multifunctional acrylates and methacrylates are successfully homopolymerized and block copolymerized by ATRP.

Multifunctional acrylates and acrylamides are suitable for homopolymerization by the RAFT process and the block copolymerizations of acrylamides were successfully performed by RAFT process.

Thus far it has been difficult to homopolymerize multifunctional methacrylamides in a controlled way.

5. EXPERIMENTAL PART

5.1. Starting materials and measurements

5.1.1. Reagents and solvents

The following reagents and solvents were used as received, without further purification.

- 1,2-diaminoethane (98%, Fluka), 2,2.2-trichloroethanol (98%, Lancaster), acryloyl chloride (97%, Fluka), methacryloyl chloride (97%, Aldrich), trimethyl-chlorosilane (98%, Fluka), *tert*-butyldimethylchlorosilane (97%, Merck), trichloroacetyl chloride (99%, Aldrich), 4-dimethylaminopyridine (DMAP, 99%, Acrōs), di-*tert*-butyl dicarbonate ($(Boc)_2$, 98%, Merck), 4-(bromomethyl)-7-methoxycumarin (97%, Aldrich), 3-aminopropanoic acid (β-alanine, 99%, Acrōs), *tert*-butanol (99%, Merck), *o*-nitrobenzyl chloride (96%, Merck), 2,6-di-*tert*-butyl-4-methyl-phenol (99%, Aldrich), 2-aminoethyl methylacrylate hydrochloride (90%, Aldrich).
- 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO, 98%, Aldrich), 2-(hydroxymethyl)-2-nitro-1,3-propanediol (98%, Aldrich), 1,1,1-triethoxy-ethane (99%, Aldrich), dioctyl-phthalate (DOP, 98%, Fluka), 2-methylpropionaldehyde (99.5%, Aldrich), ammonium chloride (NH_4Cl, 99.8% Merck), phenylmagnesiumchloride/THF solution (1.8M, Fluka), Jacobsen's catalysts [*N,N*'-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diaminocyclohexane] manganese(III) chloride, 98%, Aldrich), manganese(III) acetate hydrate ($Mn(OAc)_3$, 98%, Merck), monoglyme (dimethoxymethane, 99%, Fluka), Copper(II) trifluoromethanesulfonate ($Cu(OTf)_2$, 98%, Aldrich).
- Trifluoroacetic acid (CF_3COOH, 99%, Aldrich) and *p*-toluene sulfonic acid (*p*-TSA, $CH_3C_6H_4SO_3 \bullet H_2O$, 98%, Merck) were used as received.
- Triethylamine (99.5%, Fluka), pyridine (99.5%, Merck), imidazole (99%, Merck), *N, N'*-dicyclohexylcarbodiimide (DCC, 99%, Merck), ammonium hydroxide (NH_4OH).
- Copper chloride (II) ($CuCl_2$, 99.995%, Aldrich), copper bromide (II) ($CuBr_2$, 99.995%, Aldrich).

- 4,4'-Di-*tert*-butyl-2,2'-bipyridine (98%, Aldrich), 2,2'-bipyridine (99%, Acrōs), 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Me_4Cylam, 98%, Acrōs), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, 99%, Acrōs), tris-(2-aminoethyl-amine) (96%, Aldrich), formic acid (85%, Fluka) and formaldehyde (30%, Merck).
- Methyl 2-bromopropionate (MBrP) (98%, Aldrich), ethyl 2-bromopropionate (EBrP) (98%, Aldrich), methyl 2-chloropropionate (MClP, 97%, Aldrich), ethyl 2-bromoisobutyrate (EBriB) (98%, Aldrich).
- Sodium chloride (NaCl, 100%, J.T. Baker), anhydrous sodium carbonate (Na_2CO_3, 99.5%, J.T. Baker), sodium hydroxide (NaOH, 99%, J.T. Baker), sodium borohydride ($NaBH_4$, 96%, Fluka), saturated aqueous ($NaHCO_3$, 99%, Gruessing), anhydrous sodium sulfate (Na_2SO_4, 99.9%, J.T. Baker), anhydrous magnesium sulfate ($MgSO_4$, 99%, Gruessing), potassium fluoride (KF, 99%, Lancaster), potassium hydroxide (KOH, 88%, J.T. Baker), lithium hydroxide-monohydrate (LiOH, 56%, Merck), Zn powder (95%, Merck).
- Styrene (99%, Aldrich), *n*-butyl acrylate (99%, Fluka), 2-hydroxyethyl 2-methylacrylate (97%, Aldrich), 2-hydroxyethyl acrylate (96%, Aldrich), 2-[(trimethylsilyl)oxy]ethyl 2-methylacrylate (96%, Aldrich), were distilled under high vacuum and stored at low temperature (minus 20°C).
- Dibenzoyl peroxide (BPO, 75%, with 25% water, Merck) was dried under high vacuum and low temperature and then stored at low temperature (minus 20°C).
- 4-Hydroxy-2,2,6,6-tetramethylpiperidinyl-l-oxy (HO-TEMPO, 98%, Huels) was recrystallized from cyclohexane at 70°C prior to use.
- 2,2'-azobis(isobutyrolnitrile) (AIBN, 98%, Fluka) was recrystallized from ethanol prior to use.
- Copper bromide (I) (98%, Aldrich) and copper chloride (I) (CuCl, 99%, Aldrich) were purified by stirring over glacial acetic acid, followed by filtration and washing the remaining solid three times with methanol and twice with diethyl ether until there was no color of copper (II) and drying under vacuum for one day.

Silica gel 60 (0.040-0.063mm, Merck), aluminium oxide 90 active, neutral (0.063-0.200mm, Merck), anion exchange resin (GDR), and 4 Å molecular sieve (J.T. Baker) were used without additional cleaning.

The solvents (toluene, ethanol, pentane, ethyl acetate, dichloromethane (CH_2Cl_2), methanol (MeOH), tetrahydrofuran (THF), 1,4-dioxane, diethyl ether (Et_2O) and acetone) were purified and dried according to standard methods.

5.1.2. Analyses and measurements

Spectroscopic analyses

Infrared spectra were recorded on an AVATAR 360 FT-IR spectrometer.
^{1}H NMR spectra were recorded in solution with a Bruker AC-300P (300 MHz) and Bruker DRX 500 (500 MHz) spectrometer, with TMS proton signal as an internal standard.
^{13}C NMR spectra were recorded at 75.5 MHz on a Bruker AC-300P and at 125.5 MHz on a Bruker DRX 500 with solvent carbon signals as internal standard.
GC-MS mass spectra were obtained on an Agilent Technologies 6890N Network GC System with Agilent 5973 Network Mass Selective Detector.
MALDI-TOF mass spectra were recorded on a Kratos Kompact MALDI II.
ESR measurements were carried out on a Bruker EMX spectrometer. The nitroxide concentrations were determined by double integration of the ESR signal, and the data were calibrated under identical condition.
Photochemical deprotection was carried out using a high-pressure mercury lamp (HBO 500, Oriel) with a metal interference filter of 320 nm (Itosgembh, Germany).

Gel Permeation Chromatography (GPC)

The number (M_n) and weight average (M_w) molecular weight and the molecular weight distribution (polydispersity M_w/M_n) of the polymers were determined by GPC under different conditions:
Condition 1. WATER 600E instrument equipped with UV and RI detectors, using chloroform containing 0.1 vol.% TEA as solvent (flow rate: 1.0 ml/min). The samples were measured at 30°C with concentration of 2 mg/ml, calibrated with poly (2-vinyl pyridine). This condition was used for the polymers or block copolymers synthesized from styrene, *n*-butyl acrylate, **M13a**, **M13b**, **M9a**, **M9b**, **M15a** and **M15b**.

Condition 2. KNAUER instrument equipped with RI detectors was used with columns PL-Mixed-C for tetrahydrofuran (THF) and columns PL-Mixed-B for chloroform (flow rate: 1.0 ml/min, concentration: 3 mg/ml, r.t.). The molecular weight data are reported relative to a polymethyl methacrylate calibration. This condition was used for the polymers or block copolymers synthesized from **M12a**, **M12b**.

Condition 3. Hewlett Packard Series 1100 instrument equipped with UV and RI detectors. Column: Zorbax PSM 60 and Zorbax PSM 300, calibrated with poly (2-vinyl pyridine) standards. Solvent: *N,N*,-dimethylacetamide with 3 g/l LiCl and 2 vol.% H_2O. Concentration of the sample: 3 mg/ml, flow rate: 0.5 ml/min, r.t. This condition was used for the polymers or block copolymers synthesized from **M1a**, **M1b**, **M6a**, **M6b**, **M7a**, **M7b**.

Other measurements

Glass transition temperatures (T_g) were recorded on a Perkin-Elmer DSC 7 (with a heating rate of 5°C /min, N_2).
Atomic force microscopy (AFM) was measured by Nanoscope III, Digital Instruments.
Melting points were measured by light microscopy with a heating rate of 0.5-4°C/min. Element analyses were performed with an Euro Vector EA 3000 Elemental Analyzer.
Analytic TLC was performed on commercial Merck plates coated with Silica gel 60 F_{254} (0.20 mm). For flash chromatography Merck Silica gel 60 (0.04-0.063 mm) was employed.

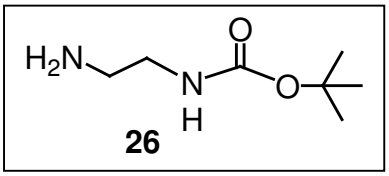
5.2. Synthesis of monomers with free and protected functional groups

5.2.1. (Meth)acrylamides with free and protected amino groups

- ***tert*-Butyl (2-aminoethyl)carbamate (26)**

A solution of di-*tert*-butyldicarbonate (17.50 g, 0.08 mol) in 1,4-dioxane (180 ml) was slowly added into a stirred solution of diaminoethane (36.0 g, 0.60 mol) in 1,4-dioxane (180 ml) at room temperature over a period of 2 h. After 2 days, the formed precipitate was filtered; 1,4-dioxane and the excess of diaminoethane were evaporated *in vacuo* from the filtrate. Bis(*N,N'*-*tert*-butyloxycarbonyl)-1,2-diaminoethane was precipitated by subsequent addition of water (300 ml) and removed by filtration. The aqueous solution was saturated with NaCl and extracted with dichloromethane (150 × 8 ml). The collected organic layer was dried over sodium sulfate and the solvent was removed under reduced pressure to give **26** as colorless oil.

Yield: 10.30 g (80.3%).



26

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3355.8 (br.m, NH_2, NH), 2974.9 (m, CH_3), 1686.4 (s, C=O), 1519.2 (s, NH).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 4.98 (br.s, 1H, N***H***Boc), 3.11-3.17 (m, 2H, C***H₂***NH), 2.75-2.79 (m, 2H, C***H₂***NH_2), 1.48 (s, 2H, NH_2), 1.41 (s, 9H, $C(CH_3)_3$).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 156.21 (C=O), 79.18 (O***C***($(CH_3)_3$), 43.28 (CH_2NH), 41.80 (CH_2NH_2), 28.37 (C(***C***$H_3)_3$).

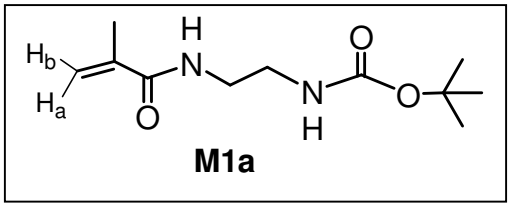
- ***tert*-Butyl [2-(methacryloylamino)ethyl]carbamate (M1a)**

To a solution of **26** (10.0 g, 0.062 mol) in dichloromethane (100 ml) anhydrous sodium carbonate (6.57 g, 0.062 mol) was added and methacryloyl chloride (6.69 g, 0.064 mol) was dropped slowly to this mixture under stirring at 0°C. After warming up to room temperature and stirring for another 2 h, the mixture was filtered and the filtrate was evaporated. Subsequently the crude product was purified by flash chromatography with ethyl acetate as eluent to give **M1a** as a white solid.

Yield: 11.61 g (81.4%).

TLC: R_f = 0.57.

Melting point: 77.5-80°C.



M1a

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3355.9 (br.m, NH, NH), 2939.4 (m, CH_3), 1682.8 (s, C=O, Boc), 1649.9 (s, C=O, amide I), 1615.2 (m, C=C), 1525.9 (br.s, NH, amide II and NHBoc).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.82 (br.s, 1H, CONH), 5.75 (s, 1H, C***H$_a$***H_b=), 5.33 (s, 1H, CH_a***H$_b$***=), 5.11 (br.s, 1H, NHBoc), 3.40-3.44 (m, 2H, CONHC***H₂***), 3.30-3.38 (m, 2H, C***H₂***NHBoc), 1.96 (s, 3H, CH_3), 1.44 (s, 9H, $C(CH_3)_3$).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 168.78 (C=O), 157.27 (C=O, Boc), 139.47 (=***C***(CH_3)), 119.88 (CH_2=), 79.71 (***C***$((CH_3)_3$), 41.51 (CONH***C***H_2), 39.88 (***C***H_2NHBoc), 28.28 (C(***C***$H_3)_3$), 18.49 (CH_3).

$C_{11}H_{20}N_2O_3$ (228.29): Calcd. C 57.87 H 8.83 N 12.27

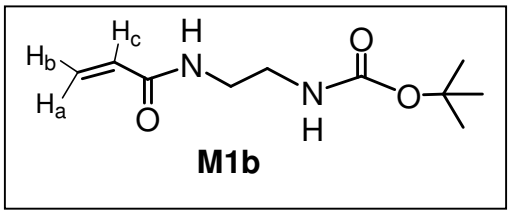
Found C 58.20 H 8.96 N 12.11

GC-MS (70 ev), m/z (%): 172 (11.9%), 155 (16.1%), 143 (8.3%), 115 (5.6%), 112 (6.2%), 111 (15.3%), 99 (53.8%), 98 (90.0%), 87 (13.0%), 86 (32.2%),

84 (30.3%), 69 (100%), 59 (NHCOO, 24.5%), 57 (94.5%), 43 (25.6%), 41 (71.8%) 39 (22.9%).

- ***tert*-Butyl [2-(acryloylamino)ethyl]carbamate (M1b)**

To a solution of **26** (16.0 g, 0.1 mol) in dichloromethane (150 ml) anhydrous sodium carbonate (10.6 g, 0.1 mol) was added and acryloyl chloride (11.0 g, 0.12 mol) was dropped under argon and stirring at 0°C to the solution. Warmed up to room temperature and stirred for 2 h, the mixture was filtered. After that the solvent was evaporated and the crude product was purified by flash chromatography with ethyl acetate as eluent to give **M1b** as a white solid.



M1b

Yield: 16.87 g (78.7%).

TLC: R_f = 0.41.

Melting point: 99.5-101.5°C.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3288.7 (br.m, NH), 1693.7 (s, C=O, Boc), 1658.6 (s, C=O, amide I), 1627.3 (s, C=C), 1545.9 (br.s, NH, amide II and NHBoc).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.55 (br.s, 1H, CONH), 6.26 (dd, $^3J_{(Ha,Hc)}$ = 17.01 Hz (*trans*), $^2J_{(Ha,Hb)}$ = 1.44 Hz, 1H, C***H***$_a$H$_b$=), 6.10 (dd, $^3J_{(Hc,Ha)}$ = 17.01 Hz (*trans*), $^3J_{(Hc,Hb)}$ = 10.12 Hz (*cis*), 1H, =C***H***$_c$), 5.64 (dd, $^2J_{(Hb,Ha)}$ = 1.44 Hz, $^3J_{(Hb,Hc)}$ = 10.12 Hz (*cis*), 1H, C***H***$_b$H$_a$=), 5.04 (br.s, 1H, NH), 3.42-3.47 (m, 2H, CONHC***H***$_2$), 3.31-3.38 (m, 2H, C***H***$_2$NHBoc), 1.44 (s, 9H, C(CH$_3$)$_3$).

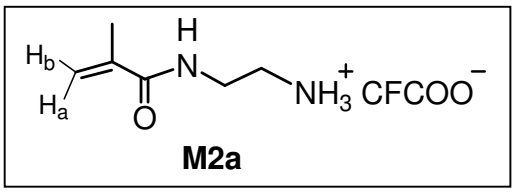
^{13}C-NMR ($CDCl_3$): δ (ppm) = 166.19 (C=O), 157.12 (C=O, Boc), 130.84 (=CH), 126.24 (CH_2=), 79.80 (***C***(CH$_3$)$_3$), 40.99 (CONH***C***H$_2$), 40.05 (***C***H$_2$NHBoc), 28.31 (C(***C***H$_3$)$_3$).

$C_{10}H_{18}N_2O_3$ (214.27):	Calcd.	C 56.06	H 8.47	N 13.07
	Found	C 55.83	H 8.51	N 12.90

GC-MS (70 ev), m/z (%): 158 (6.9%), 141 (17.7%), 112 (13.8%), 97 (10.1%), 87 (20.9%), 85 (51.4%), 84 (86.5%), 72 (16.2%), 59 (54.7%), 57 (77.3%), 56 (21.8%), 55 (100%), 44 (13.8%), 43 (26.8%), 41 (39.9%) 39 (14.7%).

- **[2-(Methacryloylamino)ethyl] ammonium trifluoroacetate (M2a)**

A solution of **M1a** (10.0 g, 0.044 mol) in dichloromethane (50 ml) was cooled to 0°C, and then trifluoroacetic acid (TFA, 45 ml) was dropped slowly. Afterwards the mixture was warmed up to room temperature and stirred for 2 h. The solvent was removed *in vacuo* to give **M2a** as a TFA salt in quantitative yield.



M2a

Melting point: 85.5-88°C.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 1661.3 (s, C=O), 1621.4 (s, C=C), 1545.5 (s, NH), 1134.2 (s, C-F).

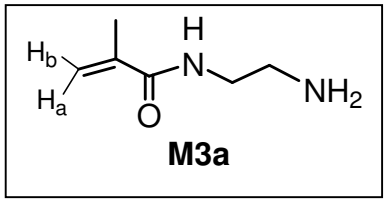
^{1}H-NMR (DMSO): δ (ppm) = 7.95 (br.s, 1H, NH), 5.72 (s, 1H, C***H*****$_a$**H$_b$=), 5.27 (s, 1H, CH$_a$***H*****$_b$**=), 3.46-3.52 (m, 2H, NHC***H*****$_2$**), 2.99-3.03 (m, 2H, C***H*****$_2$**NH$_2$), 1.86 (s, 3H, CH$_3$).

^{13}C-NMR (DMSO): δ (ppm) = 168.11 (C=O), 139.11 (=***C***(CH$_3$)), 160.3, 159.8, 169.4, 160.0 (CF$_3$***C***OO), 122.4, 119.4, 114.6, 110.3 (COO***C***F$_3$), 119.41 (CH$_2$=), 39.66 (NHCH$_2$), 36.73 (CH$_2$NH$_2$), 18.15(CH$_3$).

$C_8H_{13}N_2O_3F_3$ (242.20):	Calcd.	C 39.70	H 5.41	N 11.57
	Found	C 39.63	H 5.39	N 11.10

- ***N*-(2-Aminoethyl)-2-methylacrylamide (M3a)**

To the solution of **M2a** (0.8 g, 3.3 mmol) in water (100 ml) 80 g of anion exchange resin were added. After 3 h stirring, the solvent was removed *in vacuo* at low temperature (-15°C) to yield **M3a** as colorless oil.



M3a

Yield: 0.39 g (92.2%).

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3372.4 (br.s, NH, NH$_2$), 1665.9 (s, C=O, amide I), 1613.2 (s, C=C), 1536.1 (NH, amide II).

^{1}H-NMR (DMSO): δ (ppm) = 7.96 (br.s, 1H, CONH), 5.66 (s, 1H, C***H*****$_a$**H$_b$=), 5.23 (s, 1H, CH$_a$***H*****$_b$**=), 3.27 (br.s, NH$_2$), 3.10-3.27 (m, 2H, NHC***H*****$_2$**), 2.57-2.61 (m, 2H, C*H*$_2$NH$_2$), 1.83 (s, 3H, CH$_3$).

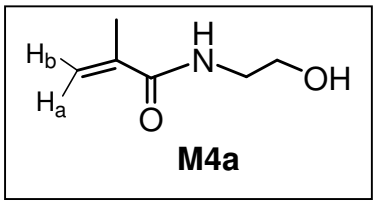
^{13}C-NMR (DMSO): δ (ppm) = 167.91 (C=O), 140.01 (=***C***(CH$_3$)), 119.09 (CH$_2$=), 42.26 (NHCH$_2$), 41.00 (CH$_2$NH$_2$), 18.65 (CH$_3$).

$C_6H_{12}N_2O$ (128.18):	Calcd.	C 56.22	H 9.44	N 21.86
	Found	C 56.57	H 9.62	N 21.18

5.2.2. (Meth)acrylamide with free and protected hydroxyl groups

- ***N*-(2-Hydroxyethyl)-2-methylacrylamide (M4a)**

Into a solution of 2-aminoethanol (24.43 g, 0.4 mol) in CH_2Cl_2 (200 ml) a mixture of 2-methacryloyl chloride (20.9 g, 0.2 mol) in CH_2Cl_2 (20 ml) was added under stirring in an argon atmosphere at 0°C. Subsequently a white precipitate appeared, the mixture was warmed up slowly to room temperature and was stirred for another 2 h. After filtration of the white precipitate, the crude product was concentrated on a rotary evaporator and further purified by flash chromatography (ethyl acetate/methanol 3:1(v/v)) to give a colorless liquid.



M4a

Yield: 19.68 g (76.2%).

TLC: R_f = 0.57.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3317.9 (br.s, OH, NH), 1654.1 (s, CO, amide I), 1608.2 (s, C=C), 1531.3 (s, NH, amide II).

^{1}H-NMR (DMSO): δ (ppm) = 7.86 (br.s, 1H, NH), 5.66 (s, 1H, C***H***$_a$H$_b$=), 5.31 (s, 1H, CH$_a$***H***$_b$=), 4.68 (br.s, 1H, OH), 3.36-3.45 (m, 2H, C***H***$_2$OH), 3.15-3.20 (m, 2H, C***H***$_2$NH), 1.85 (s, 3H, CH_3).

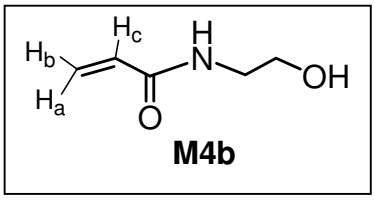
^{13}C-NMR (DMSO): δ (ppm) = 167.4 (C=O), 139.8 (=***C***(CH_3)), 118.9 (CH_2=), 59.6 (CH_2OH), 41.7 ($NHCH_2$), 18.5 (CH_3).

$C_6H_{11}NO_2$ (129.16):	Calcd.	C 55.80	H 8.58	N 10.84
	Found	C 55.33	H 8.67	N 10.58

GC-MS (70 ev), m/z (%): 129 (0.5%), 111 (9.5%), 99 (9.7%), 98 (29.3%), 86 (47.6%), 83 (10.4%), 70 (11.1%), 69 (100%), 41 (49.7%), 39 (19.4%).

- ***N*-(2-Hydroxyethyl)acrylamide (M4b)**

According to the synthesis of **M4a**, 2-aminoethanol (6.11 g, 0.1 mol) in CH_2Cl_2 (100 ml) reacted with acryloyl chloride (4.53 g, 0.05 mol) in CH_2Cl_2 (20 ml) to afford **M4b** as a colorless liquid purified by flash chromatography (ethyl acetate/methanol 3:1 (v/v)).



M4b

Yield: 4.14 g (72.0%).

TLC: R_f = 0.56.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3278.5 (br.s, OH, NH), 1654.5 (s, CO, amide I), 1622.9 (s, C=C), 1544.1 (s, NH, amide II).

^{1}H-NMR (DMSO): δ (ppm) = 6.88 (br.s, 1H, NH), 6.27 (dd, $^{3}J_{(Ha,Hc)}$ = 17.04 Hz (*trans*), $^{2}J_{(Ha,Hb)}$ = 1.92 Hz, 1H, C***H*****$_a$**H$_b$=), 6.15 (dd, $^{3}J_{(Hc,Ha)}$ = 17.04 Hz (*trans*), $^{3}J_{(Hc,Hb)}$ = 9.79 Hz (*cis*), 1H, =C***H*****$_c$**), 5.64 (dd, $^{2}J_{(Hb,Ha)}$ = 1.92 Hz, $^{3}J_{(Hb,Hc)}$ = 9.79 Hz (*cis*), 1H, C***H*****$_b$**H$_a$=), 3.94 (br.s, 1H, OH), 3.70-3.75 (m, 2H, C*H*$_2$OH), 3.42-3.49 (m, 2H, C***H*****$_2$**NH).

^{13}C-NMR (DMSO): δ (ppm) = 166.79 (C=O), 130.54 (=CH), 126.75 (CH_2=), 61.59 (CH_2OH), 42.33 ($NHCH_2$).

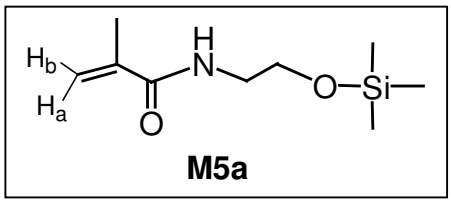
$C_5H_9NO_2$ (115.13): Calcd. C 52.16 H 7.88 N 12.17

Found C 52.63 H 7.41 N 12.38

GC-MS (70 ev), m/z (%): 115 (0.2%), 97 (9.0%), 85 (15.5%), 84 (42.9%), 72 (26.5%), 55 (100%).

- ***N*-{2-[(Trimethylsilyl)oxy]ethyl}-2-methylacrylamide (M5a)**

N-(Hydroxyethyl)-2-methylacrylamide (4.05 g, 0.031 mol) was solved in dry THF (150 ml) and slightly more than one equivalent of triethylamine (3.92 g, 0.038 mol) was added. Finally trimethylsilyl chloride (4.2 g, 0.038 mol) was added slowly while stirring. After 12 h the white precipitate was filtered. Further purification by flash chromatography with CH_2Cl_2 as eluent to yielded product **M5a**.



M5a

Yield: 2.0 g (32.1%).

TLC: R_f = 0.51.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3367.0 (br.s, NH), 2875.5 (m, CH_3), 1658.4 (s, CO, amide I), 1619.7 (s, C=C), 1536.8 (s, NH, amide II), 1251.6 (s, $Si(CH_3)_3$), 843.3 (s, $Si(CH_3)_3$).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.55 (br.s, 1H, NH), 5.61 (s, 1H, C***H*****$_a$**H$_b$=), 5.21 (s, 1H, CH$_a$***H*****$_b$**=), 3.60 (t, $^{3}J_{(H,H)}$ = 5.14 Hz, 2H, CH_2O), 3.27-3.36 (m, 2H, C***H*****$_2$**NH), 1.84 (s, 3H, CH_3), 0.00 (s, 9H, $Si(CH_3)_3$).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 169.3 (C=O), 139.8 (=***C***(CH_3)), 119.9 (CH_2=), 61.8 (CH_2O), 42.4 ($NHCH_2$), 18.5 (CH_3), -0.72 ($Si(CH_3)_3$).

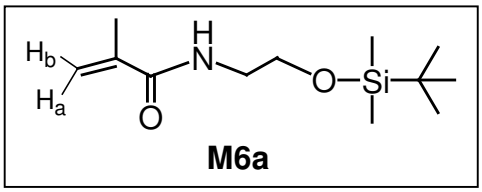
$C_9H_{19}NO_2Si$ (201.34): Calcd. C 53.69 H 9.51 N 6.96

Found C 53.82 H 9.89 N 7.11

GC-MS (70 ev), m/z (%): 129 (0.5%), 111 (9.5%), 98 (29.3%), 86 (47.6%), 69 (100%), 41 (49.7%), 39 (18.8%).

- ***N*-(2-{[*tert*-Butyl(dimethyl)silyl]oxy}ethyl)-2-methylacrylamide (M6a)**

Into a three-neck-flask equipped with a argon bleed, a stirrer, a thermometer and a condenser, *N*-(hydroxyethyl)-2-methylacrylamide (6.45 g, 0.05 mol) in THF (150 ml) was placed, and two equivalents of imidazole (6.8 g, 0.10 mol) were added. After cooling to 0°C *tert*-butyldimethylchlorosilane (7.53 g, 0.05 mol) in CH_2Cl_2 (60 ml) was added slowly under stirring. After 12 h the white precipitate was filtered, the solvent was evaporated under reduced pressure, and the residue was further purified by flash chromatography (ethylacetate/pentane 1:3 (v/v)) to give the product with a yield of 88.7%.



M6a

Yield: 10.8 g (88.7%).

TLC: R_f = 0.47.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3334.2 (br.s, NH), 2955.5 (s, CH_3), 1658.9 (s, C=O), 1620.8 (s, C=C), 1536.4 (s, NH), 1254.9 and 837.9 (s, $Si(CH_3)_2$).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.21 (br.s, 1H, NH), 5.65 (s, 1H, C***H*****$_a$**H_b=), 5.26 (s, 1H, CH_a***H*****$_b$**=), 3.65 (t, $^3J_{(H,H)}$ = 5.35 Hz, 2H, CH_2O), 3.36 (dt, $^3J_{(H,NH)}$ = 10.70 Hz, $^3J_{(H,H)}$ = 5.35 Hz, 2H, NHC***H*****$_2$**), 1.90 (s, 3H, CH_3), 0.83 (s, 9H, $C(CH_3)_3$) 0.00 (s, 6H, $Si(CH_3)_2$).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 168.2 (C=O), 139.5 (=***C***(CH_3)), 119.7 (CH_2=), 61.6 (CH_2O), 41.6 ($NHCH_2$), 25.8 ($C(\boldsymbol{C}H_3)_3$), 18.5 (CH_3), 18.1 (***C***$((CH_3)_3$), -5.5 ($Si(CH_3)_2$).

$C_{12}H_{25}NO_2Si$ (243.42):	Calcd.	C 59.21	H 10.35	N 5.75
	Found	C 59.34	H 10.66	N 5.90

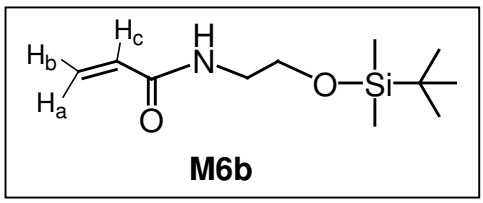
GC-MS (70 ev), m/z (%): 228 (4.9%), 187 (14.6%), 186 (100%), 142 (5.1%), 101 (3.3%), 75 (8.2%), 69 (31.4%), 41 (12.6%).

- ***N*-(2-{[*tert*-Butyl(dimethyl)silyl]oxy}ethyl)acrylamide (M6b)**

According to the synthesis of **M6a**, *N*-(hydroxyethyl)-2-acrylamide (1.15 g, 0.01 mol) in CH_2Cl_2 (60 ml) reacted with *tert*-butyldimethylchlorosilane (1.51 g, 0.01 mol) in CH_2Cl_2 (20 ml) in the presence of imidazole (1.36 g, 0.02 mol) to give the product **M6b** with a yield of 82.1%. (Flash chromatography: ethylacetate/pentane 1:2 (v/v)).

Yield: 1.88 g (82.1%).

TLC: R_f = 0.50.



M6b

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3285.0 (br.s, NH), 2929.4, 2857.5 (m, $(CH)_3$), 1657.9 (s, C=O), 1627.1 (s, C=C), 1549.6 (s, NH, amide II), 1250.9(s, $Si(CH_3)_2$), 836.3 (s, $Si(CH_3)_2$).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.21 (dd, $^3J_{(Ha,Hc)}$ = 16.98 Hz (*trans*), $^2J_{(Ha,Hb)}$ = 1.61 Hz, 1H, C***H***$_a$H$_b$=), 6.04 (dd, $^3J_{(Hc,Ha)}$ = 16.98 Hz (*trans*), $^3J_{(Hc,Hb)}$ = 10.12 Hz (*cis*), 1H, =C***H***$_c$), 5.90 (br.s, 1H, NH),5.58 (dd, $^2J_{(Hb,Ha)}$ = 1.61 Hz, $^3J_{(Hb,Hc)}$ = 10.12 Hz (*cis*), 1H, C***H***$_b$H$_a$=), 3.65 (t, $^3J_{(H,H)}$ = 5.40 Hz, 2H, CH_2O), 3.38 (dt, $^3J_{(H,NH)}$ = 10.80 Hz, $^3J_{(H,H)}$ = 5.40 Hz, 2H, NHC***H***$_2$), 0.83 (s, 9H, $C(CH_3)_3$), 0.00 (s, 6H, $Si(CH_3)_2$).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 165.4 (C=O), 130.9 (=CH), 126.2 (CH_2=), 61.7 (CH_2O), 41.6 ($NHCH_2$), 25.9 ($C(\boldsymbol{C}H_3)_3$), 18.1 ($\boldsymbol{C}((CH_3)_3$), -5.4 ($Si(CH_3)_2$).

$C_{11}H_{23}NO_2Si$ (229.40):	Calcd.	C 57.60	H 10.11	N 6.11
	Found	C 57.31	H 10.36	N 6.26

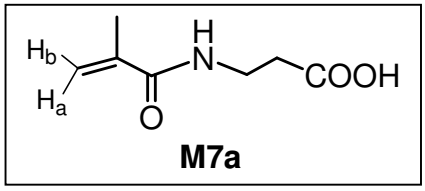
GC-MS (70 ev), m/z (%): 214 (5.0%), 173 (13.5%), 172 (100%), 128 (10.3%), 118 (8.9%), 75 (12.8%), 55 (20.6%).

5.2.3. (Meth)acrylamide with free and protected carboxyl groups

- ***N*-Methacryloyl-*β*-alanine (M7a)**

N-Methacryloyl-*β*-alanine (**M7a**) was prepared by reaction of *β*-alanine and 2-methylacryloyl chloride according to a modified literature procedure.[195] *β*-Alanine (26.73 g, 0.30 mol) and potassium hydroxide (44.8 g, 0.80 mol) were added to methanol (800 ml), and the mixture was cooled to 0°C in an ice bath. 2-Methylacryloyl chloride (34.50 g, 0.33 mol) was dropped slowly to the stirred solution, and then the mixture was warmed up to room temperature and stirred for 4 h. After the solvent was removed in vacuum, the crude product was dissolved in water (200 ml), the aqueous solution was acidified to PH = 1-2 by dropwise addition of concentrated HCl with stirring at 0°C. The solution was saturated by sodium chloride and extracted with ethyl acetate. The product was purified by repeated precipitation by pentane from ethyl acetate to give a white solid.

Yield: 35.93 g (76.2%).



M7a

Melting point: 74-76°C.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3337.9, 3078.4 (s, m, NH OH), 1710.9 (s, C=O, COOH), 1649.4 (s, C=O, amide I), 1595.7 (m, C=C), 1546.3 (s, NH, amide II).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 10.12 (br.s, 1H, COOH), 6.53 (br.s, 1H, NH), 5.70 (s, 1H, C***H***$_a$H$_b$=), 5.34 (s, 1H, CH$_a$***H***$_b$=), 3.55-3.62 (m, 2H, NHC***H***$_2$), 2.64 (t, $^3J_{(H,H)}$ = 7.17 Hz, 2H, C***H***$_2$COOH), 1.94 (s, 3H, CH_3).

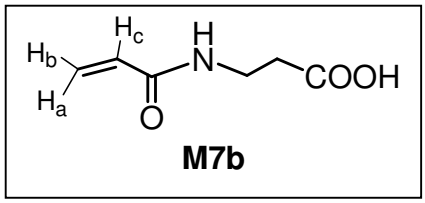
^{13}C-NMR ($CDCl_3$): δ (ppm) = 176.81 (C=O, COOH), 168.73 (C=O), 139.43 (=***C***(CH_3)), 120.34 (CH_2=), 34.94 ($NHCH_2$), 33.65 (***C***H_2COOH), 18.49 (CH_3).

$C_7H_{11}NO_3$ (157.16):	Calcd.	C 53.49	H 7.06	N 8.91
	Found	C 53.42	H 7.18	N 8.90

GC-MS (70 ev), m/z (%): 157 (14.2%), 139 (6.9%), 112 (12.7%), 98 (28.9%), 88 (28.4%), 69 (100%), 41 (59.2%), 39 (21.7%).

- ***N*-Acryloyl-*β*-alanine (M7b)**

N-acryloyl-*β*-alanine (**M7b**) was prepared by reaction of *β*-alanine (7.13 g, 0.08 mol) and acryloyl chloride (8.15 g, 0.09 mol) in the presence of potassium hydroxide (10.08 g, 0.18 mol) in methanol (200 ml) in a similar way as *N*-methacryloyl-*β*-alanine (**M7a**). The product was purified by repeated precipitation by pentane from ethyl acetate to give a white solid.



M7b

Yield: 9.36 g (81.7%).

Melting point: 92-95°C.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3252.4, 3057.7 (br.s, br.m, OH, NH), 1694.4 (s, C=O, COOH), 1649.3 (s, C=O, amide I), 1621.4 (m, C=C), 1552.5 (s, NH, amide II).

^{1}H-NMR (DMSO): δ (ppm) = 12.23 (br.s, 1H, COOH), 8.17 (br.s, 1H, NH), 6.20 (dd, $^3J_{(Hc,Ha)}$ = 17.09 Hz (*trans*), $^3J_{(Hc,Hb)}$ = 9.94 Hz (*cis*), 1H, =C***H***$_c$) 6.06 (dd, $^3J_{(Ha,Hc)}$ = 17.09 Hz (*trans*), $^2J_{(Ha,Hb)}$ = 2.41 Hz, 1H, C***H***$_a$H$_b$=), 5.56 (dd, $^2J_{(Hb,Ha)}$ = 1.44 Hz, $^3J_{(Hb,Hc)}$ = 10.12 Hz (*cis*), 1H, C***H***$_b$H$_a$=), 3.29-3.36 (m, 2H, NHC***H***$_2$), 2.41 (t, $^3J_{(H,H)}$ = 6.91 Hz, 2H, C***H***$_2$COOH).

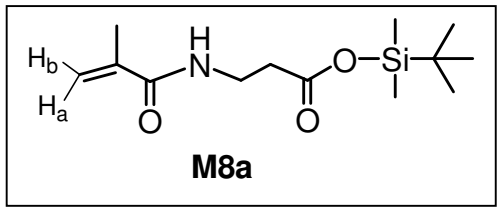
^{13}C-NMR (DMSO): δ (ppm) = 172.86 (C=O, COOH), 164.63 (C=O, $CONH_2$), 131.66 (=CH), 125.07 (CH_2=), 34.84 ($NHCH_2$), 33.76 (***C***H_2COOH).

$C_6H_9NO_3$ (143.14):	Calcd.	C 50.35	H 6.34	N 9.79
	Found	C 50.21	H 6.44	N 9.92

GC-MS (70 ev), m/z (%): 143 (2.9%), 125 (1.2%), 98 (23.3%), 88 (32.5%), 70 (11.3%), 55 (100%), 44 (9.9%).

- ***tert*-Butyl(dimethyl)silyl *N*-methacryloyl-*β*-alaninate (M8a)**

tert-Butyldimethylchlorosilane (4.52 g, 0.03 mol) was added slowly into the solution of *N*-methacryloyl-β-alanine (4.72 g, 0.03 mol) in CH_2Cl_2 (30ml) in the presence of two times of equivalent of imidazole (4.08 g, 0.06 mol) at 0°C under stirring in argon atmosphere. After 48 h the white precipitate was filtered, the solvent was evaporated under reduced pressure and the residue was further purified by flash chromatography (ethyl acetate/pentane 1:1 (v/v)) to give the product as pale yellow oil with 6.82 g yield.



M8a

Yield: 6.82 g (83.8%).

TLC: $R_f = 0.86$.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3335.5 (br.m, NH), 2931.6 (m, CH_3), 1717.1 (s, C=O, COOSi), 1657.1 (s, C=O, amide I), 1616.1 (s, C=C), 1531.4 (s, NH, amide II), 1253.9 and 826.5 (s, $Si(CH_3)_2$).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.42 (br.s, 1H, NH), 5.59 (s, 1H, C***H*****$_a$**H_b=), 5.23 (s, 1H, CH_a***H*****$_b$**=), 3.46 (dt, $^3J_{(H,NH)}$ = 11.90 Hz, $^3J_{(H,H)}$ = 5.95 Hz, 2H, NHC***H*****$_2$**), 2.50 (t, $^3J_{(H,H)}$ = 5.95 Hz, 2H, C***H*****$_2$**COO), 1.85 (s, 3H, CH_3), 0.83 (s, 9H, $C(CH_3)_3$), 0.18 (s, 6H, $Si(CH_3)_2$).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 173.25 (C=O, COO), 168.22 (C=O, CONH), 139.78 (=***C***(CH_3)), 119.66 (CH_2=), 35.41($NHCH_2$), 35.05 (CH_2COO), 25.6 ($C($***C***$H_3)_3$), 18.50 (CH_3), 17.54 (***C***$(CH_3)_3$), -4.82 ($Si($***C***$H_3)_2$).

$C_{13}H_{25}NO_3Si$ (271.44): Calcd. C 57.53 H 9.28 N 5.16

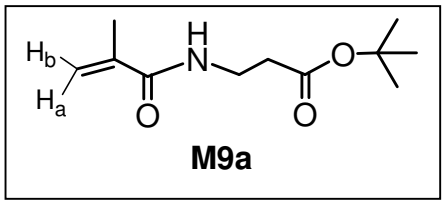
Found C 57.32 H 9.44 N 5.38

GC-MS (70 ev), m/z (%): 157 (13.6%), 139 (6.6%), 112 (12.4%), 98 (28.2%), 88 (29.3%), 70 (20.5%), 69 (100%), 41 (60.3%), 39 (21.4%).

- ***tert*-Butyl *N*-methacryloyl-*β*-alaninate (M9a)**

A solution of *N*-methacryloyl-*β*-alanine (6.29 g, 0.04 mol) and *tert*-butanol (1.48 g, 0.02 mol) in THF (40 ml) was slowly added into a stirred solution of di-*tert*-butyl dicarbonate (8.73 g, 0.04 mol) and 4-dimethylaminopyridine (DMAP) (1.80 g, 0.015 mol) in THF (150 ml) at

room temperature. After the addition of 2,6-di-*tert*-butyl-4-methyl-phenol (0.1 g, 0.45 mmol) was added, the mixture was refluxed at 50°C for 8 h. Then the mixture was cooled to room temperature, the yellow precipitate was filtered and the solvent was removed in vacuum. The crude product was purified by flash chromatography (ethyl acetate/pentane 1:1 (v/v)) to give the product as a white solid with 3.26 g yield.



M9a

Yield: 3.26 g (38.2%).

TLC: R_f = 0.45.

Melting point: 55-57°C.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3291.1 (br.m, NH), 2980.8 (m, CH_3), 2932.2 (w, CH_2), 1723.1 (s, C=O, COO), 1653.8 (s, C=O, amide I), 1611.1 (s, C=C), 1540.4 (s, NH, amide II).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.48 (br.s, 1H, NH), 5.66 (s, 1H, C***H***$_a$H$_b$=), 5.29 (s, 1H, CH$_a$***H***$_b$=), 3.48-3.54 (m, 2H, NHC***H***$_2$), 2.43-2.47 (t, $^3J_{(H,H)}$ = 6.00 Hz, 2H, C***H***$_2$COO), 1.92 (s, 3H, CH_3), 1.43 (s, 9H, $C(CH_3)_3$).

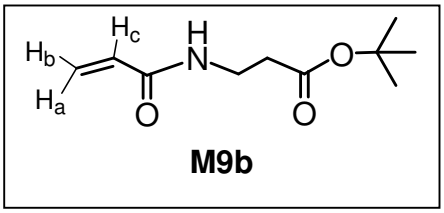
^{13}C-NMR ($CDCl_3$): δ (ppm) = 172.06 (C=O, COOH), 168.09 (C=O, CONH), 139.87 (=***C***(CH_3)), 119.50 (CH_2=), 81.07 (***C***$((CH_3)_3)$, 35.08($NHCH_2$), 34.95 (***C***H_2COO), 28.03 ($(CH_3)_3$), 18.50 (CH_3).

$C_{11}H_{19}NO_3$ (213.28):	Calcd.	C 61.95	H 8.98	N 6.57
	Found	C 62.47	H 9.36	N 6.30

GC-MS (70 ev), m/z (%): 157 (100%), 140 (76.9%), 112 (16.2%), 98 (56.9%), 88 (29.0%), 69 (81.5%), 57 (71.7%), 41 (49.2%).

- ***tert*-Butyl *N*-acryloyl-*β*-alaninate (M9b)**

According to the synthesis of **M9a**, *N*-methacryloyl-*β*-alanine (7.16 g, 0.05 mol) and *tert*-butanol (2.22 g, 0.03 mol) in THF (50 ml) reacted with di-*tert*-butyldicarbonate (11.35 g, 0.052 mol) in THF (150 ml) in the presence of 4-dimethylaminopyridine (DMAP) (1.80 g, 0.015 mol) at 60°C for 10 h to yield product **M9b** as a white solid (ethyl acetate/pentane 1:1 (v/v)) with a yield of 40.4%.



M9b

Yield: 3.22 g (40.4%).

TLC: R_f = 0.30.

Melting point: 81-82.5°C.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3232.1 (br.m, NH), 2978.8, 2885.7 (m, CH_3, CH_2), 1724.7 (s, C=O, COO), 1649.3 (s, C=O, amide I), 1616.4 (s, C=C), 1557.4 (s, NH, amide II).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.54 (br.s, 1H, NH), 6.28 (dd, $^3J_{(\boldsymbol{Ha},\mathrm{Hc})}$ = 16.95 Hz (*trans*), $^2J_{(\boldsymbol{Ha},\mathrm{Hb})}$ = 1.57 Hz, 1H, C$\boldsymbol{H_a}$H$_b$=), 6.08 (dd, $^3J_{(\boldsymbol{Hc},\mathrm{Ha})}$ = 16.95 Hz (*trans*), $^3J_{(\boldsymbol{Hc},\mathrm{Hb})}$ = 10.21 Hz (*cis*), 1H, =C$\boldsymbol{H_c}$), 5.64 (dd, $^2J_{(\boldsymbol{Hb},\mathrm{Ha})}$ = 1.57 Hz, $^3J_{(\boldsymbol{Hb},\mathrm{Hc})}$ = 10.21 Hz (*cis*), 1H, C$\boldsymbol{H_b}$H$_a$=), 3.53-3.57 (m, 2H, NHC$\boldsymbol{H_2}$), 2.50 (t, $^3J_{(\mathrm{H,H})}$ = 6.00 Hz, 2H, CH_2COO), 1.46 (s, 9H, C(CH_3)$_3$).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 172.10 (C=O, COO), 165.37 (C=O, CONH), 130.87 (=CH), 126.34 (CH_2=), 81.16 ($\boldsymbol{C}$(CH_3)$_3$), 34.94 (NHCH_2, and $\boldsymbol{C}H_2$COO), 28.07 (CH_3)$_3$).

$C_{10}H_{17}NO_3$ (199.25):	Calcd.	C 60.28	H 8.60	N 7.03
	Found	C 59.81	H 8.43	N 6.94

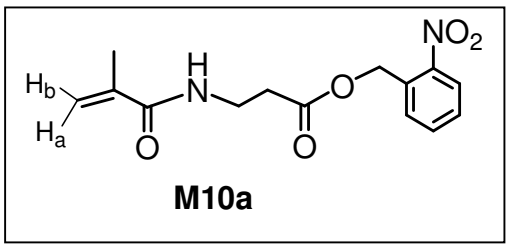
GC-MS (70 ev), m/z (%): 143 (86.3%), 126 (100%), 98 (26.8%), 88 (43.1%), 84 (70.1%), 70 (8.4%), 57 (94.1%), 55 (95.7%), 43 (12.7%), 41 (30.3%).

- **2-Nitrobenzyl *N*-methacryloyl-*β*-alaninate (M10a)**

Into a mixture of 1-(chloromethyl)-2-nitrobenzene (6.86 g, 0.04 mol), and *N*-methacryloyl-*β*-alanine (6.29 g, 0.04 mol) in dried acetone (150 ml), catalytic amounts of sodium iodide and triethyl amine (4.08 g, 0.04 mol) were added at room temperature. After that the mixture was stirred for 5 h, the yellow precipitate was filtered, and the solvent was evaporated under reduced pressure. Further purification was done by flash chromatography (acetone/pentane 2.5:1 (v/v) to give the product as a pale yellow power with 8.56 g.

Yield: 8.56 g (73.2%).

TLC: R_f = 0.38.



M10a

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3334.6 (br.m, NH), 1736.0 (s, C=O, COOCH_2), 1658.5 (s, C=O, amide I), 1615.3 (s, C=C), 1521.0 (br.s, NH, amide II, NO_2), 789.6, 728.4 (s, Ar).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.46-8.10 (m, 4H, Ar), 6.43 (br.s, 1H, NH), 5.73 (s, 1H, C$\boldsymbol{H_a}$H$_b$=), 5.51 (s, 2H, CH_2-Ar), 5.30 (s, 1H, CH$_a$$\boldsymbol{H_b}$=), 3.56-3.63 (m, 2H, NHC$\boldsymbol{H_2}$), 2.68 (t, $^3J_{(\mathrm{H,H})}$ = 5.70 Hz, 2H, C$\boldsymbol{H_2}$COO), 1.92 (s, 3H, CH_3).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 172.01 (C=O, COO), 168.30 (C=O, CONH), 147.62, 133.77, 131.52, 129.24, 129.01, 125.09 (Ar), 139.68 (=***C***(CH_3)), 119.84 (CH_2=), 63.24 (***C***H_2-Ar), 35.29($NHCH_2$), 33.84 (***C***H_2COO), 18.50 (CH_3).

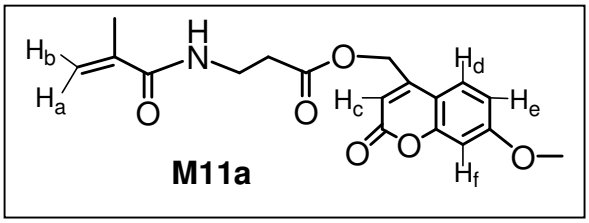
$C_{14}H_{16}N_2O_5$ (292.27): Calcd. C 57.53 H 5.52 N 9.58

Found C 57.58 H 5.78 N 9.47

GC-MS (70 ev), m/z (%): 156 (6.5%), 140 (11.5%), 136 (43.2%), 121 (12.8%), 112 (3.8%), 98 (25.4%), 78 (27.6%), 69 (100%), 41 (30.7%).

- **(7-Methoxy-2-oxo-2*H*-chromen-4-yl)methyl *N*-methacryloyl-*β*-alaninate (M11a)**

To a suspension of 4-(bromomethyl)-7-methoxycumarin (1 g, 3.7 mmol) in dried acetone (20 ml), potassium fluoride (430 mg, 7.4 mmol) and *N*-methacryloyl-β-alanine (584 mg, 3.7 mmol) were added. The mixture was stirred at room temperature for two days, then the solvent was removed in vacuo, the residue was suspended in 50 ml water and extracted with 3 × 60 ml ethyl acetate. The combined organic phases were dried with sodium sulfate; the solvent was evaporated in vacuum. Flash chromatography of the residue with dichloromethane ($CHCl_2$) yielded 1.10 g (7-methoxy-2-oxo-2*H*-chromen-4-yl)methyl *N*-methacryloyl-*β*-alaninate **(M11a)** as a pale yellow solid.



M11a

Yield: 1.10 g (86.1%).

TLC: R_f = 0.42.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3382.9 (br.m, NH), 1704.0 (s, C=O, $COOCH_2$), 1665.7 (s, C=O, amide I), 1613.9 (s, C=C), 1515.9 (s, NH, amide II, NO_2).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.37 (d, $^3J_{(\boldsymbol{He},\mathrm{Hd})}$ = 8.81 Hz, 1H, Ar, ***H*****$_e$**), 6.84 (d, $^3J_{(\boldsymbol{Hd},\mathrm{He})}$ = 8.81 Hz, 1H, Ar, ***H*****$_d$**), 6.82 (s, 1H, Ar, ***H*****$_f$**), 6.45 (br.s, 1H, NH), 6.25 (s, 1H, Ar, ***H*****$_c$**), 5.75 (s, 1H, C***H*****$_a$**H_b=), 5.30 (s, 1H, CH_a***H*****$_b$**=), 5.25 (s, 2H, C***H*****$_2$**-Ar), 3.85 (s, 3H, OCH_3), 3.58-3.63 (m, 2H, NHC***H*****$_2$**), 2.72 (t, $^3J_{(\mathrm{H,H})}$ = 8.81 Hz, 2H, C***H*****$_2$**COO), 1.91 (s, 3H, CH_3).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 171.84 (C=O, COO), 168.30 (C=O, CONH), 162.87, 160.67, 155.47, 148.77 (*tert* C, Ar), 139.56 (=***C***(CH_3)), 124.40 (CH, Ar), 119.88 (CH_2=), 112.63 (Ar, CH), 110.44 (*tert* C, Ar), 110.13, 101.15 (CH, Ar), 61.45 (***C***H_2-Ar), 55.75 (OCH_3), 34.93 ($NHCH_2$), 33.74 (***C***H_2COO), 18.47 (CH_3).

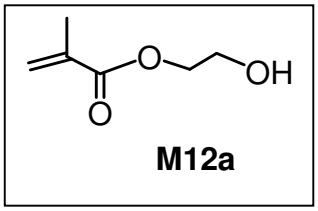
$C_{18}H_{19}NO_6$ (345.36):	Calcd.	C 62.60	H 5.55	N 4.06
	Found	C 62.83	H 5.40	N 3.96

GC-MS (70 ev), m/z (%): 345 (61.6%), 256 (26.3%), 228 (19.0%), 206 (100%), 190 (97.2%), 178 (12.7%), 161 (31.5%), 140 (94.7%), 98 (56.4%), 69 (65.8%).

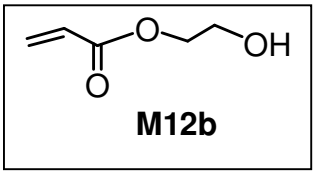
5.2.4. (Meth)acrylates with free and protected hydroxyl groups

- **2-Hydroxyethyl 2-methylacrylate (M12a) and 2-hydroxyethyl acrylate (M12b)**

Monomer **M12a** and **M12b** were commercially available. They were distilled under vacuum prior to use.



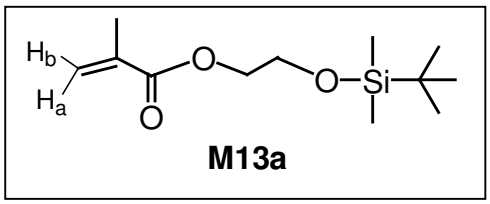
M12a



M12b

- **2-{[*tert*-Butyl(dimethyl)silyl]oxy}ethyl 2-methylacrylate (M13a)**

The same procedure as for the synthesis of **M6a** was applied. 2-Hydroxyethyl 2-methylacrylate (6.5 g, 0.05 mol) reacted with *tert*-butyldimethylchlorosilane (7.53 g, 0.05 mol) in CH_2Cl_2 (150 ml) in the presence of imidazole (6.8 g, 0.10 mol) to afford the product **M13a** with a yield of 91.7%.



M13a

Yield: 11.2 g (91.7%).

TLC: CH_2Cl_2, R_f = 0.78.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 2956.3, 2931.7, 2858.8 (m, $(CH)_3$), 1723.4 (s, C=O), 1639.0 (s, C=C), 1251.6 and 832.5 (s, $Si(CH_3)_2$).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.06 (s, H, C***H*****$_a$**H_b=), 5.50 (s, H, CH_a***H*****$_b$**=), 4.15 (t, $^3J_{(H,H)}$ = 5.10 Hz, 2H, $COOCH_2$), 3.78 (t, $^3J_{(H,H)}$ = 5.10 Hz, 2H, CH_2OSi), 1.89 (s, 3H, CH_3), 0.83 (s, 9H, $C(CH_3)_3$), 0.00 (s, 6H, $Si(CH_3)_2$).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 167.4 (C=O), 136.3 (=***C***(CH_3)), 125.5 (CH_2=), 65.9 (COO***C***H_2), 61.2 (CH_2OSi), 25.8 (C(***C***H_3)$_3$), 18.4 (CH_3), 18.3 (***C***(CH_3)$_3$), -5.4 (Si(CH_3)$_2$).

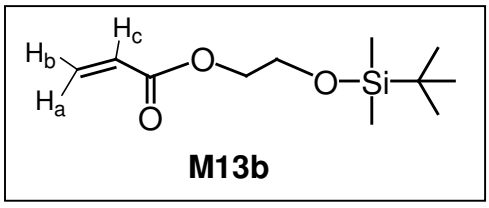
$C_{12}H_{24}O_3Si$ (244.41): Calcd. C 58.97 H 9.90

Found C 59.60 H 10.20

GC-MS (70 ev), m/z (%): 187 (31.5%), 143 (64.9%), 69 (100%), 59 (6.1%), 41 (23.3%).

- **2-{[*tert*-Butyl(dimethyl)silyl]oxy}ethyl acrylate (M13b)**

The same procedure as for the synthesis of **M6a** was applied. 2-Hydroxyethyl acrylate (5.8 g, 0.05 mol) reacted with *tert*-butyldimethylchlorosilane (7.53 g, 0.05 mol) in CH_2Cl_2 (150 ml) in the presence of imidazole (6.8 g, 0.10 mol) to give product **M13b**.



M13b

Yield: 10.7 g (92.9%).

TLC: CH_2Cl_2, R_f = 0.76.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 2953.8, 2930.9, 2857.9 (m, (CH_3)$_3$), 1727.0 (s, C=O), 1636.5 (s, C=C), 1254.4 and 831.8 (s, Si(CH_3)$_3$).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.34 (dd, $^3J_{(Ha,Hc)}$ = 17.28 Hz (*trans*), $^2J_{(Ha,Hb)}$ = 1.43 Hz, 1H, C***H***$_a$H$_b$=), 6.06 (dd, $^3J_{(Hc,Ha)}$ = 17.28 Hz (*trans*), $^3J_{(Hc,Hb)}$ = 10.39 Hz (*cis*), 1H, =C***H***$_c$), 5.76 (dd, $^2J_{(Hb,Ha)}$ = 1.43 Hz, $^3J_{(Hb,Hc)}$ = 10.39 Hz (*cis*), 1H, C***H***$_b$H$_a$=), 4.16 (t, $^3J_{(H,H)}$ = 5.00 Hz, 2H, $COOCH_2$), 3.78 (t, $^3J_{(H,H)}$ = 5.00 Hz, 2H, CH_2OSi), 0.82 (s, 9H, C(CH_3)$_3$), 0.00 (s, 6H, Si(CH_3)$_2$).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 166.1 (C=O), 130.9 (CH_2=), 129.4 (=CH), 65.7 (COO***C***H_2), 61.2 (CH_2OSi), 25.8 (C(***C***H_3)$_3$), 18.3 (***C***(CH_3)$_3$), -5.4 (Si(CH_3)$_2$).

$C_{11}H_{22}O_3Si$ (230.38): Calcd. C 57.35 H 9.63

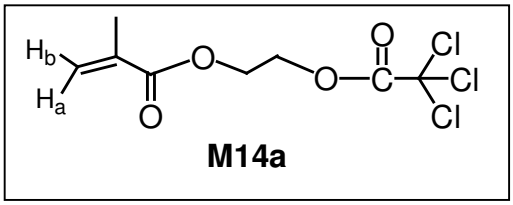
Found C 57.98 H 10.23

GC-MS (70 ev), m/z (%): 173 (29.8%), 129 (100%), 75 (21.8%), 73 (15.1%), 55 (71.6%).

- **2-[(2,2,2-Trichloroacetyl)oxy]ethyl 2-methylacrylate (M14a)**

To a solution of 2-hydroxyethyl 2-methylacrylate (7.81 g, 0.06 mol) and pyridine (9.49 g, 0.12 mol) in CH_2Cl_2 (100 ml), trichloroacetyl chloride (14.55 g, 0.08 mol) in CH_2Cl_2 (30 ml) was dropped slowly at 0°C. Warmed up to room temperature, the mixture was stirred for 2 days,

then was washed with water, dried with $MgSO_4$, and concentrated to dryness *in vacuo*. This crude product was purified by flash chromatography eluting with ethyl acetate/pentane 1:3 (v/v), to give pale yellow oil with a yield of 73.4%.



M14a

Yield: 12.14 g (73.4%).

TLC: R_f = 0.79.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 1766.9 (s, C=O), 1720.2 (s, C=O), 1637.1 (s, C=C), 750.5 (s, CCl_3).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.14 (s, H, C***H*****$_a$**H_b=), 5.61 (s, H, CH_a***H*****$_b$**=), 4.62 (t, $^3J_{(H,H)}$ = 4.66 Hz, 2H, CH_2OCO), 4.47 (t, $^3J_{(H,H)}$ = 4.66 Hz, 2H, $CH_2OCOCCl_3$), 1.95 (s, 3H, CH_3).

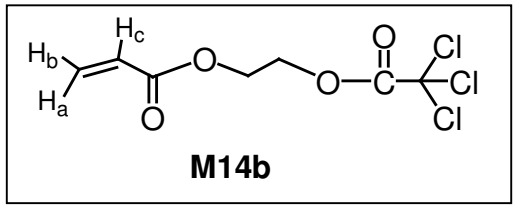
^{13}C-NMR ($CDCl_3$): δ (ppm) = 166.8 (C=O), 161.9 (***C***=$OCCl_3$), 135.7 (=***C***(CH_3)), 126.5 (CH_2=), 89.5 (CCl_3), 66.5 (COO***C***H_2), 61.4 (***C***$H_2OCOCCl_3$), 18.1 (CH_3).

$C_8H_9O_4Cl_3$ (275.52):	Calcd.	C 34.88	H 3.29	Cl 38.60
	Found	C 35.37	H 3.37	Cl 38.06

GC-MS (70 ev), m/z (%): 191 (6.8 %), 189 (2.8 %), 154 (5.3 %), 147 (4.5 %), 119 (16.2 %), 117 (16.6 %), 113 (17.3 %), 112 (23.2 %), 84 (9.9 %), 82 (7.8 %), 69 (100 %), 41 (35.6 %), 39 (17.3 %).

- **2-[(2,2,2-Trichloroacetyl)oxy]ethyl acrylate (M14b)**

Into the solution of 2-hydroxyethyl acrylate (6.97 g, 0.06 mol) in CH_2Cl_2 (100 ml) was added pyridine (9.49 g, 0.12 mol). The solution was cooled to 0°C in an ice water bath for the dropwise addition of the solution of trichloroacetyl chloride (14.55 g, 0.08 mol) in CH_2Cl_2 (30 ml). Warmed up to room temperature, the mixture was stirred for 2 days. The mixture was washed with water, dried with $MgSO_4$, and concentrated to dryness *in vacuo*. This crude product was purified by flash chromatography eluting with ethyl acetate/pentane 1:3 (v/v) to give pale yellow oil with a yield of 67.8%.



M14b

Yield: 10.64 g (67.8%).

TLC: R_f = 0.79.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 1766.4 (s, C=O), 1725.6 (s, C=O), 1636.1 (s, C=C), 751.1 (s, CCl_3).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.44 (dd, $^{3}J_{(Ha,Hc)}$ = 17.30 Hz (*trans*), $^{2}J_{(Ha,Hb)}$ = 1.40 Hz, 1H, C***H***$_a$H$_b$=), 6.15 (dd, $^{3}J_{(Hc,Ha)}$ = 17.30 Hz (*trans*), $^{3}J_{(Hc,Hb)}$ = 10.42 Hz (*cis*), 1H, =C***H***$_c$), 5.88 (dd, $^{2}J_{(Hb,Ha)}$ = 1.40 Hz, $^{3}J_{(Hb,Hc)}$ = 10.42 Hz (*cis*), 1H, C***H***$_b$H$_a$=), 4.62 (t, $^{3}J_{(H,H)}$ = 2.40 Hz, 2H, $COOCH_2$), 4.48 (t, $^{3}J_{(H,H)}$ = 2.40 Hz, 2H, $CH_2OCOCCl_3$).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 165.5 (C=O), 161.8 ($C=OCCl_3$), 131.7 (CH_2=), 127.6 (=CH), 89.4 (CCl_3), 66.5 (COO***C***H_2), 61.2 (***C***$H_2OCOCCl_3$).

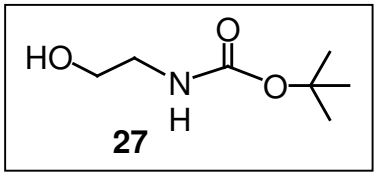
$C_7H_7O_4Cl_3$ (261.49):	Calcd.	C 32.15	H 2.70	Cl 40.67
	Found	C 32.95	H 2.77	Cl 40.17

GC-MS (70 ev), m/z (%): 190 (8.4%), 188 (8.8%), 119 (13.4%), 117 (13.6%), 99 (15.3%), 84 (4.6%), 82 (7.1%), 55 (100%).

5.2.5. (Meth)acrylate with free and protected amino groups

- ***tert*-Butyl (2-hydroxyethyl)carbamate (27)**

A solution of di-*tert*-butyldicarbonate (43.64 g, 0.20 mol) in 1,4-dioxane (350 ml) was slowly added into a stirred solution of 2-aminoethanol (45.75 g, 0.75 mol) in 1,4-dioxane (250 ml) at room temperature over a period of 3 h and stirring was continued for 2 days. After the evaporation of the 1,4-dioxane *in vacuo* the residue was redissolved in water (200 ml). The aqueous solution was saturated with NaCl and extracted with dichloromethane (150 ml x 8). The collected organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure to give **27** as colorless oil with 29.08 g.



27

Yield: 29.08 g (90.2%).

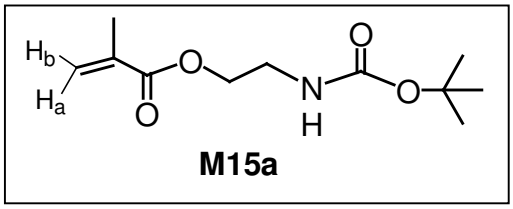
IR (neat), $\tilde{\nu}$ (cm^{-1}): 3339.9 (br.m, OH), 2976.3 (m, CH_3), 1683.1 (s, C=O, Boc), 1518.4 (s, NH).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 5.06 (br.s, 1H, N***H***Boc), 3.68-3.71 (m, 2H, C***H$_2$***OH), 3.26-3.32 (m, 2H, C***H$_2$***NH), 2.78 (s, 1H, OH), 1.45 (s, 9H, $C(CH_3)_3$).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 184.71 (C=O), 84.95 (O***C***$((CH_3)_3$), 62.30 (CH_2OH), 43.03 (CH_2NH), 28.37 ($C(\boldsymbol{C}H_3)_3$).

- **2-[(*tert*-Butoxycarbonyl)amino]ethyl 2-methylacrylate (M15a)**

Into a solution of **27** (10.0 g, 0.062 mol) in dichloromethane (100 ml) anhydrous sodium carbonate (6.57 g, 0.062 mol) was added, and 2-methacryloyl chloride (6.53 g, 0.625 mol) was slowly dropped in under argon and stirring at 0°C. After warming up to room temperature and stirring for two days, the mixture was filtered to remove the white precipitate and the filtrate was concentrated in vacuum. Further purification of the crude product was done by flash chromatography (ethyl acetate/pentane 1:2 (v/v)) to give **M15a** as a white solid.



M15a

Yield: 11.40 g (80.2%).

TLC: R_f = 0.57.

Melting point: 56.5-58.5°C.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3381.9 (br.m, NH), 2981.6 (w, CH_3), 1691.5 (s, C=O), 1632.9 (m, C=C), 1523.5 (s, NH).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.11 (s, 1H, C***H***$_a$$H_b$=), 5.57 (s, 1H, CH_a***H***$_b$=), 4.77 (br.s, 1H, NHBoc), 4.19 (t, $^3J_{(H,H)}$ = 5.10 Hz, 2H, OCH_2), 3.42-3.44 (m, 2H, C***H***$_2$NHBoc), 1.95 (s, 3H, CH_3), 1.43 (s, 9H, $C(CH_3)_3$).

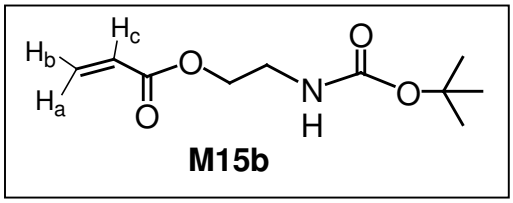
^{13}C-NMR ($CDCl_3$): δ (ppm) = 167.28 (C=O), 155.73 (C=O, Boc), 136.01 (=***C***(CH_3)), 125.91 (CH_2=), 79.63 (***C***$((CH_3)_3)$), 63.95 (O***C***H_2), 39.68 (***C***H_2NHBoc), 28.34 ($C(\boldsymbol{C}H_3)_3$), 18.29(CH_3).

$C_{11}H_{19}NO_4$ (229.28):	Calcd.	C 57.63	H 8.35	N 6.11
	Found	C 57.94	H 9.08	N 5.97

GC-MS (70 ev), m/z (%): 156 (5.9%), 143 (5.0%), 115 (5.5%), 99 (2.6%), 87 (17.3%), 69 (55.9%), 59 (18.4%), 57 (100%), 43 (22.0%), 41 (42.1%).

- **2-[(*tert*-Butoxycarbonyl)amino]ethyl acrylate (M15b)**

Into a solution of **27** (10.0 g, 0.062 mol) in dichloromethane (100 ml) anhydrous sodium carbonate (6.57 g, 0.062 mol) was added. Acryloyl chloride (5.70 g, 0.063 mol) was dropped slowly to this mixture in argon under stirring at 0°C. Afterwards the mixture was warmed up to room temperature and stirred for two days. Finally the mixture was filtered and the filtrate was concentrated under reduce pressure. Further purification of the crude product was carried out by flash chromatography (ethyl acetate/pentane 1:2 (v/v)) to give **M15b** as a white solid.



M15b

Yield: 10.90 g (81.47%).

TLC: R_f = 0.52.

Melting point: 78.5-80°C.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3364.3 (br.m, NH), 2985.0 (w, CH_3), 1693. 7 (s, C=O), 1618.8 (m, C=C), 1530.8 (s, NH).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.42 (dd, $^3J_{(Ha,Hc)}$ = 17.26 Hz (*trans*), $^2J_{(Ha,Hb)}$ = 1.43 Hz, 1H, C***H***$_a$H$_b$=), 6.12 (dd, $^3J_{(Hc,Ha)}$ = 17.26 Hz (*trans*), $^3J_{(Hc,Hb)}$ = 10.40 Hz (*cis*), 1H, =C***H***$_c$), 5.84 (dd, $^2J_{(Hb,Ha)}$ = 1.43 Hz, $^3J_{(Hb,Hc)}$ = 10.40 Hz (*cis*), 1H, C***H***$_b$H$_a$=), 4.78 (br.s, 1H, NHBoc), 4.21 (t, $^3J_{(H,H)}$ = 5.18 Hz, 2H, OCH_2), 3.42-3.44 (m, 2H, C***H***$_2$NHBoc), 1.44 (s, 9H, $C(CH_3)_3$).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 166.02 (C=O), 155.72 (C=O, Boc), 131.24 (CH_2=), 128.03 (=CH), 79.58 (***C***$((CH_3)_3$), 63.77 (O***C***H_2), 39.63 (***C***H_2NHBoc), 28.32 ($C(\boldsymbol{C}H_3)_3$).

$C_{10}H_{17}NO_4$ (215.25):	Calcd.	C 55.80	H 7.96	N 6.51
	Found	C 56.00	H 8.42	N 6.55

GC-MS (70 ev), m/z (%): 156 (0.4%), 142 (10.0%), 115 (3.4%), 99 (2.2%), 87 (17.3%), 69 (5.6%), 59 (25.4%), 57 (100%), 55 (58.5%), 43 (CONH, 21.0%), 41 (25.4%).

5.3. Synthesis of initiators for NMP

5.3.1. Synthesis of TEMPO derivatives (I1a, I1b, I1c)

- **2-Phenyl-2-[(2,2,6,6-tetramethylpiperidin-1-yl)oxy]ethyl benzoate (I1a)**

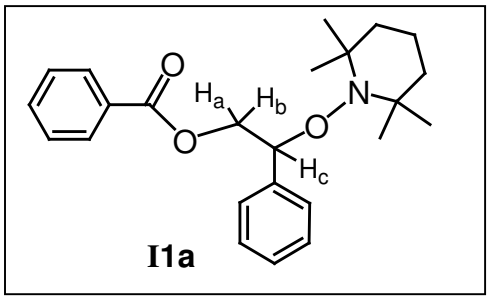
2-Phenyl-2-[(2,2,6,6-tetramethylpiperidin-1-yl)oxy]ethyl benzoate **(I1a)** was synthesized according to the literature.[54] To a solution of dibenzoyl peroxide (BPO) (1.40 g, 5.78 mmol) in distilled styrene (80 ml) was added 2,2,6,6-tetramethylpiperidinyl-l-oxy (TEMPO) (2.84 g, 18.06 mmol). The solution was degassed with argon for 30 min and heated at 80°C for 24 h. After cooling, the solution was evaporated to dryness and the residue was purified by flash chromatography with ethylacetate/pentane 1:6 (v/v) to give **I1a** as a pale yellow solid.

Yield: 0.98 g (22.2%).

TLC: R_f = 0.68.

Melting point: 71-73°C.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 2985.8, 2930.3 (m, CH_3, CH_2, CH), 1711.4 (s, C=O), 1602.2, 1583.6, 1493.0, 1450.7 (m, Ar), 1263.8(s, O-N).



I1a

^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.90-7.94 (m, 2H, Ar), 7.49-7.54 (m, 1H, Ar), 7.23-7.40 (m, 7H, Ar), 5.06 (t, $^3J_{(Hc,Ha)}$ = 6.1 Hz, $^3J_{(Hc,Hb)}$ = 5.3 Hz, 1H, C***H*****c**), 4.83 (dd, $^2J_{(Hb,Ha)}$ = 11.3 Hz, $^3J_{(Hb,Hc)}$ = 5.3 Hz, 1H, CH_a***H*****b**), 4.52 (dd, $^2J_{(Ha,Hb)}$ = 11.3 Hz, $^3J_{(Ha,Hc)}$ = 6.1 Hz, 1H, C***H*****a**H_b), 1.41-1.60 (m, 6H, $3CH_2$), 1.41, 1.20, 1.07, 0.75 (each br.s, 12H, $4CH_3$).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 166.29 (C=O), 140.68, 132.78, 129.69, 129.54, 128.24, 128.01, 127.59 (Ar), 83.94 (Ar-***C***H), 66.74 (OCH_2), 60.08 (***C***$(CH_3)_2$), 48.41 (CH_2), 34.02 (CH_3), 20.32 (CH_3), 17.13 (CH_2).

$C_{24}H_{31}NO_3$ (381.52):	Calcd.	C 75.56	H 8.19	N 3.67
	Found	C 75.26	H 8.24	N 3.92

Mass spectrum (MALDI-TOF): 382 [M + H^+].

- **2-[(4-Hydroxy-2,2,6,6-tetramethylpiperidin-1-yl)oxy]-2-phenylethyl benzoate (I1b) and 2-Phenyl-2-[(2,2,6,6-tetramethyl-4-oxopiperidin-1-yl) oxy]ethyl benzoate (I1c)**

To a solution of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl (HTEMPO) (12.5 g, 72.2 mmol) in distilled styrene (360 ml) was added dibenzoyl peroxide (BPO) (7.3 g, 30.1 mmol). The solution was degassed with argon for 30 min and heated at 80°C temperature for 35 h. After cooling, the solution was evaporated to dryness and two products (**I1b** and **I1c**) were isolated as pale yellow solids by flash chromatography with ethylacetate/pentane 1:4 (v/v).

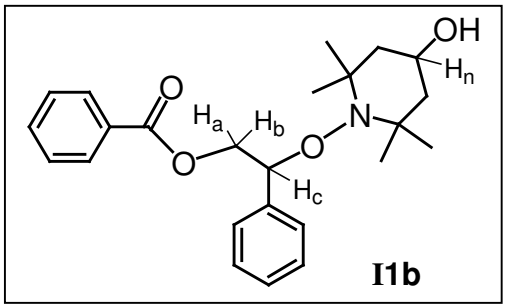
I1b

Yield: 2.05 g (8.6%).

TLC: R_f = 0.51.

Melting point: 147.5-149°C.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3506.2 (s, OH), 2999.4, 2973.3, 2937.9 (m, CH_3, CH_2, CH), 1692.2 (s, C=O), 1604.2, 1584.1, 1495.5, 1451.8 (m, Ar), 1265.0 (s, O-N).



I1b

^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.90-7.92 (m, 2H, Ar), 7.50-7.53 (m, 1H, Ar), 7.26-7.40 (m, 7H, Ar), 5.04 (t, $^3J_{(Hc,Ha)}$ = 6.0 Hz, $^3J_{(Hc,Hb)}$ = 5.7 Hz, 1H, C***H***$_c$), 4.82 (dd, $^2J_{(Hb,Ha)}$ = 11.4 Hz, $^3J_{(Hb,Hc)}$ = 5.7 Hz, 1H, CH$_a$***H***$_b$), 4.50 (dd, $^2J_{(Ha,Hb)}$ = 11.4 Hz, $^3J_{(Ha,Hc)}$ = 6.0 Hz, 1H, C***H***$_a$H$_b$), 3.91-3.97 (m, 1H, H$_n$, C***H***OH), 1.73-1.74, 1.70-1.72, 1.60-1.69, 1.47-1.49 (each, m, 4H, 2CH$_2$), 1.40, 1.24, 1.10, 0.73 (each br.s, 12H, 4CH$_3$).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 166.30 (C=O), 141.30, 132.87, 130.06, 129.53, 128.28, 128.10, 127.79, 127.64, (Ar), 84.10 (Ar-***C***H), 66.61 (OCH$_2$), 63.10 (CH-OH), 60.59, 60.42 (2***C***(CH$_3$)$_2$), 48.85, 48.78 (2CH$_2$), 34.09, 33.98, 21.27, 21.22 (4CH$_3$).

$C_{24}H_{31}NO_4$ (397.52):				
	Calcd.	C 72.52	H 7.86	N 3.52
	Found	C 71.83	H 8.05	N 3.57

Mass spectrum (MALDI-TOF): 398 [M + H$^+$], 420 [M + Na$^+$].

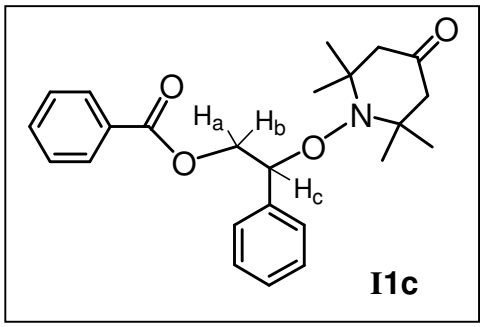
I1c

Yield: 4.40 g (18.54%).

TLC: R_f = 0.10.

Melting point: 114-116°C.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 2987.3, 2955.6, 2925.7 (m, CH$_3$, CH$_2$, CH), 1710.0 (s, C=O), 1602.1, 1584.1, 1454.3, (m, Ar), 1268.6 (s, O-N).



I1c

^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.90-7.92 (m, 2H, Ar), 7.51-7.55 (m, 1H, Ar), 7.28-7.41 (m, 7H, Ar), 5.04 (t, $^3J_{(Hc,Ha)}$ = $^3J_{(Hc,Hb)}$ = 5.7 Hz, 1H, C***H***$_c$), 4.82 (dd, $^2J_{(Hb,Ha)}$ = 11.4 Hz, $^3J_{(Hb,Hc)}$ = 5.7 Hz, 1H, CH$_a$***H***$_b$), 4.54 (dd, $^2J_{(Ha,Hb)}$ = 11.4 Hz, $^3J_{(Ha,Hc)}$ = 6.0 Hz, 1H, C***H***$_a$H$_b$), 2.60-2.63, 2.49-2.52, 2.21-2.24, 2.11-2.14 (each, d, 4H, 2CH$_2$), 1.50, 1.26, 1.10, 0.82 (each br.s, 12H, 4CH$_3$).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 208.02 (C=O), 166.28 (Ar-***C***=O), 139.59, 133.00, 129.93,129.53, 128.34, 128.25, 128.13, 127.77, (Ar), 84.30 (Ar-***C***H), 66.34 (OCH$_2$), 63.34, 63.16 (2***C***(Me)$_2$), 53.67, 53.64 (2CH$_2$), 33.59, 33.49, 22.58, 22.49 (4CH$_3$).

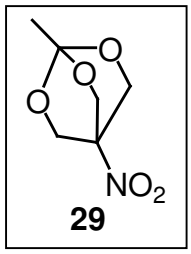
$C_{24}H_{29}NO_4$ (395.50):				
	Calcd.	C 72.89	H 7.39	N 3.54
	Found	C 72.04	H 7.42	N 3.60

Mass spectrum (MALDI-TOF): 396 [M + H$^+$], 418 [M + Na$^+$].

5.3.2. Synthesis of 2-hydroxymethyl-2-[(2-methyl-1-phenyl-propyl)-(1-phenyl-ethoxy)-amino]-propane-1,3-diol (I2a)

- **1-Methyl-4-nitro-2,6,7-trioxabicyclo[2.2.2]octane (29)**

According to the literature,[64] 2-(Hydroxymethyl)-2-nitropropane-1,3-diol (**28**) (6.04 g, 40.0 mmol) and 1,1,1-triethoxy-ethane (6.49 g, 40.0 mmol) were suspended in a mixture of dioctyl phthalate (DOP) (20 ml) and heated up to 120°C for 2 h, then 6 ml of ethanol were removed under vacuum. Additional DOP (10 ml) and a catalytic amount of *p*-toluene sulfonic acid (P-TsOH) were added, the temperature was increased to 140°C under vacuum. White crystals sublimed onto the wall of the distillation apparatus during 4 h. Washing by *n*-pentane and recrystallization of the crude product from *n*-pentane gave 1-methyl-4-nitro-2,6,7-trioxabicyclo[2.2.2]octane (**29**) as white needles.



29

Yield: 4.94 g (70.5%, lit. 45%).

Melting point: 122-123°C.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3456.03 (m, O-N), 2953.36, 2904.31 (w, CH_3, CH_2), 1546.08 (s, NO_2).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 4.39 (s, 6H, $3CH_2O$), 1.50 (s, 3H, CH_3).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 110.13 (Me***C***$(OCH_2)_3$), 75.39 (N***C***$(CH_2)_3$), 67.62 (CH_2O), 22.07 (CH_3).

$C_6H_9NO_5$ (175.14):	Calcd.	C 41.15	H 5.18	N 8.00
	Found	C 41.52	H 5.25	N 8.07

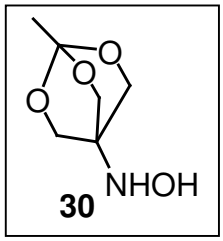
GC-MS (70 ev) m/z (%): 174 (1.0%), 145 (21.4%), 99 (100%), 43 (99.4%), 39 (8.9%).

- ***N*-(1-Methyl-2,6,7-trioxabicyclo[2.2.2] oct-4-yl)hydroxylamine (30)**

The orthoester **29** (3.00 g, 17.13 mmol) was dissolved in a mixture of CH_3CN (60 ml) and water (20 ml). After the solution was cooled to 0°C, ammonium chloride (1.01 g, 19.00 mmol) and Zn powder (4.50 g, 69.00 mmol) were added. The suspension was vigorously stirred at 0°C for 2.5 hr. The salts were then removed by filtration and the resulting solution was extracted (5 times) with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$). Removal of the solvent gave the corresponding hydroxylamine **30**. To remove the amine (formed by overreduction) the crude product was purified by flash chromatography to afford pure *N*-(1-methyl-2,6,7-trioxa-bicyclo[2.2.2] oct-4-yl)-hydroxylamine (**30**) as a white solid.

Yield: 2.23 g (80.8% (lit. 64%).

TLC: Et_2O, R_f = 0.40.



30

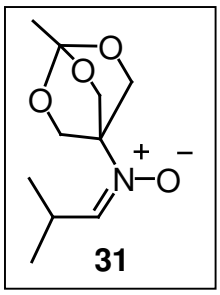
- **(*E*)-(2-Methylpropylidene)(1-methyl-2,6,7-trioxabicyclo[2.2.2]oct-4-yl) azane oxide (31)**

The hydroxylamine **30** (2.23 g, 13.84 mmol) was dissolved in CH_2Cl_2 (30 ml) and 4 Å molecular sieve (1.03 g) was added. After cooling to 0°C, 2-methylpropionaldehyde (1.51 g, 21.00 mmol) was added and stirring was continued for another 8 hr at 0°C. After filtration and evaporation the residue was redissolved in CH_2Cl_2 (30 ml) and additional 4 Å molecular sieve (350 mg) and 2-methylpropionaldehyde (0.50 g, 7.00 mmol) were added and stirring was continued for another 3.5 hr at 0°C. After the filtration and subsequent evaporation of the solvent, the nitron was recrystallized from *n*-pentane to afford **31** as a white hygroscopical solid.

Yield: 2.34 g (78.5%).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 6.20 (d, $^3J_{(H,H)}$ = 6.9 Hz, 1H, CH=N), 4.30 (s, 6H, $3CH_2O$), 3.08-3.19 (m, 1H, C***H***$(CH_3)_2$), 1.49 (s, 3H, CH_3), 1.09 (d, $^3J_{(H,H)}$ = 6.9 Hz, 6H, $2CH_3$).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 143.63 (CH=N), 109.43 (Me***C***$(OCH_2)_3$), 68,56 (CH_2O), 62.53 (N***C***$(CH_2O)_3$), 25.92 (***C***$H_3C(OCH_2)_3$), 22.80 (***C***$H(CH_3)_2$), 18.77 (***C***H_3).



31

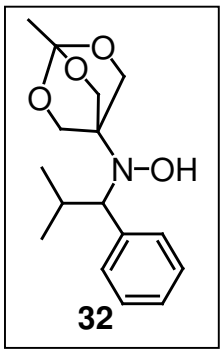
$C_{10}H_{17}NO_4$ (215.25): Calcd. C 55.80 H 7.96 N 6.51

Found C 55.41 H 7.86 N 6.60

- ***N*-(2-Methyl-1-phenylpropyl)-*N*-(1-methyl-2,6,7-trioxabicyclo[2.2.2] oct-4-yl)-amin-*N*-oxyl (33)**

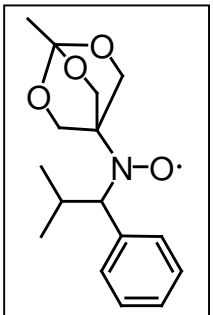
The nitrone **31** (12.00 g, 55.75 mmol) was dissolved under argon atmosphere in dry THF (80 ml) and cooled down to 0°C. A phenylmagnesium chloride solution in THF (76.3 ml, 1.8 M, 137.50 mmol) was slowly added during one period of 1 h and the mixture was allowed to warm up to r.t.. The resulting suspension was stirred at room temperature for 12 h. After

addition of 200 ml saturated aqueous NH_4Cl, the mixture was extracted 5 times with 150 ml Et_2O. The combined organic extracts were washed with brine and dried ($MgSO_4$). Removal of the solvent gave the crude hydroxylamine (**32**) (yellowish oil).



32

The crude hydroxylamine (**32**) was dissolved in MeOH (250 ml). A solution of ammonium hydroxide (70 ml) and $Cu(OAc)_2$ (0.60 g, 3.00 mmol) were added. The solution was vigorously stirred for 4 h while oxygen was bubbled through the mixture. The solvent was evaporated and the residue was treated with 100 ml 2 N NaOH. Extraction with 100 ml CH_2Cl_2 (5 times) and washing of the combined organic layers with brine afforded a yellow solution. After drying by $MgSO_4$ and evaporation of the solvent, the further purification by flash chromatography (Et_2O/Penthane1:1(v/v)) yielded *N*-(2-Methyl-1-phenyl-propyl)-*N*-(1-methyl-2,6,7-trioxa-bicyclo[2.2.2]oct-4-yl)-amin-*N*-oxyl (**33**) as a yellow solid.



33

Yield:	11.63 g (71.3%).			
TLC:	R_f = 0.63.			
Melting point:	111-113°C.			
IR (neat): $\tilde{\nu}$ (cm^{-1})	2958.35, 2897.38 (m, CH_3, CH_2, CH), 1492.26 (m), 1470.51 (m), 1455.60 (m), and 723.65 (s, Ar).			
ESR analysis:	g = 2.0061; α_N = 14.54 G; $\alpha_{\beta\text{-}H}$ = 2.75 G.			
$C_{16}H_{22}NO_4$ (292.36)	Calcd.	C 65.73	H 7.58	N 4.79
	Found	C 65.09	H 7.69	N 4.73

Mass spectrum (MALDI-TOF): 394 [M + H^+].

- ***N*-(2-Methyl-1-phenylpropyl)-*N*-(1-methyl-2,6,7-trioxabicyclo[2.2.2]oct-4-yl)-*O*-(1-phenylethyl)hydroxylamine (36)**

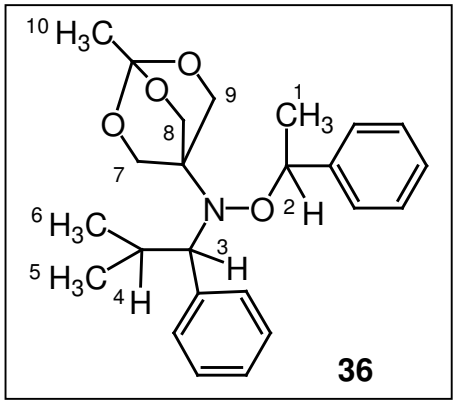
A round bottom three-neck flask was charged with a mixture of toluene/ethanol (1:1(v/v), 200 ml) and air was bubbled through for 1 hour. Styrene (5.34 g, 5.13 mmol) and the free nitroxide **33** (2.5 g, 8.55 mmol) were added sequentially to the solution. Afterwards Jacobsen's catalyst (2.72 g, 4.28 mmol) was added in one portion followed immediately by $NaBH_4$ (0.97 g, 25.65 mmol) also added in one portion. The dark brown reaction mixture was bubbled through with air for 4 hr. After additional 2.0 g (19.20 mmol) of styrene and 1.0 g (26.44 mmol) of $NaBH_4$,

the mixture was bubbled with air for another 4 hr. After that time the solvent was evaporated, the residue dissolved in 50 ml of CH_2Cl_2 and filtered through silica gel with 500 ml of CH_2Cl_2 as eluent. The solvent was evaporated and the residue dried under vacuum. The crude product was purified by flash chromatography with CH_2Cl_2 as eluent. 3.08 g of a white solid product (*N*-(2-methyl-1-phenylpropyl)-*N*-(1-methyl-2,6,7-trioxabicyclo[2.2.2]oct-4-yl)-*O*-(1-phenyl ethyl)hydroxylamine **36** as 1:1-mixture of the diastereomer). Further purification by precipitation from CH_2Cl_2 to pentane gave the product as a white solid.

Total Yield: 3.08 g (90.6%).

TLC: CH_2Cl_2, R_f = 0.52.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 2973.82, 2899.57 (m, CH_3, CH_2, CH), 1493.31 (m), 1467.37 (m), 1452.05 (m), and 702.93 (s) (Ar).



36

$C_{24}H_{31}NO_4$ (397.52): Calcd. C 72.52 H 7.86 N 3.52

Found C 72.03 H 8.14 N 3.64

Mass spectrum (MALDI-TOF): 399 $[M + H^+]$.

Additional 500 mg of the alkoxyamine **36** were separated by further flash chromatography eluting with Et_2O/n-pentane 3:1 (v/v) to afford two diastereomers.

Diastereomer I:

Yield: 236 mg (47%).

TLC: 3:1(v/v) Et_2O/n-pentane, R_f = 0.55.

^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.50-7.10 (m, 10H, Ar), 4.80 (q, $^3J_{(H2,H1)}$ = 6.6 Hz, 1H, CHO), 4.03-4.07 and 3.87-3.91 (m, 6H, CH_2O), 2.85 (d, $^3J_{(H3,H4)}$ = 10.6 Hz, 1H, CHN), 1.56 (d, $^3J_{(H1,H2)}$ = 6.6 Hz, 3H, C***H***$_3$CHO), 1.52 (m, 1H, C***H***$(CH_3)_2$), 1.39 (s, 3H, C***H***$_3$C$(OCH_2)_3$), 0.92 (d, $^3J_{(H5,H4)}$ = 6.3 Hz, 3H, C***H***$_3$C(CH_3)HCHN), 0.27 (d, $^3J_{(H6,H4)}$ = 6.6 Hz, 3H, CH_3C(C***H***$_3$)HCHN).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 140.24, 130.36, 128.34, 128.19, 127.99, 127.53, 126.82 (Ar), 108.28 (CH_3***C***$(OCH_2)_3$), 83.47 (CHO), 73.81 (CHN), 68.46 (CH_2O),

57.34 (ON***C***$(CH_2O)_3$), 31.37 (***C***H$(CH_3)_2$), 22.84 (***C***$H_3C(OCH_2)_3$), 22.75 (***C***H_3CHO), 22.01 (***C***$H_3C(CH_3)HCHN$), 20.91 (CH_3C(***C***H_3)HCHN).

Diastereomer II:

Yield: 224 mg (44%).

TLC: 3:1(v/v) Et_2O/n-pentane, R_f = 0.48.

^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.50-7.10 (m, 10H, Ar), 4.80 (q, $^3J_{(H2,H1)}$ = 6.6 Hz, 1H, CHO), 3.62-3.66 and 3.40 (m, 6H, CH_2O), 2.97 (d, $^3J_{(H3,H4)}$ = 10.7 Hz, 1H, CHN), 2.29-2.37 (m, 1H, C***H***$(CH_3)_2$), 1.63 (d, $^3J_{(H1,H2)}$ = 6.6 Hz, 3H, C***H***$_3$CHO), 1.32 (d, $^3J_{(H5,H4)}$ = 6.3 Hz, 3H, C***H***$_3C(CH_3)HCHN$), 1.21 (s, 3H, C***H***$_3C(OCH_2)_3$), 0.56 (d, $^3J_{(H6,H4)}$ = 6.6 Hz, 3H, CH_3C(C***H***$_3$)HCHN).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 143.16, 130.36, 128.68, 128.18, 127.86, 127.35, 126.63 (Ar), 108.57 (CH_3***C***$(OCH_2)_3$), 83.83 (CHO), 74.02 (CHN), 68.20 (CH_2O), 57.34 (ON***C***$(CH_2O)_3$), 31.37 (***C***H$(CH_3)_2$), 22.92 (***C***$H_3C(OCH_2)_3$), 22.68 (***C***H_3CHO), 21.78 (***C***$H_3C(CH_3)HCHN$), 21.10 (CH_3C(***C***H_3)HCHN).

- **2-(Hydroxymethyl)-2-[(2-methyl-1-phenylpropyl)(1-phenylethoxy) amino]propane-1,3-diol (I2a)**

Alkoxyamine **36** (2.56 g, 6.44 mmol) was dissolved in CH_2Cl_2 (60 ml), then water (1.2 ml) and *p*-TsOH (60.8 mg) were added. The reaction mixture was stirred for 1 h at r.t.. Afterwards the mixture was washed with saturated aqueous $NaHCO_3$ (70 ml) and brine (the aqueous phase was back-extracted 5 times with 100 ml CH_2Cl_2 each. Drying of the combined organic layers ($MgSO_4$) and evaporation of the solvents afforded the corresponding diol ester 2-[(1,1-dihydroxyethoxy)methyl]-2-[(2-methyl-1-phenylpropyl)(1-phenylethoxy)amino] propane-1,3-diol, which was subsequently dissolved at r.t. in monoglyme (60 ml). 1N LiOH (13 ml) was added, the solution was stirred for 3 h at r.t.. After addition of saturated aqueous $NaHCO_3$ (50 ml), the mixture was extracted with CH_2Cl_2 (5 × 100 ml). Drying of the combined organic layers ($MgSO_4$) and evaporation of the solvents afforded the crude product, which was purified by flash chromatography (Et_2O/*n*-pentane 3:1 (v/v)) to yield the pure initiator **I2a** as a white solid. The initiator 2-(hydroxymethyl)-2-[(2-methyl-1-phenylpropyl)(1-phenylethoxy) amino]propane-1,3-diol (**I2a**) is a 1:1 mixture of two diastereomers.

Yield: 2.18 g (90.5%, lit. 88%).

TLC: $R_f = 0.28$.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3387.88-3344.34 (m, OH), 2958.99, 2868.77 (m, CH_3, CH_2, CH), 1492.33 (m), 1451.12 (m), and 700.11 (s) (Ar).

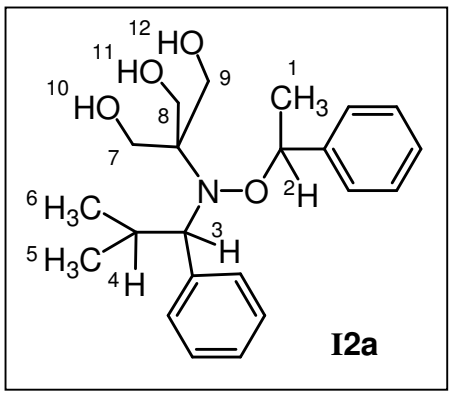
$C_{22}H_{31}NO_4$ (373.50): Calcd. C 70.75 H 8.37 N 3.75

Found C 71.18 H 8.41 N 3.80

Mass spectrum (MALDI-TOF): 375 $[M + H^+]$.

Additional 500 mg of initiator **I2a** were separated by further flash chromatography eluting with Et_2O/n-pentane 3:1 (v/v) to afford two diastereomers.

Diastereomer I



I2a

Yield: 236 mg (47%).

TLC: $R_f = 0.31$.

Melting point: 111-113°C.

^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.60-7.25 (m, 10H, Ar), 5.01 (q, $^3J_{(H2,H1)} = 6.6$ Hz, 1H, CHO), 3.61 (d, $^3J_{(H3,H4)} = 10.4$ Hz, 1H, CHN), 3.30 (s, 6H, CH_2O), 2.41-2.46 (m, 1H, C***H***$(CH_3)_2$), 2.22 (br.s, 3H, OH), 1.70 (d, $^3J_{(H1,H2)} = 6.6$Hz, 3H, C***H***$_3$CHO), 1.41 (d, $^3J_{(H5,H4)} = 6.3$ Hz, 3H, C***H***$_3$C(CH_3)HCHN), 0.60 (d, $^3J_{(H6,H4)} = 6.6$ Hz, 3H, CH_3C(C***H***$_3$)HCHN).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 142.84, 141.13, 128.95, 128.70, 128.23, 127.47, 126.63 (Ar), 83.98 (CHO), 72.89 (CHN), 68.40 (***C***$(CH_2OH)_3$), 64.80 (CH_2O), 32.18 (O***C***HAr), 23.09 (***C***H_3CHAr), 21.93 (***C***H_3C(CH_3)HCHN), 21.35 (CH_3C(***C***H_3)HCHN).

Diastereomer II:

Yield: 225 mg (45.0%).

TLC: $R_f = 0.25$.

Melting point: 115-118°C.

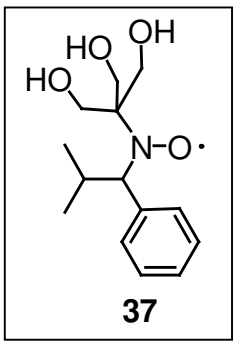
^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.50-7.20 (m, 10H, Ar), 4.96 (q, $^3J_{(H2,H1)} = 6.6$ Hz, 1H, CHO), 3.72-3.75 and 3.65-3.70 (m, 6H, CH_2O), 3.29 (d, $^3J_{(H3,H4)} = 10.7$ Hz, 1H,

CHN), 2.47 (br.s, 3H, OH), 1.62 (d, $^3J_{(H1,H2)}$ = 6.6 Hz, 3H, C***H*****$_3$**CHO), 1.48-1.58 (m, 1H, C***H***$(CH_3)_2$), 0.93 (d, $^3J_{(H5,H4)}$ = 6.3 Hz, 3H, C***H*****$_3$**C(CH_3)HCHN), 0.26 (d, $^3J_{(H6,H4)}$ = 6.9 Hz, 3H, CH_3C(C***H*****$_3$**)HCHN).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 143.04, 140.63, 128.49, 128.15, 128.01, 127.33, 126.83 (Ar), 84.10 (CHO), 72.54 (CHO), 69.46 (***C***$(CH_2OH)_3$), 64.08 (CH_2O), 31.75 (O***C***HAr), 22.93 (***C***H_3CHAr), 21.83 (***C***H_3C(CH_3)HCHN), 20.96 (CH_3C(***C***H_3)HCHN).

- ***N*-(2-Methyl-1-phenylpropyl)-*N*-[2,2,2-tris(hydroxymethyl)methane]-amine-N-oxyl (37)**

The free nitroxide **33** (250 mg, 0.855 mmol) was dissolved in CH_2Cl_2 (10 ml), then water (0.4 ml) and *p*-toluenesulfonic acid (*p*-TsOH, 10.0 mg) were added. The reaction mixture was stirred for 1 hr at r.t.. Afterwards the mixture was washed with saturated aqueous $NaHCO_3$ (15 ml) and brine (15 ml) (the aqueous phase was back-extracted with CH_2Cl_2 (5 × 40 ml). Drying of the combined organic layers ($MgSO_4$) and evaporation of the solvents afforded the corresponding diol ester, which was subsequently dissolved at r.t. in monoglyme (15 ml). LiOH (1N, 3 ml) was added, the solution was stirred for 2 h at r.t.. After addition of saturated aqueous $NaHCO_3$ (15 ml), the mixture was extracted with CH_2Cl_2 (5 × 30 ml). Drying of the combined organic layers ($MgSO_4$) and evaporation of the solvents afforded the crude product, which was purified by flash chromatography (Et_2O/pentane 3:1 (v/v)) to yield the pure trihydroxy nitroxide.



37

Yield: 210.3 mg (91.7%).

TLC: R_f = 0.20.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3362.98 (br.m, OH), 2957.00, 2923.57 (br.m, CH_3, CH_2, CH), 1490.19 (m), 1454.20 (m), and 696.95 (s) (Ar).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 7.32-7.49 (m, 5H, Ar), 3.65 (br.s, 1H, CH-N), (m, 6H, CH_2O), 1.70 (br.s, 1H, C***H***$(CH_3)_2$), 1.25 (s, 6H, CH_3).

$C_{14}H_{22}NO_4$ (268.34):	Calcd.	C 62.67	H 8.26	N 5.22
	Found	C 62.41	H 8.13	N 5.02

Mass spectrum (ESI): 269 [M + H^+], 291 [M + Na^+].

5.3.3. ESR measurements of initiator I2a

The ESR experiments of the initiator **I2a** were carried out in *tert*-butylbenzene, DMF and 1,2,4-trichlorobenzen (1×10^{-3} mol/l). All the sample solutions were heated up onto the designed temperature (85°C and 120°C respectively) within 3 min. The signal of the nitroxide radical **37** reflects the initiator decomposition. The temporal changes of concentration of the nitroxide radical **37** were traced and the obtained ESR signals of **37** were double integrated. For the detailed data see the discussion part.

5.4. Radical polymerization of acryl- and methacryl derivatives

5.4.1. Traditional radical polymerization initiated by AIBN

General procedure 1

In a polymerization bottle, 0.5 g of the monomer and AIBN (the ratio of monomer to initiator of 40:1 (mol/mol) were dissolved in dry 1,4-dioxane or *N,N*-dimethylformamide (DMF) (the concentration of monomer of 0.1 g/ml), degassed with argon by three freeze-pump-thaw cycles and sealed. The solution was stirred for certain time (0-24 h) at 70°C under argon. The homopolymers were purified by precipitation, and dried *in vacuo* to a constant weight.

5.4.2. Radical polymerization by NMP

General procedure 2

In a Schlenk flask, 0.5 g of the monomer and nitroxide-mediated initiator or macroinitiator (1.0 mol% of monomers) were dissolved in dry DMF, degassed with argon by three freeze-pump-thaw cycles and then the flask was sealed. The solution was stirred at room temperature for 10 min and then placed in an oil bath at 120°C to start the reaction. Cooling with liquid nitrogen stopped the polymerization. The homopolymers and block-copolymers were purified by precipitation in a suitable solvent, and dried *in vacuo* to a constant weight.

5.4.3. Radical polymerization by ATRP

- **Synthesis of tris(2-dimethylaminoethyl)amine (Me_6TREN)**

Tris-(2-dimethylaminoethyl)amine (Me_6TREN) (Figure 5.1) was used successfully as a ligand for the ATRP of many monomers. This ligand was synthesized according to procedures described in the literature.[259]

10 ml Tris(2-aminoethyl)amine were added drop-wise to a solution of 52.44 ml formic acid (85%) and 44.57 ml formaldehyde (30%) in 7.8 ml distilled water. The mixture was stirred at room temperature for 30 minutes and then stirred at 95°C for 12 hours. The reddish liquid was dissolved in 100 ml water and reacted with anion exchange resin. Subsequently it was distilled at 140°C *in vacuo* to yield colorless oil.

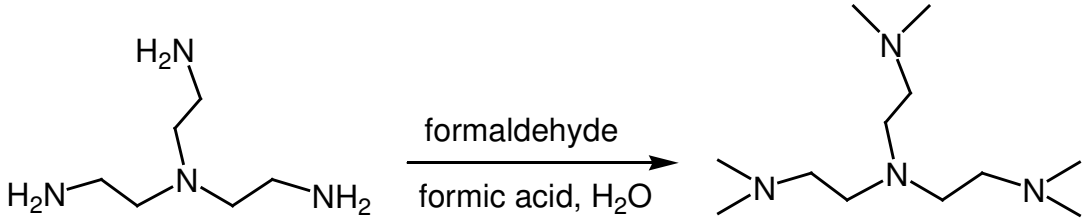


Figure 5.1 Synthesis of tris(2-dimethylaminoethyl).

Yield: 11.4 g (100%).

IR (neat), $\tilde{\nu}$ (cm^{-1}): 2941.6, 2815.1, 2763.7 (m, CH_3, CH_2).

^{1}H-NMR ($CDCl_3$): δ (ppm) = 2.60-2.65 (m, 6H, CH_2), 2.36-2.42 (m, 6H, C***H₂***N$(CH_3)_2$), 2.24 (s, 18H, CH_3).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 57.59 (CH_2), 53.15 (***C***$H_2N(CH_3)_2$), 45.83 (CH_3).

($C_{12}H_{30}N_4$) (230.36):				
	Calcd.	C 62.56	H 13.13	N 24.31
	Found	C 62.24	H 13.45	N 24.60

GC-MS (70 ev), m/z (%): 172 (49.0%), 72 (100%), 58 (44.9%), 42 (9.8%).

- **Radical polymerization by ATRP**

General procedure 3

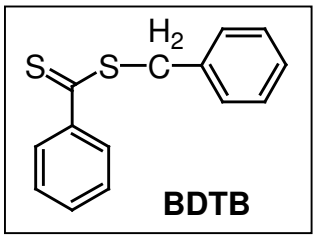
The initiator or macroinitiator was placed in a Schlenk flask and dissolved in the corresponding solvent, subsequently the monomer and the ligand were added, the mixture was degassed by three freeze-pump-thaw cycles. Under stirring at 25°C for 20 min, CuCl or CuBr was added and the flask was placed in a thermostated bath to start the reaction. Cooling with

liquid nitrogen and opening the flask stopped the polymerization. The reaction mixture was diluted and eluted through a column filled with neutral alumina or silica gel to remove the copper complex. The solvent was removed under vacuum at room temperature and the polymer solution was repeatedly precipitated into methanol/water or diethyl ether. Finally the homopolymer or block-copolymer was dried *in vacuo* to a constant weight.

5.4.4. Radical polymerization by RAFT

- **Synthesis of benzyl dithiobenzoate (BDTB)**

According to Benicewicz's report[256] a mixture of benzoic acid (1.22 g, 10 mmol), benzyl mercaptan (1.24 g, 10 mmol), and phosphorus pentasulfide (P_4S_{10}, 0.88 g, 2 mmol) in toluene (40 ml) was refluxed at 110°C for 6 h. A dark red color appeared immediately after heating. After the reaction was completed, it was cooled to room temperature and the product was purified by column chromatography on neutral alumina, eluting with toluene. Removal of the solvent by distillation gave the red-colored oil benzyl dithiobenzoate.



Yield: 2.24 g (92%).

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3057.85, 1493.97, 1222.86, 1040.56, 1025.72, 875.37, 757.57.

^{1}H-NMR ($CDCl_3$): δ (ppm) = 4.60 (s, 2H, CH_2), 7.30- 7.41 (m, 7H, Ar), 7.49-7.55 (m, 1H, Ar), 7.98-8.01 (m, 2H, Ar).

^{13}C-NMR ($CDCl_3$): δ (ppm) = 42.28 (CH_2), 121.00, 126.90, 127.75, 128.34, 129.30, 132.40, 134.99, 144.77 (Ar), 224.23 (C=S).

($C_{14}H_{12}S_2$) (244.38):	Calcd.	C 68.81	H 4.95	S 26.24
	Found	C 69.06	H 4.76	S 26.03

GC-MS (70 ev), m/z (%): 244.1 (54.2%), 211.1 (26.1%), 121.1 (100%), 91.1 (74.3%), 77.1 (45.0%), 65.1 (18.5%), 51.1 (14.9%).

- **Radical polymerization by RAFT**

General procedure 4

The monomer, the solvent and the chain transfer agent CTA or macroCTA were added into a Schlenk flask and degassed by three freeze-pump-thaw cycles. After that the flask was heated

to 70°C for 10 min, the initiator was added and the flask was sealed to start the reaction. Cooling with liquid nitrogen stopped the polymerization. The homopolymer or block-copolymer was isolated by twice precipitation from methanol/water or diethyl ether and dried *in vacuo* to a constant weight.

5.5. Deprotection of the functional groups in the polymers

5.5.1. Deprotection of the protected amino groups

5.5.1.1. Removal of the Boc group from *poly*{*tert*-butyl [2-(methacryloylamino)ethyl] carbamate} (P1a) to *poly*{*N*-(2-aminoethyl)-2-methylacrylamide} (dP1a)

- ***Poly*{[2-(methacryloylamino)ethyl] ammonium trifluoroacetate} (dP2a)**

A solution of **P1a** (1.0 g, 4.4 mmol) in DMF (20 ml) was cooled to 0°C and trifluoroacetic acid (TFA, 20 ml) was dropped in slowly, and then the mixture was warmed to room temperature and stirred for 2 h. The solvent was removed *in vacuo* to give **dP2a** as its TFA salt in quantitative yield.

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3373.6 (br.m, NH), 1681.4 (s, C=O), 1532.5 (s, NH), 1133.7 (s, C-F).

^{1}H-NMR (DMSO): δ (ppm) = 8.06 (br.s, 4H, NH, NH_3^+), 3.22 (br.s, 2H, NHC***H*****$_2$**), 2.86 (m, 2H, C***H*****$_2$**NH_3^+), 1.40-1.80 (m, 2H, CH_2), 0.60-1.26 (m, 3H, CH_3).

^{13}C-NMR (DMSO): δ (ppm) = 175.7 (C=O), 159.2, 158.8, 158.4, 157.9 (CF_3***C***OOH), 122.6, 118.6, 114.7, 110.8 (***C***F_3COOH), 44.8 (*tert* C), 36.5-39.0 (N***C***H_2***C***H_2N), 17.0-18.5 (CH_3).

$(C_8H_{13}N_2O_3F_3)_n$ (242.20)$_n$	Calcd.	C 39.67	H 5.42	N 11.56
	Found	C 38.21	H 5.98	N 11.02

- ***Poly*{*N*-(2-amino-ethyl)-2-methacrylamide} (dP1a)**

dP2a (0.61 mg, 2.5 mmol) was dissolved in water (50 ml) and was poured into anion exchange resin in water, and reacted for 3 h. The solvent was removed *in vacuo* to yield the white solid **dP1a**.

Yield: 284 mg (88.6%).

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3368.2 (br.s, NH, NH_2), 1661.6 (s, C=O).

^{1}H-NMR (DMSO): δ (ppm) = 7.87 (br.s, 1H, NH), 2.90-3.50 (br.s, 4H, NHC***H₂***C***H₂***NH_2), 1.50-1.92 (m, 2H, CH_2), 0.70-1.40 (m, 3H, CH_3).

^{13}C-NMR (DMSO): δ (ppm) = 180.6 (C=O), 55.3 (CH_2), 47.2 (*tert* C), 46.5 ($NHCH_2$), 40.2 (CH_2NH_2), 15.1 (CH_3).

$(C_6H_{12}N_2O)_n$ $(128.18)_n$	Calcd.	C 56.22	H 9.44	N 21.86
	Found	C 53.45	H 9.87	N 21.34

5.5.2. Deprotection of the protected hydroxyl group

5.5.2.1. Removal of the TMS group from *poly*{*N*-{2-[(trimethylsilyl)oxy]ethyl}-2-methylacrylamide} (P5a) to give *poly*{*N*-(2-hydroxyethyl)-2-methylacrylamide} (dP5a)

- ***Poly*{*N*-(2-hydroxyethyl)-2-methylacrylamide} (dP5a)**

10 ml 0.01 N HCl were dropped into the solution of *poly*{*N*-{2-[(trimethylsilyl)oxy] ethyl}-2-methylacrylamide} (**P5a)** (300 mg) in DMF (8 ml) under stirring at room temperature. After 2 hours the solvent was removed *in vacuo* and the product **dP5a** was purified by precipitation from acetone into diethyl ether as a white solid.

Yield: 280 mg (100%).

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3321.2 (br.s, OH, NH), 1627.3 (s, CO), 1528.5 (s, NH).

^{1}H-NMR (DMSO): δ (ppm) = 9.04 (br.s, 1H, OH), 7.45 (br.s, 1H, NH), 3.54 (br.s, 2H, C***H₂***OH), 3.20 (br.s, 2H, NHC***H₂***), 1.50-2.15 (m, 2H, CH_2), 0.70-1.50 (m, 3H, CH_3).

^{13}C-NMR (DMSO): δ (ppm) = 176.8 (C=O, CONH), 59.2 (CH_2OH), 44.94 (*tert* C), 41.9 ($NHCH_2$), 16.1 (CH_3).

$(C_6H_{11}NO_2)_n$ $(129.16)_n$	Calcd.	C 55.80	H 8.58	N 10.84
	Found	C 52.28	H 9.29	N 11.44

5.5.2.2. Removal of the TBS goup from *poly*{*N*-(2-{[*tert*-butyl(dimethyl)silyl]oxy}ethyl)-2-methylacrylamide} (P6a) to obtain *poly* {*N*-(2-hydroxyethyl)-2-methylacrylamide} (dP6a)

- ***Poly*{*N*-(2-hydroxyethyl)-2-methylacrylamide} (dP6a)**

10 ml 0.01 N HCl were dropped into a solution of *poly*{*N*-(2-{[*tert*-butyl(dimethyl)silyl]oxy} ethyl)-2-methylacrylamide} **(P6a)** (846 mg) in DMF (50 ml) under stirring at 50°C. After 5 hours the product was purified by precipitation from water into diethyl ether.

Yield: 690 mg (96 %).

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3316.8 (br.s, OH, NH), 1630.2 (s, CO), 1525.5 (s, NH).

^{1}H-NMR (DMSO): δ (ppm) = 7.92 (br.s, 1H, NH), 3.71 (br.s, 1H, OH), 3.57 (br.s, 2H, C***H*****$_2$**OH), 2.84 (br.s, 2H, NHC***H*****$_2$**), 1.45-2.10 (m, 2H, CH_2), 0.55-1.45 (m, 3H, CH_3).

^{13}C-NMR (DMSO): δ (ppm) = 176.7 (C=O, CONH), 59.5 (CH_2OH), 44.9 (*tert* C), 41.9 ($NHCH_2$), 16.3 (CH_3).

$(C_6H_{11}NO_2)_n$ $(129.16)_n$	Calcd.	C 55.80	H 8.58	N 10.84
	Found	C 52.55	H 8.11	N 10.81

5.5.2.3. Deprotection of *poly*{2-[(2,2,2-trichloroacetyl)oxy]ethyl 2-methylacrylate} (P 15a) to yield *poly*{2-hydroxyethyl 2-methylacrylate} (dP15a)

- ***Poly*{2-hydroxyethyl 2-methylacrylate} (dP15a)**

P15a (0.3 g, 1.1 mmol) was dissolved in 8 ml EtOH/DMF (1:1), NH_4OH (0.15 g, 1.1 mmol) was added at 0 °C. After having warmed up to 25°C, the reaction solution was stirred for 6 hours. Subsequently the solvent was removed *in vacuo* and the product was purified by precipitation from CH_2Cl_2 into diethyl ether.

Yield: 143.2 mg (93.0%).

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3451.7 (br.m, OH), 1717.1 (s, C=O).

^{1}H-NMR (DMSO): δ (ppm) = 4.80 (br.s, 1H, OH), 3.89 (br.s, 2H, $COOCH_2$), 3.58 (br.s, 2H, C***H*****$_2$**OH), 1.50-2.30 (m, 2H, CH_2), 0.60-1.50 (m, 3H, CH_3).

^{13}C-NMR (DMSO): δ (ppm) = 177.0 (C=O), 66.1 (OCH_2), 58.4 (CH_2OH), 52.8 (CH_2), 44.4 (*tert* C), 16.0-17.9 (CH_3).

$(C_6H_{10}O_3)_n$ 130.14)$_n$	Calcd.	C 55.37	H 7.75	
	Found	C 53.97	H 7.90	

5.5.3. Deprotection of the protected carboxyl group

5.5.3.1. Removal of the TBS group from *poly*{*tert*-butyl(dimethyl)silyl *N*-methacryloyl-*β*-alaninate} (P8a) to achieve *poly*{*N*-methacryloyl-*β*-alanine} (dP8a)

- ***Poly*{*N*-methacryloyl-*β*-alanine} (dP8a)**

12 ml of acetic acid-water (3:1) was dropped into a solution of **P8a** (180 mg, 0.66 mmol) in DMF (4.0 ml) at room temperature under stirring. After 4 hours the product was purified by precipitation from water into diethyl ether.

Yield: 94 mg (90.6%).

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3354.5 (br.m, NH, OH), 1712.9 (s, C=O, COOH), 1620.4 (s, C=O, amide I), 1523.4 (s, NH, amide II).

^{1}H-NMR (DMSO): δ (ppm) = 12.13 (br.s, 1H, COOH), 7.30 (br.s, 2.1H, NH), 3.15 (br.s, 2H, NHC***H₂***), 2.35 (br.s, 2H, CH_2COO), 1.22-2.00 (m, 2 H, CH_2), 0.40-1.22 (m, 3H, CH_3).

^{13}C-NMR (DMSO): δ (ppm) = 176.90 (C=O, CONH), 173.34 (C=O, COOH), 54.55 (CH_2), 45.19 (*tert* C), 35.63 ($NHCH_2$), 33.00 (***C***H_2COO), 16.45-17.74 (CH_3).

$(C_7H_{11}NO_3)_n$ $(157.16)_n$	Calcd.	C 53.49	H 7.06	N 8.91
	Found	C 50.05	H 7.49	N 8.13

5.5.3.2. Removal of the *tert*-butyl group from *poly*{*tert*-butyl *N*-methacryloyl-*β*-alaninate} (P9a) to give *poly*{*N*-methacryloyl-*β*-alanine} (dP9a)

- ***Poly*{*N*-methacryloyl-*β*-alanine} (dP9a)**

P9a (250 mg, 1.16 mmol) was dissolved in DMF (20.0 ml) and cooled to 0°. Then trifluoroacetic acid (20 ml) was dropped in slowly under stirring. Warmed up to room temperature the solution was stirred for 4 hours. The product was purified by precipitation from dioxane into diethyl ether.

Yield: 166 mg (91.1%).

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3359.2 (br.m, NH, OH), 1712.7 (s, C=O, COOH), 1622.9 (s, C=O, amide I), 1522.9 (s, NH, amide II).

^{1}H-NMR (DMSO): δ (ppm) = 12.13 (br.s, 1H, COOH), 7.30 (br.s, 2.1H, NH), 3.15 (br.s, 2H, NHC***H₂***), 2.36 (br.s, 2H, CH_2COO), 1.30-2.15 (m, 2 H, CH_2), 0.40-1.30 (m, 3H, CH_3).

^{13}C-NMR (DMSO): δ (ppm) = 176.92 (C=O, CONH), 173.33 (C=O, COOH), 54.38 (CH_2), 44.69 (*tert* C), 35.62 ($NHCH_2$), 33.00 (***C***H_2COO), 16.49-17.76 (CH_3).

$(C_7H_{11}NO_3)_n$ $(157.16)_n$	Calcd.	C 53.49	H 7.06	N 8.91
	Found	C 50.35	H 7.10	N 8.09

5.5.3.3. Removal of the ONB group from *poly*{2-nitrobenzyl *N*-methacryloyl-*β*-alaninate} (P10a) to yield *poly*{*N*-methacryloyl-*β*-alanine} (dP10a)

- ***Poly*{*N*-methacryloyl-*β*-alanine} (dP10a)**

The homopolymer (200 mg) *poly*{2-nitrobenzyl *N*-methacryloyl-*β*-alaninate} (**P10a**) was dissolved in a solution of water and DMF (v:v = 5 ml:50 ml), degassed by argon for 30 min, and then irradiated by UV light (320 nm, I = 100 W) with stirring at room temperature for 10 hours. The product **dP10a** was purified by precipitation from water into diethyl ether.

Yield: 101 mg (94.4 %).

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3362.1 (br.m, NH, OH), 1716.4 (s, C=O, COOH), 1632.9 (s, C=O, amide I), 1524.2 (s, NH, amide II).

^{1}H-NMR (DMSO): δ (ppm) = 12.18 (br.s, 1H, COOH), 7.30 (br.s, 2.1H, NH), 3.16 (br.s, 2H, NHC***H₂***), 2.36 (br.s, 2H, CH_2COO), 1.35-2.00 (m, 2 H, CH_2), 0.40-1.35 (m, 3H, CH_3).

^{13}C-NMR (DMSO): δ (ppm) = 176.85 (C=O, CONH), 173.34 (C=O, COOH), 54.37 (CH_2), 44.58 (*tert* C), 35.61 ($NHCH_2$), 33.30 (CH_2COO), 16.41 (CH_3).

$(C_7H_{11}NO_3)_n$ $(157.16)_n$	Calcd.	C 53.49	H 7.06	N 8.91
	Found	C 51.28	H 7.22	N 8.63

5.5.3.4. Removal of the cumarine group from *poly*{(7-methoxy-2-oxo-2*H*-chromen-4-yl)methyl *N*-methacryloyl-*β*-alaninate} (P11a)

- ***Poly*{*N*-methacryloyl-*β*-alanine} (dP11a)**

The homopolymer *poly*{(7-methoxy-2-oxo-2*H*-chromen-4-yl)methyl *N*-methacryloyl-*β*-alaninate} (**P11a**) (400 mg, 1.16 mmol) was dissolved in a solution of water and DMF (v:v = 20 ml:80 ml), degassed with argon for 30 min, and irradiated by UV light (320 nm, I = 100 W) with stirring at room temperature for 80 min. The product was purified by precipitation from CH_2Cl_2 into diethyl ether as a pale yellow solid.

Yield: 173.3 mg (95.2%).

IR (neat), $\tilde{\nu}$ (cm^{-1}): 3342.2 (br.m, NH, OH), 1719.8 (s, C=O, COOH), 1630.2 (s, C=O, amide I), 1526.4 (s, NH, amide II).

^{1}H-NMR (DMSO): δ (ppm) = 12.03 (br.s, 1H, COOH), 7.62 (br.s, 2.1H, NH), 3.33 (br.s, 2H, NHC***H₂***), 2.55 (br.s, 2H, CH_2COO), 1.50-2.05 (m, 2 H, CH_2), 0.40-1.50 (m, 3H, CH_3).

^{13}C-NMR (DMSO): δ (ppm) = 178.52 (C=O, CONH), 174.77 (C=O, COOH), 54.89 (CH_2), 45.87 (*tert* C), 36.26 ($NHCH_2$), 33.28 (CH_2COO), 17.45 (CH_3).

$(C_7H_{11}NO_3)_n$ $(157.16)_n$	Calcd.	C 53.49	H 7.06	N 8.91
	Found	C 52.14	H 7.24	N 8.59

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7. ACKNOWLEDGEMENT

The Ph. D work was performed under the guidance and help of Doz. Dr. W. D. Habicher. My warmest thanks for his academic supervision, valuable discussions, interesting research theme and kind support.

I am especially grateful to Prof. Dr. B. Voit for her friendly and kind support, interesting ideas and helpful suggestions.

I gratefully acknowledge Prof. Dr. W. T. Yang for his help and support in my study in Germany and his concern for this work.

I would like to thank Prof. Dr. T. Wolff for his kind permission to use the UV lamp and to thank Dr. D. Kuckling and Mr. D. Voigt for their kind permission to use GPC equipment, and to Prof. Dr. L. Dunsch for his permission to measure ESR.

Special thanks are due to Dr. I. Bauer and Dr. G. Whitener for their valuable discussions, reading the manuscript and a great deal of help.

I would also like to thank my colleagues Mr. M. Messerschmidt and Mr. T. Krause their friendly cooperation and helpful discussions and to Mrs. G. Theumer for MALDI-TOF-MS measurements and a lot of help, as well as to other co-workers in our group for their discussions and help.

I am very thankful for the great help and many useful suggestions of Dr. Y. Z. Wang, Dr. X. L. Yu, and many Chinese friends.

I gratefully acknowledge the assistance of the following co-workers:

Dr. M. Gruner, Mrs. K. Böhler and Mrs A. Rudolph for many NMR measurements, Mrs. P. Treppe, Mr. D. Seifert and Cong-Duan Vo for GPC measurements, Dr. H. Kroschwitz for GC-MS measurements, Mrs. L. Rössler for IR measurements, Mrs A. Peritz for element analyses, Mrs I. Poitz for DSC measurements, Dr. S. L. Gao for AFM measurements.

My special thanks to my family for their love, care and all the support.

Financial support by the Deutsche Forschungsgemeinschaft (DFG) (Sonderforschungsbereich 287/A15 "Reaktive Polymeres") is gratefully acknowledged.

8. LIST OF SYMBOLS AND ABBREVIATIONS

AFM	atomic force microscopy
AIBN	2,2'-azobis(isobutyronitrile)
ATRA	atom transfer radical addition
ATRP	atom transfer radical polymerization
BDTB	benzyl dithiobenzoate
bipy	2,2'- bipyridine
$(Boc)_2O$	di-*tert*-butyldicarbonate
Boc	*tert*-butyloxycarbonyl
BPO	benzoyl peroxide
br.	broad
Cat	catalyst
Con.	concentration
CRP	controlled radical polymerization
CTA	chain transfer agent
CuBr	copper bromide
CuCl	copper chloride
d	doublet
dd	double doublet from doublet
DCC	*N,N'*-dicyclohexylcarbodiimide
DMAc	dimethyl acetamide
DMF	*N, N'*-dimethylformamide
DMSO	dimethyl sulfoxide
DOP	dioctyl phthalate
DSC	differential scanning calorimetry
DTB-bipy	4,4'-di-*tert*-butyl-2,2'-bipyridine
EBrP	ethyl 2-bromopropionate
EBriB	ethyl 2-bromoisobutyrate
ESR	electron spin resonance-spectroscopic
Et	ethyl group

e.g.	for example (Latin: *exempli gratia*)
GC-MS	gas chromatography mass spectroscopy
GPC	gel permeation chromatography
HTEMPO	4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl
h	hour
Hz	herz
I	initiator
i.e.	that is (Latin: *id est*)
IR	infrared spectroscopy
J	coupling constant
k_a	activation rate constant
k_d	deactivation rate constant
k_p	propagation rate constant
k_t	termination rate constant
l	liter
L	ligand
LiCl	lithium chloride
M	monomer
m	multiplet (NMR) or medium (IR)
MacroCTA	macrochain transfer agent
MacroI	macroinitiator
MALDI-TOF-MS	matrix-assisted laser distortion ionization-time of flight-mass spectroscopy
MCM	(7-methoxy-2-oxo-2*H*-chromen-4-yl)methyl
MClP	methyl 2-chloropropionate
MBrP	methyl 2-bromopropionate
Me	methyl group
MeOH	methanol
Me_6TREN	tris[2-(dimethylamino)-ethyl]amine
Me_4Cyclam	1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane
ml	millimole
mol	mole
mol%	mole per cent
M_n	number average molecular weight

mp	melting point
MS	mass spectrometry
M_w	weight average molecular weight
M_w/M_n	polydispersity
nm	nanometer
NMP	nitroxide mediated polymerization
NMR	nuclear magnetic resonance spectroscopy
ONB	*o*-nitrobenzyl
PMDETA	*N*,*N*,*N*',*N*'',*N*''-pentamethyldiethylenetriamine
ppm	parts per milion
PRE	persistent radical effect
Pst	polystyrene
R·	radical specie
RAFT	reversible addition-fragmentation chain transfer polymerization
R_f	retention factor
r.t.	room temperature
s	singlet (NMR) or strong (IR)
ss	strong strong
sec	second
SFRP	stable free radical polymerization
t	triplet (NMR), time (reaction)
TB	*tert*-butyl
TBDMS	*tert*-butyldimethylsilyl
TCA	2,2,2-trichloroacetyl
TEMPO	2,2,6,6-tetramethylpiperidine-1-oxyl
THF	tetrahydrofuran
T_g	glass transition temperature
TLC	thin layer chromatography
TMS	trimethylsilyl
q	quadruplet
UV	ultraviolet
w	weak
wt	weight
λ	wavelength of light

Versicherung

Hiermit versichere ich, dass ich die vorliegende Arbeit ohne unzulässige Hilfe Dritter und ohne Benutzung anderer als der angegebenen Hilfsmittel angefertigt habe; die aus fremden Quellen direkt oder indirekt übernommenen Gedanken sind als solche kenntlich gemacht. Die Arbeit wurde bisher weder im Inland noch im Ausland in gleicher order ähnlicher Form einer anderen Prüfungsbehörde vorgelegt.

Yin, Meizhen

Erklärung

Die vorliegende Arbeit wurde unter der wissenschaftlichen Betreuung von Herrn Doz. Dr. Wolf D. Habicher in der Zeit von Januar 2001 bis März 2004 im Institut für Organisch Chemie der Technischen Universität Dresden angefertigt. Es haben keine frühen erfolglosen Promotionsverfahren stattgefunden.

Ich erkenne die Promotionsordnung der Fakultät Mathematik and Naturwissenschaften der Technischen Universität Dresden vom 16.04.2003 in vollem Umfang an.

Dresden, den 22 März 2004

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