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MODIFIKASI PERMUKAAN PET DENGAN POLIMER-POLIMER FUNGSIONAL DARI AGEN RAFT UNTUK MENCAPAI SIFAT ANTIBAKTERI

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MODIFICATION OF PET SURFACES WITH END-FUNCTIONALIZED POLYMERS PREPARED FROM RAFT AGENTS TO ACHIEVE ANTIBACTERIAL PROPERTIES

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MODIFIKASI PERMUKAAN PET DENGAN POLIMER-POLIMER FUNGSIONAL DARI AGEN RAFT UNTUK MENCAPAI SIFAT ANTIBAKTERI

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ABSTRAK

Modifikasi permukaan PET dengan polimer-polimer fungsional dari polimerisasi RAFT telah diteliti sebelumnya. Polimerisasi awal menggunakan stirena telah diteliti untuk mengetahui perbandingan antara polimerisasi radikal bebas konvensional (CFRP) dan polimerassi transfer rantai adisi-fragmenasi secara reversible (RAFT) Tiga tipe dari agen RAFT diantaranya asam pentanoat (4-siano-4-fenilkarbonotioltio), 2-siano-2-propil dodesil tritiokarbonat, dan 2-siano-2-propil benzoditioat. Ketiga macam agen RAFT tersebut telah diuji coba pada polimerisasi awal dan bisa menghasilkan konversi tertinggi dari monomer-monomer. Agen transfer kontrol (CTA) dari golongan tritiokarbonat terpilih untuk disintesis kemudian difungsionalisasi dengan succinimide..

Monomer-monomer stirena, N,N-dimetilaminoetil metakrilat (DMAEMA) and 2-laktobionamidoetil metacrilat dipolimerisasi dengan teknik polimerisasi RAFT menggunakan succinimid-CTA sebagai agen RAFT. Massa molar terkontrol dan polidispersitas dar polimer-polimer fungsional dikarakterisasi menggunakan kromatografi ekslusi ukuran (SEC).

Permukaan PET diaminolisis terlebih dahulu menggunakan polietilenimin (PEI) dan 1,6-diaminoheksana sebelum proses *grafting*. Gugus-gugus amin yang terdapat pada permukaan PET dikarakterisasi dengan pengukuran sudut kontak dan spektroskopi fotoelektron X-ray (XPS). Penurunan sudut kontak terjadi antara permukaan PET teraminolisis dan tetesan air (dari Θ_{ref} = 64° ke Θ = 48°). Grafting PS dan poli-LAMA sebagai polimer-polimer fungsional pada permukaan PET teraminolisis dilakukan dengan teknik *grafting-to*. Perubahan sifat permukaan setelah proses *grafting* dikarakterisasi dengan pengukuran sudut kontak. *Grafting* PS pada permukaan PET teraminolisis menghasilkan peningkatan sudut kontak (Θ = 63°) karena sifat hidrofobik. Di sisi lain, *grafting* poli-LAMA pada permukaan PET teraminolisis menghasilkan penurunan sudut kontak (Θ = 39°) karena sifat hidrofilik.

Keywords: PET, polimerisasi RAFT, Suc-CTA, polistirena, poli-DMAEMA, poli-LAMA, teknik *grafting-to*.

MODIFICATION OF PET SURFACES WITH END-FUNCTIONALIZED POLYMERS PREPARED FROM RAFT AGENTS TO ACHIEVE ANTIBACTERIAL PROPERTIES

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ABSTRACT

Modification of PET surfaces with end-functionalized polymers prepared from RAFT polymerization were investigated. Preliminary polymerizations of styrene were prepared to establish the comparison of conventional free radical polymerizations (CFRP) and reversible addition-fragmentation chain transfer (RAFT) polymerizations. Three types of RAFT agents (4-cyano-4-(phenylcarbonothioylthio) pentanoic acid **(1)**, 2-cyano-2-propyl dodecyl trithiocarbonate **(2)**, and 2-cyano-2-propyl benzodithioate **(3)**) that could obtain the highest conversion of monomers were investigated in the preliminary polymerizations. Controlled transfer agent (CTA) from trithiocarbonate groups were chosen to be synthesized then functionalized with succinimide groups. Monomers of styrene (St), N,N-dimethylaminoethyl methacrylate (DMAEMA), and 2-lactobionamidoethyl methacrylate (LAMA) were polymerized by RAFT polymerization technique using succinimide-CTA (Suc-CTA) as RAFT agent. The controlled molar masses and narrow polydispersities of end-functionalized polymers were characterized by size exclusion chromatography (SEC). PET surfaces were aminolized first by polyethylenimine (PEI) and 1,6-diaminohexane before grafting process. The amine functions on PET surfaces were characterized by contact angle measurements and X-ray photoelectron spectroscopy (XPS). Decreasing of contact angle between aminolized PET surfaces and a droplet of water occured (from Θ_{ref} = 64° to Θ = 48°). Then grafting of PS and poly-LAMA as end-functionalized polymers on aminolized PET surfaces were prepared by "grafting-to" technique. The change of surface properties after grafting process was characterized by contact angle measurements. Grafting of PS on aminolized PET surfaces obtained the increasing of contact angle (Θ = 63°) because of their hydrophobic properties. In otherwise, grafting of poly-LAMA on aminolized PET surfaces obtained the decreasing of contact angle (Θ = 39°) because of their hydrophilic properties.

Keywords: PET, RAFT Polymerizations, Suc-CTA, polystyrene, poly-DMAEMA, poly-LAMA, grafting-to.

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LISTS OF ABBREVIATIONS

ACVA	4,4'-azobis-(4-cyanovaleric acid)
AIBN	2,2'-azobis-(isobutyronitrile)
ATRP	Atom transfer radical polymerization
CFRP	Conventional free radical polymerization
CLRP	Controlled/living radical polymerization
CTA	Controlled transfer agent
DCC	Dicyclohexyl carbodiimide
DCM	Dichloromethane
HCl	Hydrochloric acid
DMAEMA	N,N-diethylaminoethyl methacrylate
DMF	Dimethyl formamide
DSA	Drop shape analysis
FT-IR	Fourier transform infra red
ICMMO	"Institut de chimie moléculaire et des matériaux d'Orsay"
LAMA	2-lactobionamidoethyl methacrylate
MAM	More activated monomer
Mn,exp	Experimental number molecular weight
Mn,th	Theoritical number molecular weight
NHS	N-hydrosuccinimide
NMP	Nitroxide-mediated polymerization
NMR	Nuclear magnetic resonance
PDI	Polydispersities index
PEI	Poly-ethylenimine
PET	Poly-ethylene terephtalate
PMMA	Poly methyl methacrylate
Poly-DMAEMA	Poly(N,N-diethylaminoethyl methacrylate)
Poly-LAMA	Poly(2-lactobionamidoethyl methacrylate)
PS	Polystyrene
RAFT	Reversible addition-fragmentation chain transfer
SEC	Size exclusion chromatography
St	Styrene
Suc-CTA	Succinimide based controlled transfer agent
TFA	Trifluoroacetic acid
TMS	Tetramethylsilane
UMR	"Unité mixte de recherche"
XPS	X-ray photoelectron spectroscopy

CHAPTER 1
INTRODUCTION

1.1 Background

Polymers have became an essential thing in our daily life. They exist in many field like industry of textile, food, medicine, and also we can find it in the human body as biomacromolecules. The most widely used synthetic materials in the world is polyethylene terephtalate (PET), as shown in Figure 1.1. Its high cristallinity and high melting point are responsible for its toughness, excellent fibers and film-forming properties. PET is relatively inert and hydrophobic without functional groups. Majority, this polymer was used in packaging industry such food and drinks, cosmetics, household chemicals, toiletries, and pharmaceuticals. The other field of PET also was found in biomedical engineering as a material for artificial blood vessels, tendons, hard tissue prostheses, and surgical thread[1].

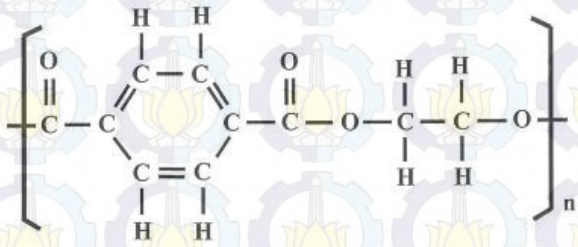


Figure 1.1 Chemical structure of PET

Based of their broad applications, treatments of functional PET surface with reactive groups or environment-sensitive groups have attracted much attention[2]. Microorganisms such bacteria have a strong tendency to develop on surfaces, giving rise to a complex and strongly adhering microbial community named “biofilm”. Biofilms are difficult to eradicate using conventional cleaning and desinfection treatments. It needs to design surfaces which will not allow settlement of microbes at the very first place. Consequently, preventing biofilm

formation by incorporating antimicrobial products on surface materials would be better option than treating it[3]. There are two principles in designing antimicrobial surfaces, repel the microbes or kill them on contact, as shown in Figure 1.2. Both of principles make bacteria very hard to attach by decreasing bacterial adhesion. Repelling surfaces are generally prepared by modifying the surface with either neutral polymers which prevent bacterial adhesion by steric hindrance or anionic polymers which repel the negatively charged cell membrane[1]. While contact killing surfaces could be designed by modification of the surface with cationic polymers which strongly interact with cell membrane and cause the disruption[4].

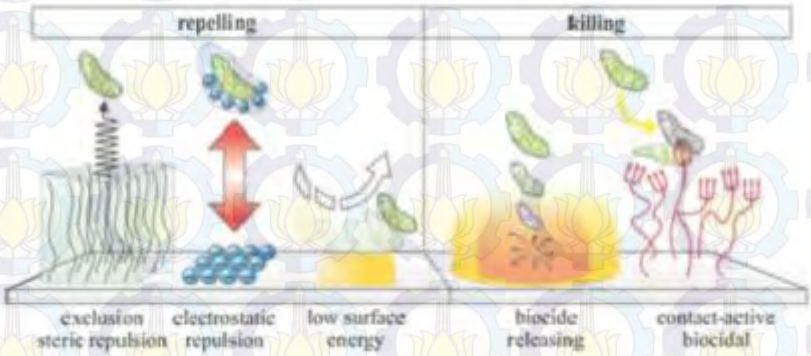


Figure 1.2 Representation of repelling and killing bacteria surfaces[5]

Surface modification is great importance, as it can alter the properties of the surface dramatically and control the interaction between materials and their environment. Due to the wide applications of polymers in many areas, as told above, surface modification by grafting end-functionalized polymers have much developped. The inert nature of most commercial surface such PET caused it must undergoes surface prior to attachment of a bioactive compounds from end-functionalized polymers. One of the methodes usually used were introduce the primary amine groups by thermally induced aminolysis, which is reaction of an organic amine groups with the ester bonds along a polymer chain[6].

Surfaces modification with end-functionalized polymers can be applied in three forms, as shown in Figure 1.3. It's separated by two great principle, first is simple physical absorption without any covalent attachment and the second is the covalent attachment of the biocidal polymer to the surface. The first principle

have a high risk with such coatings of biocide leaching out to the surrounding in some instances, which may lead to a loss of antimicrobial activity over a short time. While the second principle is classified in two technique, “grafting-to” and “grafting-from”. The antimicrobial surfaces created by this methodology do not allow the biocide to leach easily and long-term non-leachable antimicrobial coatings could be designed.

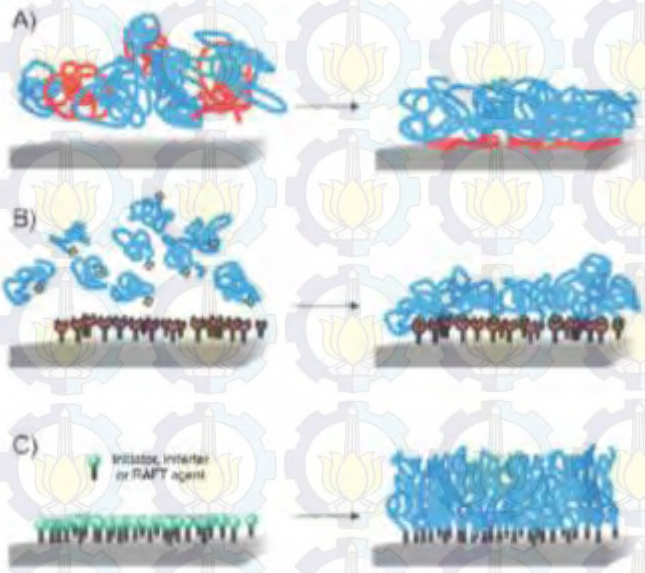
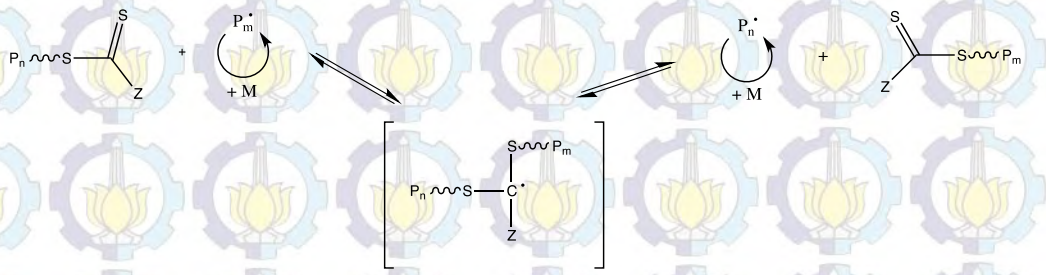


Figure 1.3 Main polymer immobilization schemes (A) Physical adsorption by non-covalent, (B) “grafting-to” methods by creating covalend bonds with the surface, and (C) “grafting-from” or surface initiated polymerization via synthesis of antimicrobial coating from initiators[7]

Polymers with one functional end group are usually grafted on the surfaces by “grafting-to” or “grafting-from” techniques[8]. The advance polymerization technique which prepared the well-defined polymers with precisely designed molecular architectures and predictable molar masses, has been developped[9]. It was famous called with Controlled/Living Radical Polymerization (CLRP). Among the two techniques of CLRP (Nitroxide-mediated Polymerization/NMP and Atom Transfer Radical Polymerization/ATRP), Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization is the

most recent of the living/controlled free radical methodologies that have revolutionized the field of free radical. Compared with NMP and ATRP, the RAFT polymerization is suitable for much more monomers and in principle, all classic radical polymerization can be used with the RAFT process in the presence of efficient RAFT agents. While for NMP and ATRP, the synthesis of polymers with well-defined structures, such as some block copolymers and other complex architecture, has some limitations because the processes are not compatible with certain monomers or reaction conditions[10].

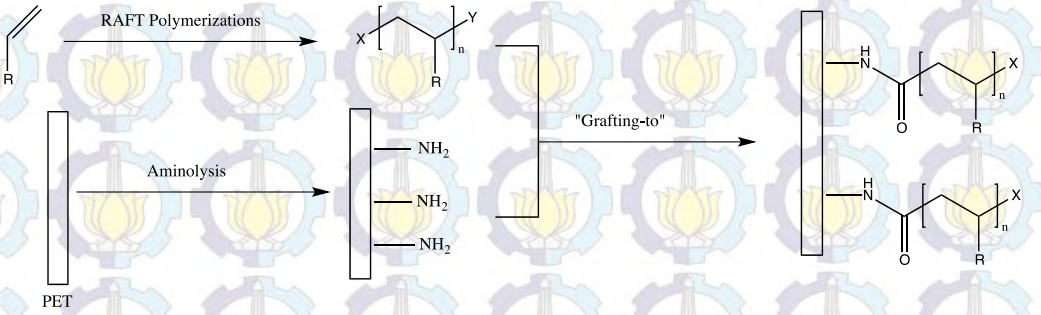
The functional groups can be easily introduced into the chain ends of the polymers by adjusting the structure of the RAFT agent. Selection of the RAFT agent for the monomers and reaction conditons is crucial for the succes of a RAFT polymerization. RAFT agents, denoted Z-C(=S)SR, act as transfer agents by two steps of addition-fragmentation mechanism, as shown in Scheme 1.1. The RAFT group is typically a thiocarbonylthio group such as dithioester (Z = alkyl), trithiocarbonate (Z = S-alkyl), xanthate (Z = O-alkyl) or dithiocarbamate (Z = $N(alkyl)_2$)[11]. The effectivenes of RAFT agents is determined by substituents R and Z[12]. The Z group should activate the C=S towards radical addition, while the R group should be a good free-radical leaving group and be capable of reinitiating free-radical polymerizations[13]. Fast equilibrium between propagating radicals and dormant species is needed to achieve well-defined polymers with low polydispersity.



Scheme 1.1 General mechanism of RAFT Polymerization

The aim of this work is to prepared antibacterial PET surfaces with the end-functionalized polymers by “grafting-to” technique, as shown in Scheme 1.2.

End-functionalized polymers were prepared by RAFT polymerization technique in presence of an initiator and a RAFT agent based on succinimide groups. The succinimide compounds give the ester bonds in polymer chains that will be very reactive to incorporate with amine groups on PET surfaces. Amino groups will be incorporated on PET surfaces by aminolysis reaction. After grafting, PET surfaces will be subjected in bacterial tests to study the bacteria adhesion.



Scheme 1.2 General overview of surface modification of PET with end-functionalized polymers prepared from RAFT polymerizations

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1.2 Objectives of Research

Generally, the objective of this study is to prepared antibacterial PET surfaces with the end-functionalized polymers by "grafting-to" technique. The objective classification of each work will be explained on the specific objectives.

1.2.1 Specific objectives

1. To synthese the controlled transfer agents (CTA) based on succinimide groups (Suc-CTA)
2. To get the end-functionalized polymers using RAFT polymerization technique.
3. To give the amine function on PET surfaces by aminolysis
4. To graft end-functionalized polymers on aminolized PET surfaces by "grafting-to" method

CHAPTER 2
LITERATURE REVIEW

2.1 Polyethylene terephtalate (PET)

PET is a major polymer used in the packaging industry and is used to package both carbonated and non carbonated drinks by an injection moulding and strecth blow moulding process. It is the polymer of choice to pack a wide variety of products from food and drinks to cosmetics, household chemicals, toiletries and pharmaceuticals. Packaged drinks include soft drinks, waters, fruit juices, wine, spirits and beer. Packaged foods include edible oils, vinegars, fruit, meat and fresh pasta. PET is also used to manufacture tough, clear industrial sheet which can be thermoformed[14].

The characterizations of PET are high cristallinity and high melting point. They are responsible for its toughness and its excellent fiber and film forming properties. As are most synthetic polymers, PET is relatively inert and hydrophobic without functional groups able to take part in covalent enzyme immobilization. To overcome this drawback chemical modifications have been attempted to alter the surface properties of the material[1]. The structure of PET was showed in Figure 2.1.

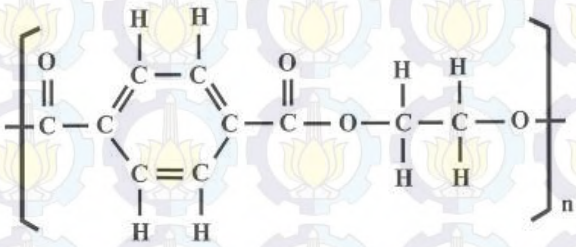


Figure 2.1 Chemical structure of PET

2.2 Functional Polymers

Functional polymers are the basis for the most important trends in polymer science in the las decade. They have properties that are not only derived from the macromolecular structure, but depend to a significant extent or even

entirely on the functional group substituents on the macromolecules. The high demand on the design and the actual tailormaking of such macromolecular materials require a great deal of imagination and detailed knowledge in synthesis and structure or property relationships (macromolecular architecture and macromolecular engineering). In the last decade, research in polymer chemistry and production in the polymer-related industries have shifted from the emphasis on polymers based on raw material availability and high cost efficiency to market and use-oriented tailor-made polymeric materials.

In the design of macromolecular structures with functional groups, it is not only necessary to be concerned with the macromolecule and the functional group, but it is becoming of further importance to be concerned with the spacing of the functional groups with respect to the macromolecular backbone chain. Nature has carefully designed natural macromolecular structures and has placed functional amino acid units with spacer groups in sugar units in polysaccharides to obtain macromolecular structures with opimal biological activity. With clever structure design, sequence, and spacer arrangements, nature has designed enzymes, biologically and immunologically active macromolecular structure. Much could be done in the design of synthetic macromolecular with proper knowledge of the intricacies and interrelations of macromolecular backbone chains, functionalities, and spacer groups[15].

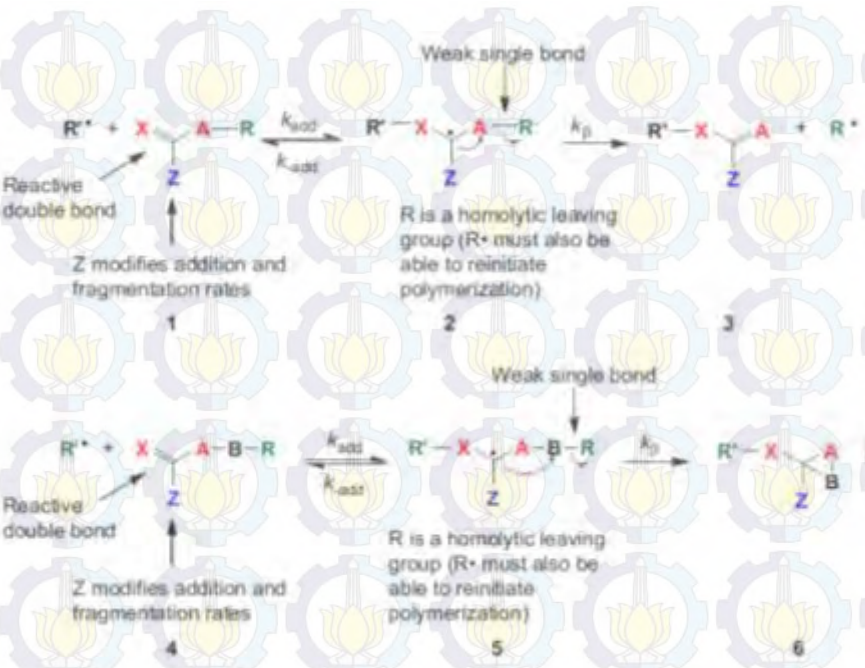
2.3 Reversible Addition-Fragmentation Chain Transfer (RAFT) Polymerization

The RAFT process is the most recent of the living/controlled free radical methodologies that have revolutionized the field of free radical polymeriation. The RAFT process employs a fundamentally different conceptual approach compared to nitroxide-mediated polymerization (NMP) and atom transfer radical polymerization (ATRP) in that it relies on a degenerative chain transfer process and does not make use of a persistent radical effect to establish control. Such an approach has the important consequence that the RAFT process feature quasi-identical rates of polymerization, apart fro deviations caused by the chain legnth dependence of some rate coefficients as the respective conventional free radical

polymerization processes. Among the other unique features of the RAFT process is high tolerance to functional monomers such as vinyl acetate and acrylic acid which can be polymerized with living characteristics with ease. The RAFT process is an equally powerful tool for the coalmost instruction of complex macrromolecular architectures via variable approaches, Z and R group designs, that allow for limitless possibilities in the synthestic protocols in terms of the low molecular weight[16].

2.3.1 Addition-fragmentation chain transfer

Addition—fragmentation transfer agents and mechanisms whereby these reagents provide addition-fragmentation chain transfer during polymerization are shown in Scheme 2.1. Unsaturated compounds of general structure 1 or 4 can act as transfer agents by a two-step addition-fragmentation mechanism. In these compounds C=X should be a double bond that is reactive towards radical addition. X is most often CH_2 or S. Z is a group chosen to give the transfer agent an appropriate reactivity towards propagating radicals and convey appropriate stability to the intermediate radicals (2 or 5, respectively). Examples of A are CH_2, CH_2=$CHCH_2$, O or S. R is a homolytic leaving group and R· should be capable of efficiently reinitiating polymerization. In all known examples of transfer agents 4, B is O. Since functionality can be introduced to the products 3 or 6 in either or both the transfer (typically from Z) and reinitiation (from R) steps, these reagents offer a route to a variety of end-functional polymers including telechelics.



Scheme 2.1 Mechanism for addition-fragmentation chain transfer

In addition-fragmentation chain transfer, the rate constant for chain transfer (k_{tr}) is defined in terms of the rate constant for addition (k_x) and a partition coefficient (Φ) which defines how the adduct is partitioned between products and startig materials, as shown in Scheme 2.2 as Eqs (1) and (2)[17].

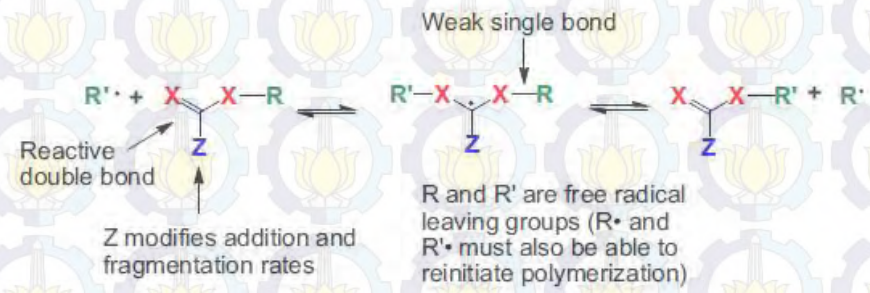
$$k_{tr} = k_{add}\frac{k_\beta}{k_{-add} + k_\beta} = k_{add}\phi \qquad (1)$$

$$\phi = \frac{k_\beta}{k_{-add} + k_\beta} \qquad (2)$$

Scheme 2.2 Equations of chain transfer rate

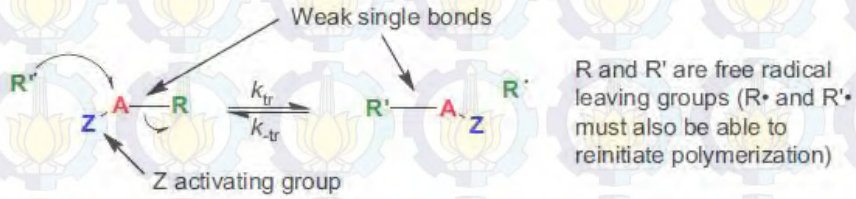
2.3.2 Reversible addition-fragmentation chain transfer (RAFT)

Macromonomers have been known as potential reversible transfer agents in radical polymerization since the mid 1980s, as shown in Scheme 2.3. However, radical polymerizations which involve a degenerate reversible chain transfer step for chain equilibration and which display at least some characteristics of living polymerization were not reported until 1995[18,19].

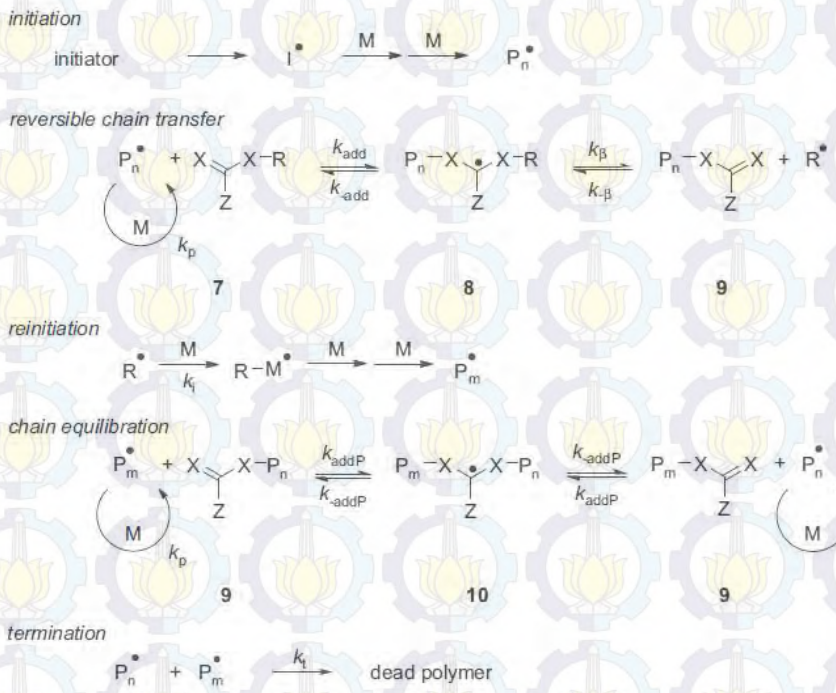


Scheme 2.3 Reversible addition-fragmentation chain transfer

Reversible chain transfer may, in principle, involve homolytic substitution as shown in Scheme 2.4 or addition-fragmentation (RAFT) as shown in Scheme 2.5 or some other transfer mechanism[20]. An essential feature is that the product of chain transfer is also a chain transfer agent. The overall process has also been termed degenerate or degenerative chain transfer since the polymeric starting materials and products have equivalent properties and differ only in molecular weight (where R· and R'· are both propagating chains).



Scheme 2.4 Reversible homolytic substitution chain transfer



Scheme 2.5 Mechanism of RAFT polymerization

2.4 Surface Modification

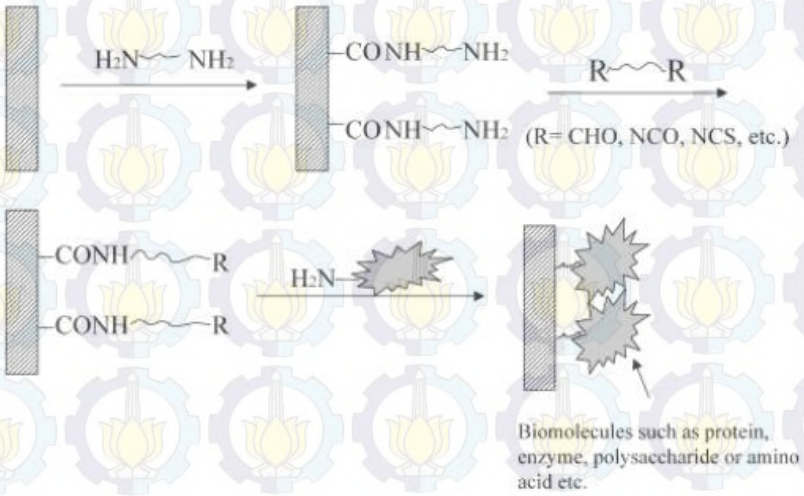
Several surface modification techniques have been developped to improve wetting, adhesion, and printing of polymer surfaces by introducing a variety of polar groups, with little attention to functional group specificity. However, when surface modification is a precursor to attache a bioactive compound, these techniques must be tailored to introduce a specific functional group. Techniques that modify surface properties by introducing random, non-specific groups or by coating the surface are less useful in bioconjugation to polymer surfaces[21].

2.4.1 Surface Modification Technique of PET via Aminolysis

Many methods of modification of PET surface have been proposed, among them are controlled chemical breaking of ester bonds[22,23], surface grafting polymerization[24,25] and plasma treatment[26,27]. The first group of methods induces reaction of PET with low molecular weight substances containing hydroxyl, carboxyl, or amine groups thus incorporating corresponding functionalities onto

the surface. Such action increased the hydrophility of the polymer and created the anchor functionalities for subsequent reactions. The main problem however is to find the proper parameters of these processes, parameters that do not cause high degradation or significant decrease of the mechanical properties of the sample. The same processes but in much more severe conditions are applied also for chemical recycling of PET[28,29].

Primary amine groups are often introduced by thermally induced aminolyis, which is reaction of an organic amine agent with the ester bonds along a polymer chain, as shown in Scheme 2.6[30]. Among the most often used amines are hydrazine, ethylenediamine, and 1,6-diaminohexane[31].



Scheme 2.6 The schematic representation of aminolysis and further immobilization of biomolecules on a membrane

2.4.2 Surface Characterization

2.4.2.1 Water Contact Angle

Water contact angle measures surface hydrophilicity by measuring how much a droplet of water spreads on surface. As shown in Figure 2.2, the lower the contact angle, the more hydrophilic the surface is. As a surface becomes more oxidized, or has more ionizable groups introduced to it, hydrogen bonding with the water becomes more facile and the droplet spreads along the hydrophilic surface, resulting in a lower contact angle.

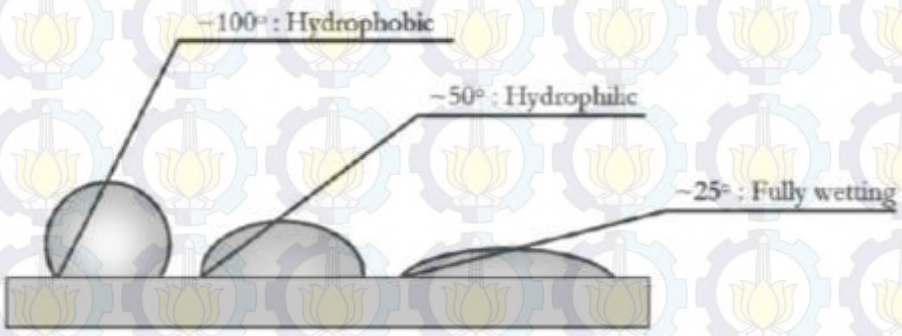


Figure 2.2 Measurement of contact angle

By taking contact angle with a range of buffered aqueous solutions varying in pH value, one can identify the surface pKa, which can be used to identify if a surface contains acidic or basic functionalities[32]. Knowing surface pKa not only helps identify the nature of the surface functional groups, but it aids in determining the proper pH for a conjugation buffer in order to optimize covalent bonding. While contact angle is a simple and rapid measure of the change of a surface's hydrophilicity, it is limited by its inability to distinguish between different hydrophilic functional groups and by many ways error can be introduced into the measurement, including the following: difference in operator measurement, inconsistent water Ph and hardness, and changes in environmental temperature and humidity[33].

2.4.2.2 X-ray photoelectron spectroscopy (XPS)

XPS, or Electron Spectroscopy for Chemical Analysis (ESCA), determines the atomic composition of a solid's top several nanometers. Upon exposure to X-ray photons, a surface emits photoelectrons whose bindingenergies can be compared to known values to identify the element and its oxidation state[34]. The resulting spectrum is a plot of intensity versus binding energy (Ev). The intensity of the ejected photoelctrons relates directly to the material surface atomic distribution and can therefore be used to quantify percent atomic composition and stoichiometric ratios[35]. In addition to quantifying change in surface atomic composition, XPS can be used to estimate extents of reaction by dividing

measured atomic concentrations by theoritical values calculated by assuming complete conversion[36].

In polymer surface modification, it is of interest to identify the presence of specific functional groups. Curve synthesis can be used on high resolution scans to better understand the nature of a bond, but curve fitting models must be chosen carefully, functionalities are typically present in low concentration, and fitted curves overlap, making quantification complex[37]. A different approach to identifying presence of specific functional groups in through the use of chemical derivitizing agents[38]. For example, Kingshott et al. Derivitized hydroxyl and carboxylic acid groups of oxidized PET with trifluoroacetic acid and pentafluorophenol, respectively, and analyze the resulting F/C ratios to better understand the nature of the surface, samples must be handled carefully as even minor surface contamination is pronounced in the resulting spectrum.

CHAPTER 3
METHODOLOGY

3.1 Materials

Preliminary experiment for styrene polymerization by RAFT technique used the commercial CTA of 4-cyano-4-(phenylcarbonothioylthio) pentanoic acid **(1)**, 2-cyano-2-propyl dodecyl trithiocarbonate **(2)**, and 2-cyano-2-propyl benzodithioate **(3)**. Succinimide-CTA (Suc-CTA) grafted in PET films were prepared as reported in literature. Monomers of styrene and dimethylaminoethyl methacrylate (DMAEMA) were purified under reduced pressure before use. While the monomer of 2-lactobionamidoethyl methacrylate (LAMA) were synthesized as reported in literature. 2,2'-azobis-(isobutyronitrile) (AIBN) was used as initiator for polymerization of styrene and DMAEMA while 4,4'-azobis-(4-cyanovaleric acid) (ACVA) was for polymerization of LAMA. PET films of melinex OD with surfaces thickness 175 μm were traited by aminolysis with polyethylenimine (PEI) and 1,6-diaminohexane. Before it, films were washed in mixture solution of ethanol/acetone (1/1 v/v) for at least 1 h then dried with argon gases. All other chemicals such as 2-methyl-1-propanethiol, carbon disulfide (CS_2), aqueous NaOH solution, acetone, chloroform, HCl, tricaprylmethylammonium chloride, N-hydrosuccinimide (NHS), dry dichloromethane, dicyclohexyl carbodiimide (DCC), N,N-dimethylaminoethyl methacrylate (DMAEMA), lactobionic acid, methanol, trifluoroacetic acid (TFA), 2-aminoethyl methacrylate hydrochloride, triethylamine, hydroquinone, and dimethyl formamide (DMF), were used without further purification.

3.2 Methods

3.2.1 Preliminary Polymerizations

3.2.1.1 Conventional Free Radical Polymerization (CFRP) of Styrene

2,2'-azo-bis-(isobutyronitrile) (AIBN, 143 mg, 0.87 mmol) dissolved in styrene (1 mL, 8.7 mmol). The mixture was stirred in different times (2, 4, and 6 h) under argon atmosphere at temperature of 70 °C. After that times, the polymer solution was cooled in ambient temperature and then precipitated with cold methanol. The white polymer solid was filtered and dried under vacum.

3.2.1.2 RAFT Polymerization of Styrene

Three RAFT agents was tried in this preeliminary experiments. Each of compounds **(1) (**244mg, 0.09 mmol), compounds **(2)** (30.2 mg, 0.9 mmol), and compounds **(3)** (19.3 mg, 0.09 mmol) was added to 2,2'-azo-bis (isobutyronitrile)/ AIBN (1.4 mg, 0.009 mmol). Then, it was solubilized in 1 mL of styrene. The mixture was stirred under Argon atmosphere at temperature of 70 °C and will be compared in the polymerization time of 24 h. After that, the polymer solution was cooled in ambient temperature and then precipitated with methanol. The solid polymer was filtered and dried under vacum. Each of polymer solid from RAFT agents of compounds (1), (2), and (3) had white, yellow, and pink colours.

3.2.2 Synthesis of Functional Chain Transfer Agent (CTA)

3.2.2.1 Synthesis of 2-(1-isobutyl) sulfanylthiocarbonyl-sulfanyl-2-methyl propionic acid (CTA), (4)

An aqueous NaOH solution (4 mL, 50 wt%, 50 mmol) was added dropwise to a solution of 2-methyl-1-propanethiol (4.8 mL, 44 mmol), acetone (28 mL, 380 mmol) and tricaprylmethylammonium chloride (0.8 mL, 4.5 mmol). It kept at 5-10 °C in an ice water bath under argon atmosphere. The mixture solution was stirred for 20 min. 2.8 mL of carbon disulfide solution in 8 mL acetone was added dropwise and stirred again for 30 min. 5.6 mL of chloroform was added in one portion then followed by dropwise addition of aqueous NaOH solution (13 mL, 50% wt, 163 mmol). Then, the solution was stirred overnight at ambient temperature under argon atmosphere. 65 mL of water then followed by 33 mL of

concentrated HCl 37% was added in solution to check the pH range of 1-2. Acetone was removed by evaporation. Then, the solid was filtrated and washed with water 5 mL for three times. The orange solid was collected and recrystallized from 7 mL of acetone/hexane (1/10 v/v). It was filtrated again and washed with about 3 mL hexane. The yellow solid was dried in desiccator. The product was obtained as a bright yellow solid in 36% yield.

^{1}H NMR (250 MHz, $CDCl_3$), δ (ppm from TMS) : 1.03 (d, J = 6.1 Hz, 6H, CH-$(CH_3)_2$), 1.74 (s, 6H, $C(CH_3)_2$), 2 (m, 1H, CH_2-CH-$(CH_3)_2$), 3.22 (d, J = 6.8 Hz, 2H, S-CH_2-CH).

3.2.2.2 Synthesis of Succinimide based CTA (Suc-CTA), (5)

A suspension of N-hydroxysuccinimide (1 g, 8.7 mmol) in 40 mL of dichloromethane was added dropwise, at temperature of -10 °C in argon atmosphere, to a solution containing compounds **(4)** (1.6 g, 6.4 mmol) and dicyclohexylcarbodiimide (DCC, 1.8 g, 8.7 mmol) in 50 mL of dry dichloromethane. The mixture was allowed to stir overnight at ambient temperature. Then, it was purified by column chromatography with ethyl acetate/petroleum ether (1/2 v/v) as eluent. The product was obtained as a bright yellow solid in 31.5 %.

^{1}H NMR (360 MHz, $CDCl_3$), δ (ppm from TMS) : 1.03 (d, J = 6.8 Hz, 6H, CH-$(CH_3)_2$), 1.88 (s, 6H, $C(CH_3)_2$), 2.02 (m, 1H, CH_2-CH-$(CH_3)_2$), 2.82 (s, 4H, (C=O)-CH_2-CH_2-(C=O)), 3.25 (d, J = 6.5 Hz, 2H, S-CH_2-CH).

3.2.3 Synthesis of 2-Lactobionamidoethyl methacrylate (LAMA), (6)

White solid of lactobionic acid (5 g, 14 mmol) was solubilized in 100 mL methanol and added by 2-3 drops of trifluoroacetic acid (TFA). The solvent was evaporated and the sugar was done again in the same treatment as before for three times. The formed sugar was analysed by FT-IR instruments. The formed sugar was solubilized in 150 mL methanol and stirred at T = 45 °C under argon atmosphere. After the sugar dissolved, the solution was kept in ambient temperature. 2-aminoethyl methacrylate hydrochloride (5 g, 30 mmol), triethylamine (5 mL, 36 mmol), and hydroquinone (0.1 g, 1 mmol) was added in

sugar solution. The solution was stirred at ambient temperature under argon atmosphere overnight. The solvent was evaporated and the formed sugar was solubilized in the mixture solution of methanol/isopropanol (2/3 v/v). It was stirred for 1 h to precipitate then filtrated and dried. The product was obtained as white solid in 88 %.

^{1}H NMR (250 MHz, D_2O), δ (ppm from TMS) : 1.78 (s, 3H, $C(CH_3)$), 3.84 (m, 26H, CH-OH of sugar), 5.85 (s, 1H, CH_2=C).

FT-IR (cm-1) : 3439 (O-H), 2920 (C-H), 1734 (C=O), 1070 (C-O).

3.2.4 Preparation of End-Functionalized Polymers via RAFT Polymerization

3.2.4.1 RAFT Polymerization using Suc-CTA, (5)

Compounds **(5)** as RAFT agents (30.4 mg, 0.09 mmol), 2,2'-azobis-(isobutyronitrile) (AIBN, 1.4 mg, 0.009 mmol) was solubilized in styrene (1 mL, 8.7 mmol). The solution was mixed by stirring for 15 min in ambient temperature under argon atmosphere then continued stirring at T = 80 °C in different times. Polymer solution was precipitated in 100 mL cold methanol, then filtrated and dried under vacum. The yellow solid was obtained as polymers.

The similar methods was also applied in polymerization of dimethylaminoethyl methacrylate (DMAEMA, 1 mL, 5.94 mmol) [DMAEMA]:[Suc-CTA **(5)**]:[AIBN] = 100:1:0.3) and 2-lactobionamidoethyl methacrylate (LAMA, 469 mg, 1 mmol) in solution of H_2O/DMF (5/1 v/v) with ACVA as intiator ([LAMA]:[Suc-CTA **(5)**]:[ACVA] = 100:5:1).

3.2.4.2 RAFT Polymerization using CTA, (4)

Compouds **(4)** as RAFT agents (12.6 mg, 0.05 mmol), 4,4'-azobis-(4-cyanovaleric acid) (ACVA, 2.8 mg, 0.01 mmol), and 2-lactobionamidoethyl methacrylate **(6)** (LAMA, 469 mg, 1 mmol) was solubilized in 3 mL solution of water/DMF (5/1 v/v). The solution was mixed by stirring for 15 min in ambient temperature under argon atmosphere then continued stirring at T = 80 °C in different times (0.5, 1, 2, and 3 h). Polymer solution was precipitated in 100 mL

cold methanol, then filtrated and dried under vacum. The white solid was obtained as polymers.

3.2.4.3 Acetylation of poly-LAMA

Poly-LAMA (10 mg, 0.02 mmol) was solubilized in acetic anhydride (0.5 mL, 5.3 mmol) and pyridine (1 mL, 12.4 mmol). The solution was stirred overnight in temperature 50 °C to acetylate hidroxyl groups of glycopolymers. About 5 mL of toluene was added to the solution then evaporated to get the acetylated glycopolymers. The obtained glycopolymers need to be purified again by extraction with water/DCM then cleaned with NaCl solution and $MgSO_4$. The solvent was evaporated and the protected glycopolymers was dried. It was preparated for SEC analysis.

3.2.5 Surface Modification of PET

3.2.5.1 Aminolysis Reaction

A pair of washed PET films were added to tubes containing of 5 mL solution of 1,6-diaminohexane (5.8 g, 50 mmol) in 50 mL methanol. Then, it was thermostated at T = 50 °C in different times (1, 3, 5, 7, and 24 h). The solution was removed from the films by washing with methanol in 3-4 times then dried in vacum at ambient temperature for at least 8 h. The films were analysed by contact angle measurements of water.

The similar methods was also applied in surface modification of PET using polyethyleneimine (PEI) 11.6 % in methanol.

3.2.5.2 "grafting-to" of End-functionalized Polymers in Aminolized PET Surfaces

PS (50 mg, ~0.025 mmol) were added to tubes containing 5 mL solution of THF/triethylamine (98/2, v/v). A film of aminolized PET surfaces was added to the tubes then stirred at ambient temperature for 2 days. The aminolized PET surfaces was analysed by contact angle measurements of water to see the difference of surface properties before and after of treatment.

The similar methods was also applied in “grafting-to” of poly-LAMA using the solvent of water/triethylamine (9/1, v/v) at 40 °C for 2 days.

3.2.6 Characterization

The molar masses and polydispersities of all formed polymers were determined by Size Exclusion Chromatography (SEC). THF/Et_3N (98/2, v/v) was used as the eluent at a flow rate of 1.0 mL min^{-1} operated at 30 °C. Special treatment just for poly-LAMA that needs to be protected with acetyl groups before solubilize in THF. PS standard was used for sample measurements.

Determination of structure were recorded by ^1H NMR spectra of the polymers were recorded on 350 MHz nuclear magnetic resonance intrument, using TMS as the internal standard.

Surface modification of PET was characterized by X-ray photoelectron spectroscopy (XPS) and drop shape analysis (DSA). The water dropped was 3 μL. An Kα X-ray source was used. In DSA, a drop of water was used to measure the contact angle in aminolized PET surfaces.

Fourier transform-infra red (FT-IR) analysis was used for detect the functional groups in LAMA synthesis. The module used was vertex 70 ATR pike germanium.

CHAPTER 4
RESULTS AND DISCUSSION

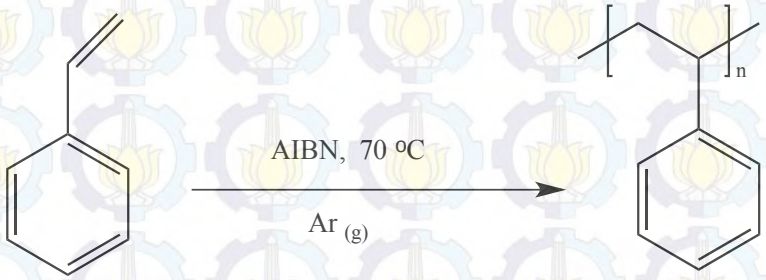
4.1 Preliminary Polymerizations

4.1.1 Conventional Free Radical Polymerization (CFRP) of Styrene

CFRP of styrene using AIBN as an intiator at 70 °C were prepared with the reaction ratios [St]:[AIBN] = 100:1 and in the bulk conditions. Polymerizations were done with different reaction time (2, 4, and 6 h) until the monomer conversion reach the highest value. The results are shown in Table 4.1 and polymerization reaction can be seen in Scheme 4.1.

Table 4.1. Results for CFRP of St at 70 °C ([St]:[AIBN]=100:1)

No. Sample	Time (h)	Conversion (%)		Mn,exp (g/mol)	PDI
		^{1}H NMR	Precipitation		
SADIA 22	2	45	33	26300	1.76
SADIA 26	4	68	49	11200	2.13
SADIA 28	6	100	72	8500	3.14



Scheme 4.1. CFRP reaction of St at 70 °C ([St]:[AIBN]=100:1)

As shown in Table 4.1, Mn,exp was decreased in the increasing on polymerization time, for example 26300 g/mol for polymerization time of 2 h and only 8500 g/mol for polymerization time of 6 h. It showed that CFRP without an inhibitor in bulk condition cause the reaction hard to control. It produces premature radicals with high reactivity which will fastly initiate polymerization of vinyl monomer, as styrene. It usually called autoacceleration or *Tromsdorff effects*. This effect accelerate the initiation reaction so the number-average molecular weight (Mn) decrease in the increasing of conversion or polymerization time. Beside that, the uncontrolled process in CFRP of styrene also produce polydispersities index (PDI) broad as 3.14 for monomer conversion of 100 %.

4.1.2 RAFT Polymerization of Styrene

Three types of commercial CTA were used in these preliminary experiments. The aim is to compare and chose the most suitable CTA type for St polymerizations, as shown in Figure 4.1. These Polymerizations also used AIBN as an initiator at 80 °C with the presence of the three CTA. The polymerizations results are shown in Table 4.2, 4.3, and 4.4.

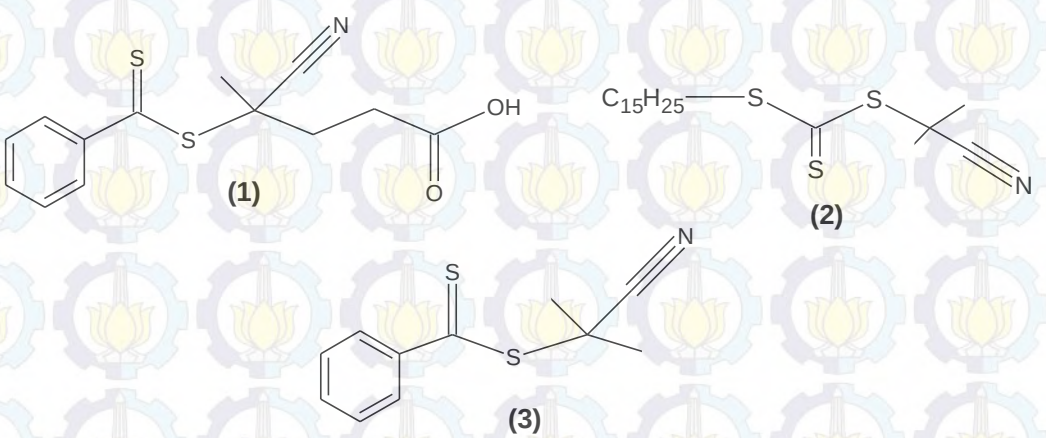


Figure 4.1 Chemical structure of three types of CTA, **(1)** 4-cyano-4-(phenylcarbonothioylthio) pentanoic acid, **(2)** 2-cyano-2-propyl dodecyl trithiocarbonate, and **(3)** 2-cyano-2-propyl benzodithioate

Table 4.2 Results for RAFT polymerization of St with CTA **(1)** at 80 °C ([St]:[CTA **(1)**]:[AIBN] = 100:1:0.3)

No. Sample	T	Time	NMR Yield		Precipitation Yield		Mn, exp (g/mol)	PDI
	(°C)	(h)	^{1}H NMR (%)	Mn, theo (g/mol)	Masse (%)	Mn, theo (g/mol)		
SADIA 18	80	2	12.5	1580	-	-	-	-
SADIA 20	80	4	30	3400	2	690	1025	1.03
SADIA 30	80	6	26	2980	16.5	2000	1540	1.08
SADIA 16	80	24	57.5	6260	26	2980	3375	1.19

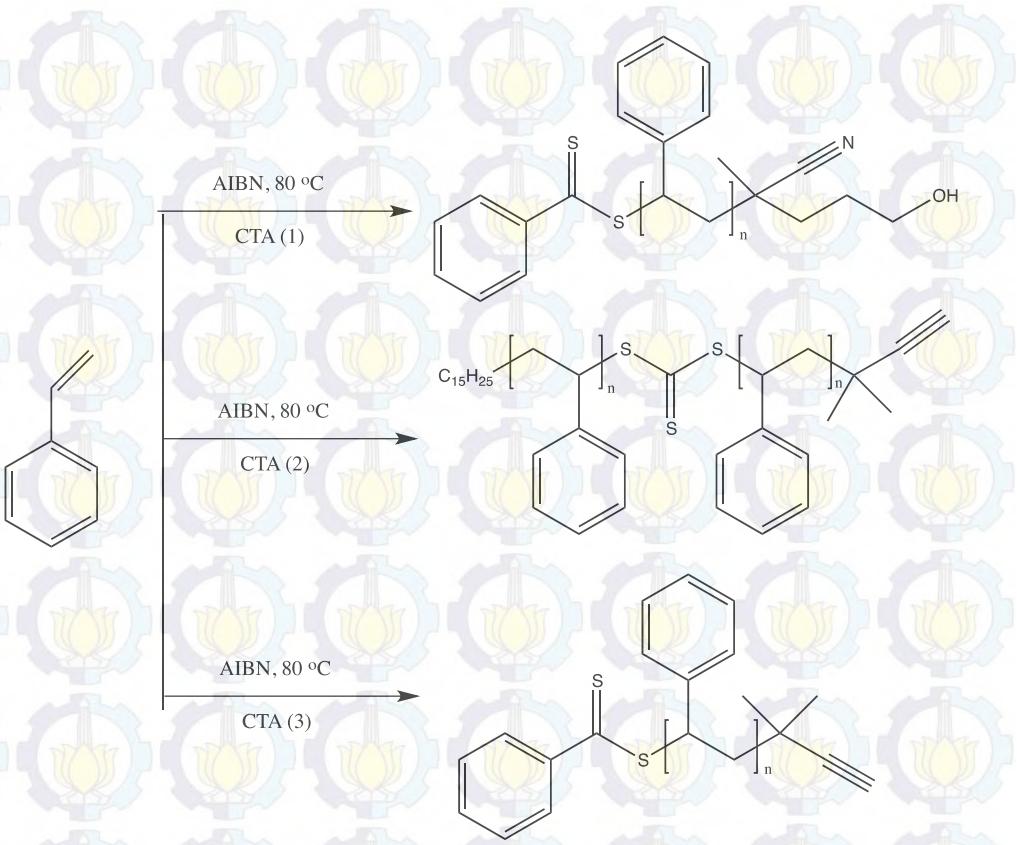
Table 4.3 Results for RAFT polymerization of St with CTA **(2)** at different temperatures ([St]:[CTA **(2)**]:[AIBN] = 100:1:0.1)

No. Sample	T	Time	NMR Yield		Precipitation Yield		Mn, exp (g/mol)	PDI
	(°C)	(h)	^{1}H NMR (%)	Mn, theo (g/mol)	Masse (%)	Mn, theo (g/mol)		
SADIA 36	60	24	32	3670	17	2100	1745	1.11
SADIA 42	70	24	56	6170	31	3570	2380	1.09
SADIA 50	80	24	77	8350	58	6380	5400	1.10

Table 4.4 Results for RAFT polymerization of St with CTA **(3)** at different temperature ([St]:[CTA **(3)**]:[AIBN] = 100:1:0.1)

No. Sample	T	Time	NMR Yield		Precipitation Yield		Mn, exp (g/mol)	PDI
	(°C)	(h)	^{1}H NMR (%)	Mn, theo (g/mol)	Masse (%)	Mn, theo (g/mol)		
SADIA 38	60	24	14	1680	18	2100	1130	1.05
SADIA 34	70	24	34	3760	21	2400	1730	1.12
SADIA 48	80	24	43	4700	25	2800	2750	1.12

As shown in Table 4.2 up to 4.3, the highest conversion in the same time (24 h) and temperature (80 °C) of RAFT polymerization for St reached by CTA **(2)** with the conversion 77 % from NMR yield, Mn exp. = 5400 g/mol, and PDI = 1.10. CTA from trithiocarbonate type, for example CTA **(2),** was the best CTA agent in CLRP for activated monomers, as a styrene[39]. We can also see from the three table that the number-average molecular weight (Mn, exp) had the linear relationship with the increasing of monomer conversion. It's so different with the FRP, as previously described. In CLRP, there is an equilibrium between propagating radicals $Pm^{\cdot}$, $Pn^{\cdot}$, and dormant polymeric RAFT agent via the intermediate macro-RAFT radical. This equilibrium passed so fast which cause the polymeric radical propagate with the same probability and achieve polymers with low polydispersities[40], as shown in Table 4.1 until 4.3 (PDI<1.20). This process proved that CLRP is more controlled than FRP. The polymerization reaction of St with each of CTA was shown in Scheme 4.2.



Scheme 4.2. St Polymerization reaction with CTA **(1), (2),** and **(3)**

Kinetic study for RAFT polymerization of St was also studied by using CTA **(2)** at 80 °C ([St]:[CTA **(2)**]:[AIBN] = 100:1:0.1). It is proposed to establish relationship between the polymerization time (t) with the logaritmic conversion ($\ln [M]_0/[M]$), as shown in Figure 4.2.

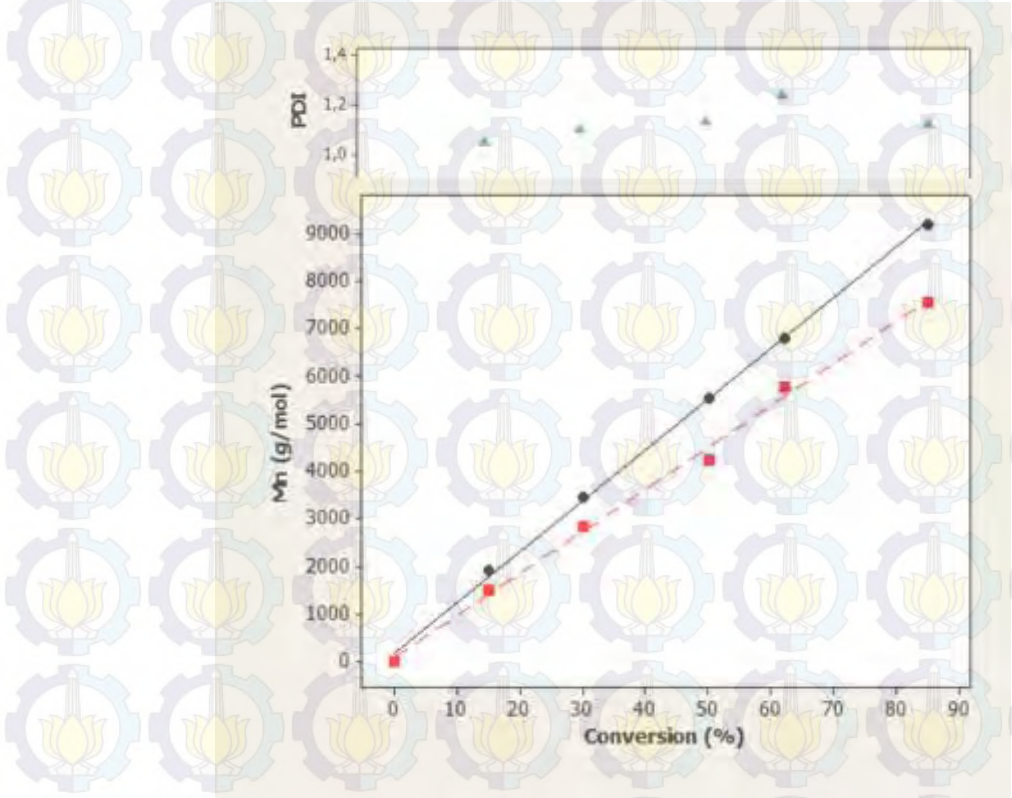


Figure 4.2 Relationships between molar masses and polydispersities to the monomer conversion for RAFT polymerization of St at 80 °C ([St]:[CTA **(2)**]:[AIBN] = 100:1:0.1)

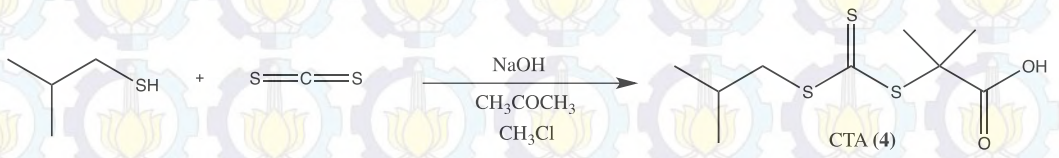
As shown in Figure 4.2, the relationship between ln ($[M]_0/[M]$) and the reaction time for RAFT polymerizations is linear. It's the indication of controlled/living radical polymerizations. The number-average molecular weight (Mn, exp) values also increased almost linearly with monomer conversion and were close to the calculated value (Mn, th).

4.2 Synthesis of Functional Chain Transfer Agent (CTA)

Functionalized chain transfer agents (CTA) was needed for grafting polymers on aminated PET surfaces. Succinimide based CTA (Suc-CTA) was choosen as functional CTA in this work because it will give the ester groups in the polymers chain which be very reactive with amine agents on PET surfaces.

4.2.1 Synthesis of 2-(1-isobutyl) sulfanylthiocarbonyl-sulfanyl-2-methyl propionic acid (CTA), (4)

This method was first step to synthesize the functional CTA based on succinimide (will be discussed later). The CTA was chosen from trithiocarbonate type because in the preeliminary experiments, it was very suitable to RAFT polymerization of St that had given the high monomer conversion. CTA was conveniently prepared from 2-methyl-1-propanethiol with carbon disulfide in acetone then continued by oxidation process to be carboxylic acid groups, as shown in scheme 4.3. The product was obtained as a bright yellow solid in 36% yield.

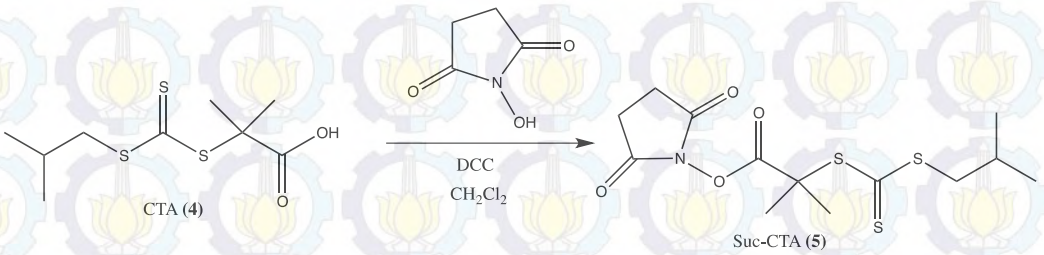


Scheme 4.3 Synthesis of 2-(1-isobutyl) sulfanylthiocarbonyl-sulfanyl-2-methyl propionic acid (CTA), (4)[41]

The structure of CTA was confirmed by ^{1}H NMR revealed the presence of the characteristic signals of equivalent methyl in the position between carbonyl group and thiol (s, 1.7 ppm).

4.2.2 Synthesis of Succinimide based CTA (Suc-CTA), (5)

The Suc-CTA was designed to activate the carboxyl group required in aminolyzed PET surface grafting, that will be discussed later. Suc-CTA was conveniently prepared from N-hydroxysuccinimide (NHS) and activated ester of CTA, **(4)**, as shown in scheme 4.4. The product was obtained as a bright yellow solid in 32 %.

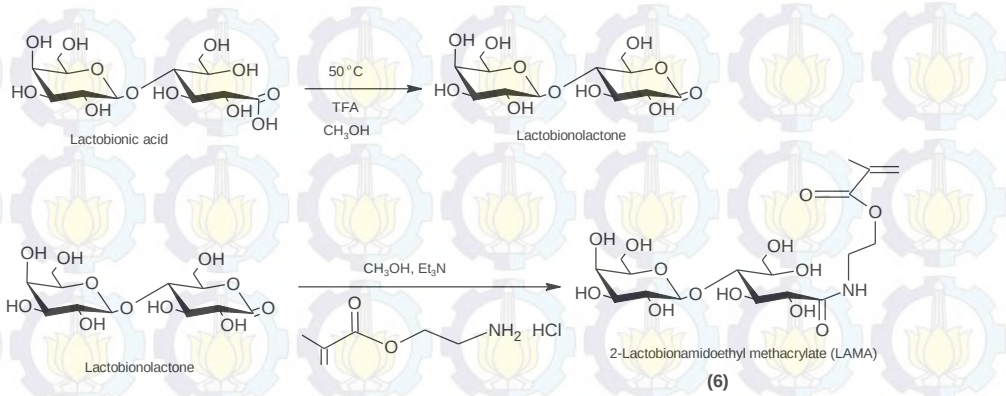


Scheme 4.4 Synthesis of Succinimide based CTA (Suc-CTA), (5)[42]

The structure of Suc-CTA was confirmed by ^{1}H NMR recorded in $CDCl_3$ at 25 °C. The spectrum revealed the presence of the characteristic signals of the succinimide unit (2,8 ppm) and the other spectrum shown the structure of CTA, **(4).**

4.3 Synthesis of 2-Lactobionamidoethyl methacrylate (LAMA), (6)

LAMA was prepared for RAFT polymerization from glycomonomers groups. This glycomonomer was designed with methacrylate groups. LAMA was prepared from lactobionic acid by a very facile synthetic approach without using any protecting group chemistry, as shown in scheme 4.5. The product was obtained as white solid in 88 %.



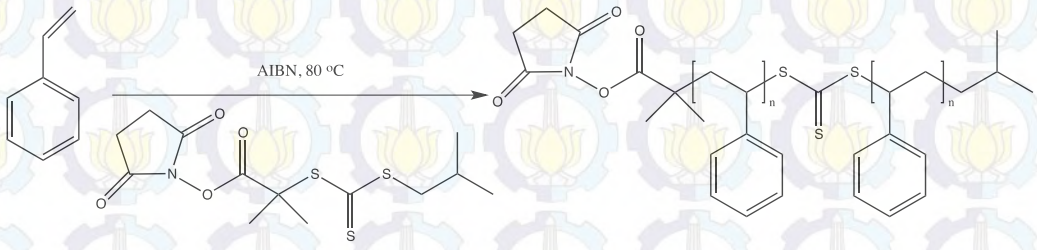
Scheme 4.5 Synthesis of 2-Lactobionamidoethyl methacrylate (LAMA), (6)[43]

The structure of LAMA was confirmed by ^{1}H NMR. The spectrum revealed the presence of the characteristic signals of the carbohydrate groups (3.2 – 4.4 ppm) and vinyl of methacrylates groups (5.6 and 6 ppm).

4.4 End-Functionalized Polymers via RAFT Polymerization

4.4.1 RAFT Polymerization of Styrene using Suc-CTA (5)

RAFT polymerization of St was promoted using Suc-CTA **(5)**. The polymerizations was prepared in bulk conditions same as preliminary experiments. It was initiated by AIBN in the presence of Suc-CTA **(5)** at 80 °C in the different time ([St]:[Suc-CTA **(5)**]:[AIBN] = 100:1:0.1), as shown in Scheme 4.6.



Scheme 4.6 RAFT polymerization reaction of St using Suc-CTA at 80 °C ([St]:[Suc-CTA **(5)**]:[AIBN] = 100:1:0.1)

From the Figure 4.3, we can see that there was linear relationship between ln $[M]_0/[M]$ and polymerization time. Also, it show us that there was also linear relationship between between number-average molecular weight (Mn,exp) and monomer conversion from NMR yields. It indicated that Suc-CTA could play an essential role as RAFT agent in controlled/living radical polymerizations of St. The free radical from RAFT agents remained constant during the polymerizations and there was fast equilibrium between active and dormant species during addition-fragmentation reactions[44]. By seeing good results of functionalized PS prepared from Suc-CTA, it tell us that functionalized PS can be grafted in PET surfaces, will be described later.

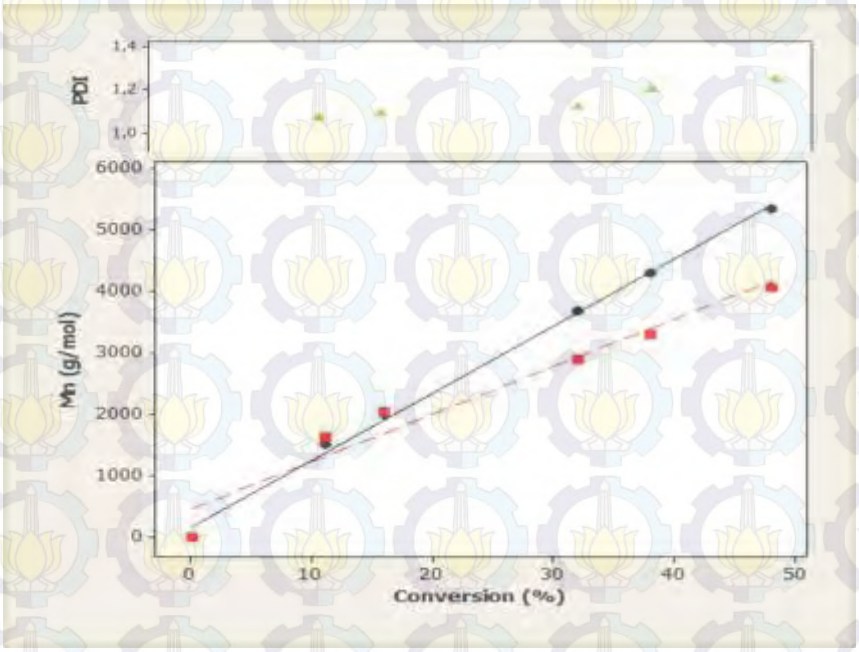
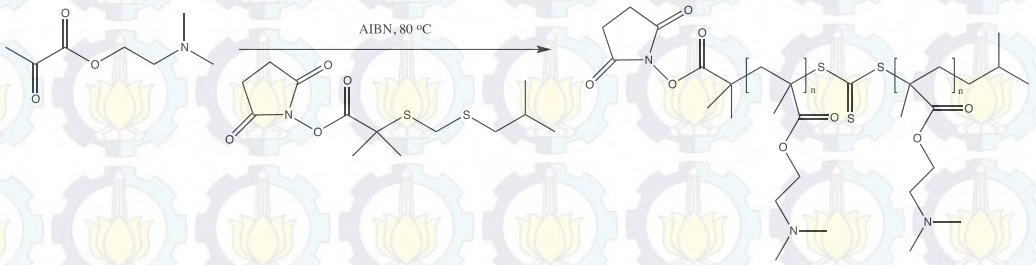


Figure 4.3 Relationships between molar masses and polydispersities to the monomer conversion for RAFT polymerization of St using Suc-CTA at 80 °C ([St]:[Suc-CTA **(5)**]:[AIBN] = 100:1:0.1)

4.4.2 RAFT Polymerization of DMAEMA using Suc-CTA (5)

DMAEMA also was promoted by RAFT polymerization using Suc-CTA **(5)** as RAFT agents. This polymerization was prepared in bulk conditions with AIBN act as initiator. DMAEMA was polymerized at 80 °C in the different time [DMAEMA]:[Suc-CTA **(5)**]:[AIBN] = 100:1:0.3), as shown in Scheme 4.7.



Scheme 4.7 RAFT polymerization reaction of DMAEMA using Suc-CTA at 80 °C ([DMAEMA]:[Suc-CTA **(5)**]:[AIBN] = 100:1:0.3)

There was linear relationship between ln $[M]_0/[M]$ and polymerization time, as shown in Figure 4.4. But nothing formed precipitate of poly-LAMA could be obtained. Some solvents have been tried to precipitate poly-DMAEMA (like methanol, petroleum ether, and n-hexane) but nothing results. DMAEMA polymerization at lower temperature as 60 °C also have been tried but nothing formed polymers. The experiment molar masses and polydispersities of poly-DMAEMA couldn't be observed by size exclusion chromatography (SEC).

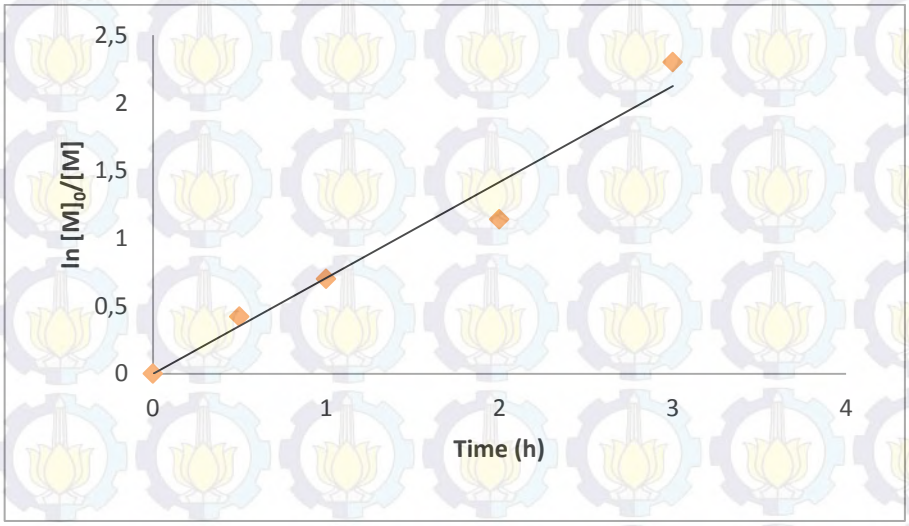


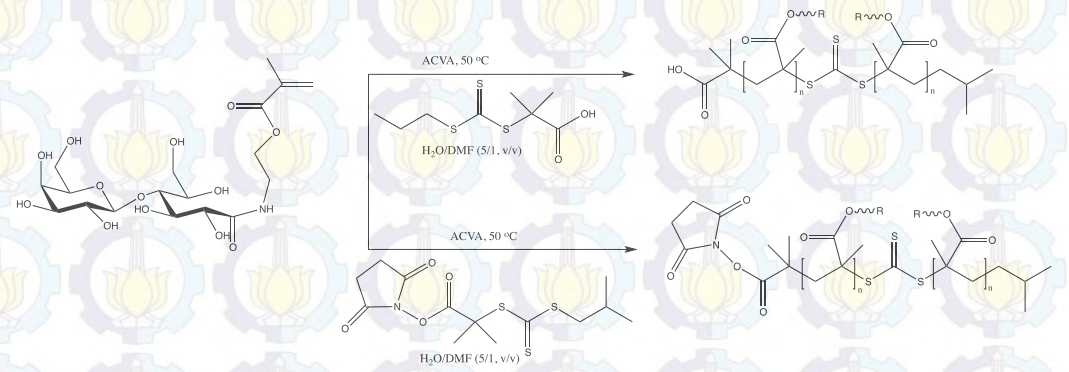
Figure 4.4 Relationships between ln $[M]_0/[M]$ and the polymerization time for RAFT polymerization of DMAEMA using Suc-CTA at 80 °C ([DMAEMA]:[Suc-CTA **(5)**]:[AIBN] = 100:1:0.3)

4.4.3 RAFT Polymerization of LAMA using CTA (4) and Suc-CTA (5)

RAFT polymerizations using CTA **(4)** and Suc-CTA **(5)** was specially prepared for glycomonomers of LAMA. Glycomonomers of LAMA contained two reactive groups, carbohydrate and methacrylates, so they have two type of properties in their structure. Many hydroxyls in carbohydrate groups give hydrophilic properties while methacrylate groups give hydrophobic properties. Based on two different properties in LAMA glycomonomers, it needs to be tried doing RAFT polymerization using CTA **(4)** that is more suitable with hydrophilic properties and Suc-CTA **(5)** that is more suitable with hydrophobic properties.

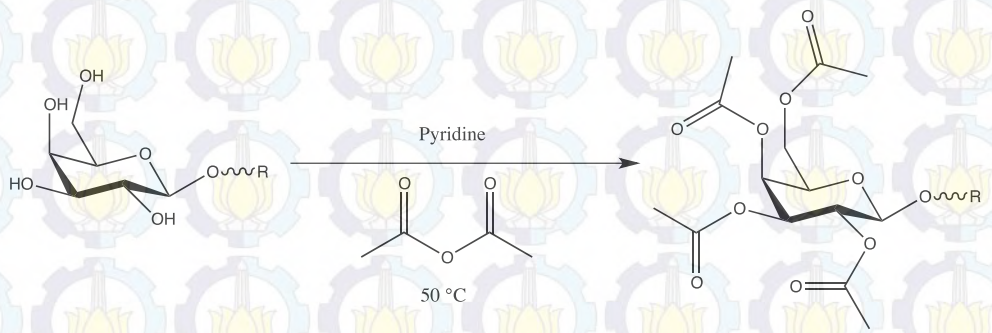
RAFT polymerization of LAMA couldn't be prepared in bulk conditions. Due to the presence of the unprotected hydroxyl groups of the carbohydrate moieties, it would be more interesting to investigate the RAFT polymerization in water. However, due to the low solubility of the chain transfer agents in pure water, the polymerizations was conducted in mixtures of water and *N,N'*-dimethylformamide (DMF), (H_2O/DMF = 5/1)[45]. It was initiated by ACVA in the

presence of CTA at 80 °C ([LAMA]:[CTA **(4)**]:[ACVA] = 100:5:1 and ([LAMA]:[Suc-CTA **(5)**]:[ACVA] = 100:5:1, as shown in Scheme 4.8.



Scheme 4.8 RAFT polymerization reaction of LAMA using CTA **(4)** and Suc-CTA **(5)** at 80 °C ([LAMA]:[CTA **(4)**]:[ACVA] = 100:5:1 and [LAMA]:[Suc-CTA **(5)**]:[ACVA] = 100:5:1)

Poly-LAMA couldn't be characterized directly by SEC using the organic solvent of THF/Et_3N. Glycopolymers wasn't possible to dissolve in the organic solvents. It needs to be prepared by acetylation reactions using anhydride acetic and pyridine, as shown in Scheme 4.9. Hydroxyl groups of poly-LAMA will be protected by acetyl groups which will be easy to dissolve in the organic solvents. The molar masses and polydispersities of protected glycopolymers also could be characterized by SEC, as shown in Table 4.5.



Scheme 4.9. Acetylation reaction of sugar compound

Table 4.5. Results for RAFT polymerizations of LAMA using CTA **(4)** and Suc-CTA **(5)** at 80 °C ([LAMA]:[CTA **(4)**]:[ACVA] = 100:5:1 and [LAMA]:[Suc-CTA **(5)**]:[ACVA] = 100:5:1)

No. Sample	RAFT agents	Time (h)	NMR Yield		Precipitation Yield		Mn, exp (g/mol)	PDI
			^{1}H NMR (%)	Mn, th (g/mol)	Masse (%)	Mn, th (g/mol)		
SADIA 146	CTA (4)	0,5	75	35430	47	22295	12570	1.42
SADIA 140	CTA (4)	3	100	47150	48	22760	13840	1.54
SADIA 164	Suc-CTA (5)	3	100	47250	48	22860	9300	1.88

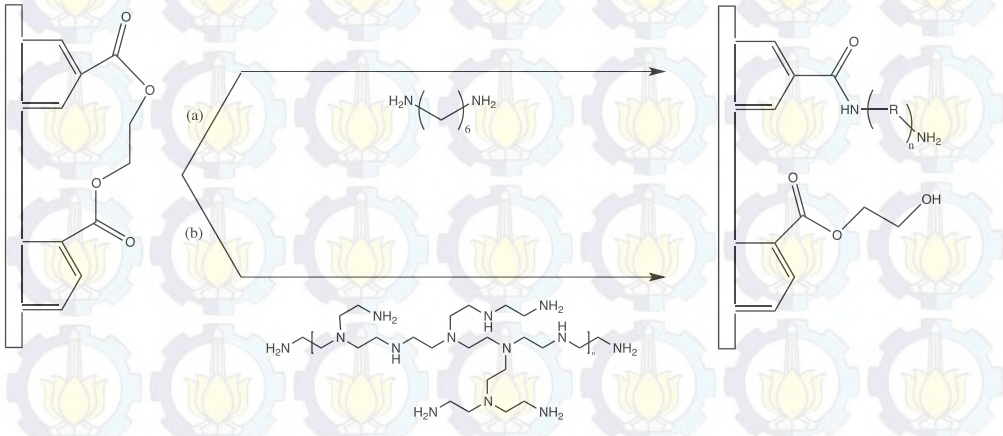
Table 4.8 shows us that poly-LAMA using CTA **(4)** and Suc-CTA **(5)** as RAFT agents reached the highest conversion of monomers, 100 %, in the same polymerization time (3 h). But, both of them have the difference value of average number-molecular weigh (Mn,exp) and polydispersity indexs (PDI). In the

polymerization time of 3 h, poly-LAMA using CTA **(4)** had the molar masses higher than poly-LAMA using Suc-CTA **(5)** (13840 > 9300, g/mol). In otherwise, poly-LAMA using CTA **(4)** had the polydispersities lower than poly-LAMA using Suc-CTA **(5)** (1.54 < 1.88). It means that RAFT agents of CTA **(4)** was more suitable for RAFT polymerization of LAMA.

4.5 Surface Modification of PET

4.5.1 Aminolysis Reaction

PET surfaces were prepared by aminolysis reactions with 1,6-diaminohexane and polyethylenimine (PEI). This treatment was proposed to give the amine functions on PET surfaces. The aminolized PET surfaces will be very reactive to incorporate covalently the ester bonds of end-functionalized polymers in grafting process. By thermally induced aminolysis at 50 °C, the amine groups from 1,6-diaminohexane and polyethylenimine (PEI) in methanol solution will form the covalent bonds with carbonyl groups on PET surfaces, as shown in Scheme 4.10.



Scheme 4.10 Aminolysis reactions of PET with (a) 1,6-diaminohexane, (R = $(CH_2)_6$) and (b) PEI, (R = $(PEI)_n$)[46]

PET surfaces were characterized by water contact angle measurements and X-ray photoelectron spectroscopy (XPS). Both of measurements were performed on PET surfaces before and after aminolysis reaction, as shown in Table 4.6 and 4.7.

Table 4.6 Aminolysis reaction of PET with polyethylenimine (PEI) at 50 °C

Time (h)	Θ_{H2O} (°)
0	64.4 ± 6.0
1	50.4 ± 0.5
4	47.9 ± 3.8
24	48.4 ± 1.9

Table 4.7 Aminolysis reaction of PET with 1,6-diaminohexane at 50 °C

Time (h)	Θ_{H2O} (°)
0	64.4 ± 6.0
1	56.9 ± 1.9
3	50.4 ± 2.4
7	48.6 ± 1.9
24	22.4 ± 5.2

The measurements of contact angle show us that aminolized PET surfaces had the lower angle contact than the PET references. It means that amine groups either from PEI and 1,6-diaminohexane have been succesfully attacked by carbonyl groups on PET surfaces. It also was proved by XPS results that there was a new peak of nitrogen (N1s) on PET surfaces after aminolysis reactions, as

shown in Figure 4.5 Although, there was degradation on aminolized PET surfaces prepared from 1,6-diaminohexanes for aminolysis time of 24 h. Consequently, it couldn't be grafted by end-functionalized polymers. The surface degradation didn't occur in aminolized PET surfaces prepared from 1,6-diaminohexane for aminolysis time of 24 h.

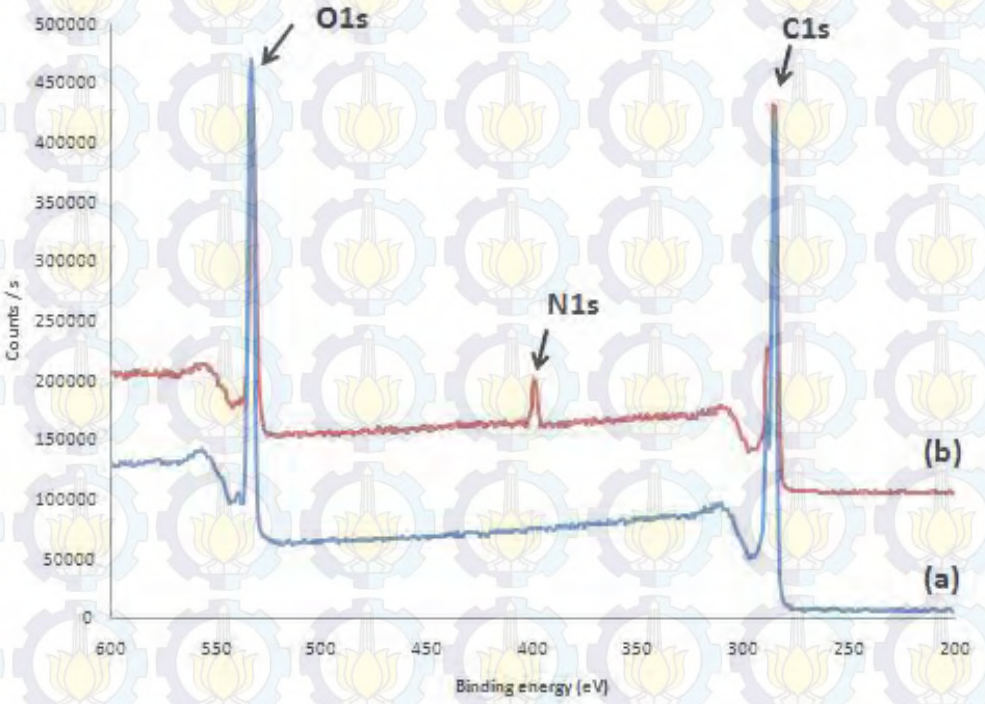
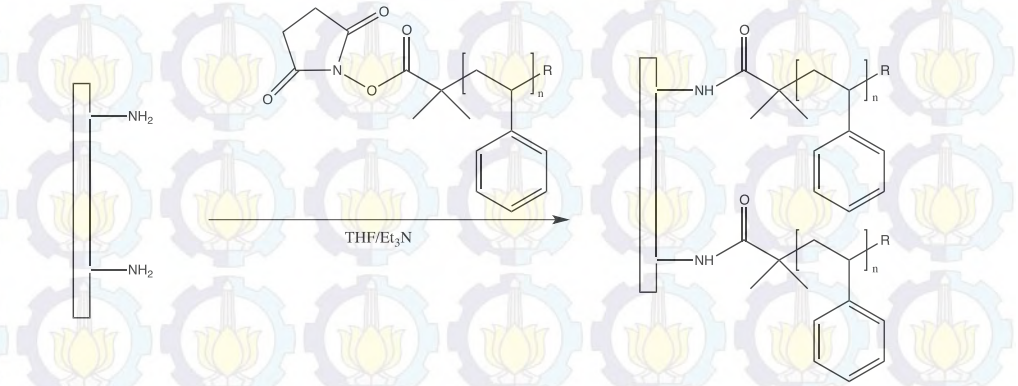


Figure 4.5 XPS spectra of PET surfaces (a) before and (b) after aminolysis reaction with PEI

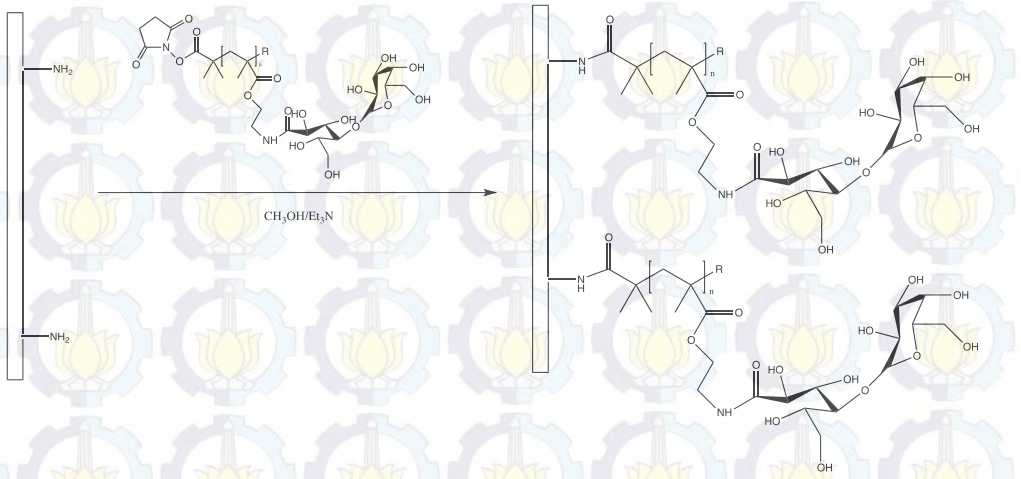
4.5.2 Grafting *"to"* of End-functionalized Polymers on Aminolized PET Surfaces

PS and poly-LAMA as end-functionalized polymers were grafted on aminolized PET surfaces by "grafting-to" technique. Poly-DMAEMA couldn't be grafted on aminolized PET surfaces by "grafting-to" technique because of nothing formed precipitated of polymers. Grafting of PS from the monomers conversion

64 % was prepared in the solution of THF/Et_3N (98/2, v/v) at ambient temperature for 48 h, as shown in Scheme 4.11. While grafting of poly-LAMA from the monomers conversion 100 % was prepared in the solution of CH_3OH/Et_3N (9/1, v/v) at 40 °C for 24 h, as shown in Scheme 4.12. Triethylamine (Et_3N) was used as base functions to prepare the formation of amide groups from end-functionalized polymers on aminolized PET surfaces.



Scheme 4.11 Grafting of PS on aminolized PET surfaces



Scheme 4.12 Grafting of poly-LAMA on aminolized PET surfaces

Grafting of end-functionalized polymers on aminolized PET surfaces was characterized by contact angle measurements, as shown in Table 4.8. Both of PET surfaces either were grafted by PS or poly-LAMA show the difference of contact angle with aminolized PET surfaces without grafting (PET reference, $\Theta = 48°$). Grafting of PS on aminolized PET surfaces obtained the higher contact angle than PET reference because of the hydrophobic properties of PS. While grafting of poly-LAMA on aminolized PET surfaces obtained the lower contact angle than PET reference because of the hydrophobic properties of poly-LAMA. Although, grafting of PS and poly-LAMA on aminolized PET surfaces still didn't reach the angle contact of standard hydrophobic and hydrophilic materials ($\Theta_{hydrophobic} = 110°$)[47] and ($\Theta_{hydrophilic} = 14°$)[48]. Preliminary results of "grafting-to" obtained the conditions which need to be optimized.

Table 4.8 Grafting of PS (in the solution of THF/Et_3N (98/2, v/v)) and poly-LAMA (in the solution of CH_3OH/Et_3N (9/1, v/v)) on aminolized PET surfaces by "grafting-to" technique

Grafting of	**Time (h)**	**Temperature (°C)**	Θ_{H2O} **(°)**
PS	48	ambient	63.3 ± 2.9
poly-LAMA	24	40	39.1 ± 3.2

CHAPTER 5
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

End-functionalized polymers have been prepared by RAFT polymerization technique. A new RAFT agent prepared from succinimide compounds was designed and used to mediate homopolymerizations of styrene, DMAEMA, and LAMA. Controlled molar masses and narrow polydispersities were observed by SEC.

Surface modification of PET also have been prepared by aminolysis reactions. PET surfaces was incorporated with amine groups from 1,6-diaminohexane and PEI. The hydrophilic properties of aminolized PET surfaces was observed by contact angle and XPS.

Grafting end-functionalized polymers on aminolized PET surfaces was prepared by "grafting-to" technique. Only PS and poly-LAMA could be grafted on aminolized PET surfaces by "grafting-to" technique because of nothing formed precipitate of poly-LAMA. The properties of PET surfaces after grafting process were characterized by water contact angle measurements. Grafting of PS on aminolized PET surfaces obtained the increasing of contact angle (Θ = 63°) because of their hydrophobic properties. In otherwise, grafting of poly-LAMA on aminolized PET surfaces obtained the decreasing of contact angle (Θ = 39°) because of their hydrophilic properties. As the comparison, the water contact angle with aminolized PET surfaces without grafting is equal to 48°. By this results, modification of PET surfaces with end-functionalized polymers prepared from RAFT agents can be proposed to antibacterial tests.

For the comparison, the future work will focus on the grafting end-functionalized polymers on aminolized PET surface by "grafting-from" technique. By this technique, grafting of end-functionalized polymers on PET surfaces is expected can give the higher antibacterial properties than by "grafting-to" technique. Two main potential advantages of "grafting-from" technique are a higher bioconjugation efficiency which is anticipated due to a lower steric hindrance and the purification of the final materials is easier as only small molecules have to be

removed such as unreacted monomers, in contrast to preformed polymer for the "grafting-to" approach.

5.2 Recommendations

1. Optimize grafting end-functionalized polymers by "Grafting-to" method.
2. Grafting end-functionalized polymers on aminolized PET surfaces by "Grafting-from" method.
3. Do antibacterial test to see the properties of modified surface.

APPENDIX

Table 1. Results for RAFT polymerization of St at 80 °C ([St]:[CTA **(2)**]:[AIBN] = 100:1:0.1)

Sample	Time (h)	NMR Yield		Precipitation Yield		Mn,exp (g/mol)	PDI
		^{1}H NMR (%)	Mn,th (g/mol)	Masse (%)	Mn, th (g/mol)		
SADIA 56	1	2	560	15	1900	1500	1.05
SADIA 60	3	25	3000	30	3465	2845	1.10
SADIA 54	5	37	4260	50	5550	4220	1.13
SADIA 64	7	46	5140	62	6800	3770	1.24
SADIA 52	24	73	7900	85	9185	7570	1.12

Table 2. Results for RAFT polymerization using Suc-CTA of St at 80 °C ([St]:[CTA **(5)**]:[AIBN] = 100:1:0.1)

No. Sample	T	Time	NMR Yield		Precipitation Yield		Mn, exp (g/mol)	PDI
	(°C)	(h)	^{1}H NMR (%)	Mn, th (g/mol)	Masse (%)	Mn, th (g/mol)		
SADIA 78	80	1	22	2640	11	1500	1640	1.07
SADIA 80	80	3	28	3260	16	2000	2040	1.09
SADIA 82	80	5	42	4700	32	3680	2900	1.12
SADIA 84	80	7	51	5650	38	4300	3300	1.20
SADIA 76	80	24	64	7000	48	5340	4070	1.25

Table 3. Results for RAFT polymerization using Suc-CTA of DMAEMA at 80 °C ([St]:[CTA **(5)**]:[AIBN] = 100:1:0.3)

No. Sample	T	Time	NMR Yield	
	(°C)	(h)	^{1}H NMR (%)	Mn, th (g/mol)
SADIA 98	80	0,5	34	5700
SADIA 100	80	1	50	8200
SADIA 150	80	2	68	11205
SADIA 92	80	3	90	14480

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