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Oxidative coupling polymerization of primary aromatic diamines

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Chapter 1

Introduction and outline of the thesis

Introduction

Properties of azo polymers

Azo polymers contain -N=N- (azo) groups within the polymer structure. Depending on the position of the azo group a subdivision in main-chain and side-chain azo polymers can be made. Especially the so-called aromatic azo polymers, where the azo group connects two aromatic units, have interesting properties. These brightly coloured aromatic azo polymers have good mechanical and thermal properties and a low flammability [1]. Moreover, these polymers can be liquid-crystalline and can have non-linear optical properties [2]. A very well-known reaction is the *cis-trans* isomerization of the aromatic azo group. The *cis-trans* isomerization, which occurs thermally or/and photochemically, was first studied with azo dye molecules in solution or dispersed in polymers [3] and is still a subject of research [4-8]. The *cis-trans* isomerization reaction of azobenzene and azobenzene derivatives, covalently bound within the main- or side-chain of a polymer, was also investigated extensively [9-14]. Reversible photocontrolled *cis-trans* isomerization also causes a reversible change in the physical properties. Therefore especially aromatic azo polymers with relatively stable *cis* isomers are used in switching devices [2].

In liquid-crystalline aromatic azo polymers, the azobenzene unit acts as a rigid mesogenic group. Flexible spacers (mostly methylene units) are used to provide the mesogenic group with sufficient conformational freedom to form stacks or organized domains. For side-chain azo polymers the flexible groups connect the aromatic azo groups with the polymer backbone. The backbone of these side-chain liquid-crystalline polymers can be e.g. poly(hydrocarbons) [15-22], poly(esters) [23], poly(amides) [24] or poly(phosphazenes) [25]. For the main-chain liquid-crystalline polymers [26-30] the backbone contains azobenzene units connected by flexible spacers.

A material with noncentrosymmetric bulk ordering of the azobenzene unit, bearing an electron-donor and -acceptor group, can exhibit second-order nonlinear optical (NLO) properties. To obtain a noncentrosymmetric bulk ordering a polymer matrix is often used. In order to circumvent the low solubility and fast thermal relaxation to a centrosymmetric bulk ordering of the NLO-active group dispersed in a polymer matrix, the NLO-active groups are often covalently bound in the main-chain [31-34] or side-chain [35-41] of the polymer.

Synthesis of azo polymers

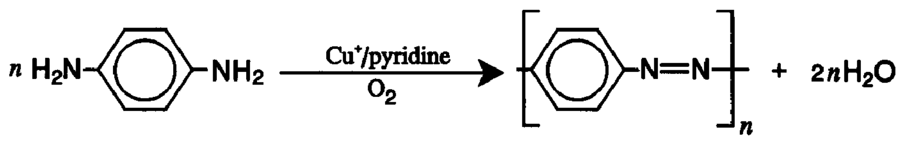
Side-chain aromatic azo polymers have been synthesized either by modification of a preformed polymer [42-46] or by copolymerization of an aromatic azo containing monomer with a simple monomer like methyl methacrylate or styrene [11,46-54].
Main-chain aromatic azo polymers can be synthesized by polymerization with and without the formation of the azo linkage. Polymerization without formation of the azo group is performed with monomers that already contain the aromatic azo group [11,13,30,55-66]. For the polymerization with formation of the aromatic azo group a few methods are used: i) coupling of diazonium salts [67-71]; ii) coupling of azide groups [72]; iii) conversion of nitrosamides into their azo ester, followed by decomposition resulting in the formation of the aromatic azo group [68,73-76]; iv) coupling of primary aromatic diamines either by hydrogen abstraction by free radicals [77] or oxidatively by an iron [78] or copper [79-97] catalyst.

Oxidative coupling polymerizations

Oxidative coupling polymerization, with a metal complex serving as a catalyst, is the result of coupling of radicals or ions formed by oxidation of the monomer through coordination with this metal complex. Because of the ability to repeat this procedure after reoxidation by dioxygen, the metal complex is a catalyst. Monomers, easily polymerized oxidatively to their corresponding polymers, have at least two labile hydrogen atoms. A very well known example is the oxidative coupling polymerization of 2,6-disubstituted phenols to high-molecular-weight linear poly(2,6-disubstituted phenylene oxide)s, first reported by Hay et al. [98]. In our Laboratory the oxidative coupling polymerization of 2,6-disubstituted phenols by using (polymer-bound) copper-amine complexes and the mechanism of this reaction have been intensively investigated [99-104]. Other monomers used for catalytic oxidative coupling (polymerization) are, for instance, diacetylenes [105,106], thiophenol [107] and organic molecules containing activated CH groups for carbon-carbon coupling [105].

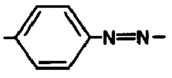
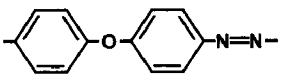
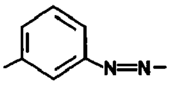
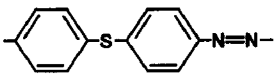
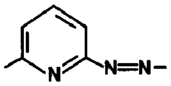
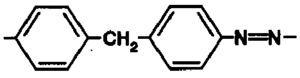
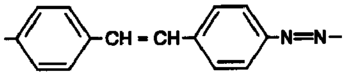
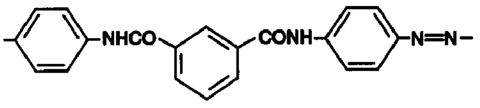
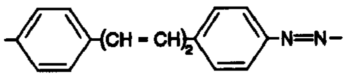
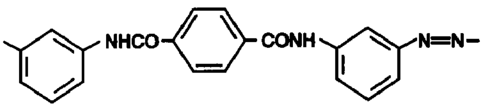
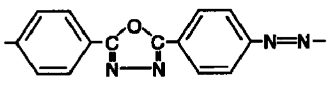
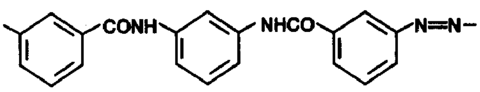
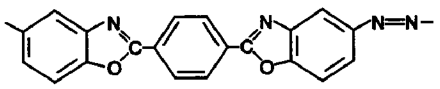
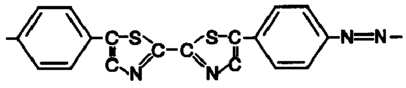
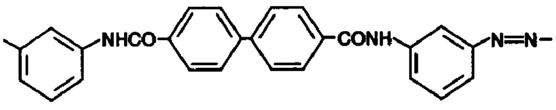
Oxidative coupling polymerization of primary aromatic diamines

The oxidative coupling of aniline to azobenzene by a catalyst prepared from copper(I) chloride, pyridine (py) and dioxygen was first reported by Terent'ev and Mogilyanskii [108]. In the mid sixties Kotlyarevsii et al. [97] and Bach [94] used this catalytic system to prepare a large number of conjugated and non-conjugated main-chain aromatic azo polymers. The repeating units of these azo polymers are shown in Tab. 1.1, and the overall reaction for the oxidative coupling polymerization of 1,4-diaminobenzene is shown in Eq. 1.1.



(1.1)

Table 1.1. *Examples of azo polymers*

Conjugated	Non-conjugated
	
	
	
	
	
	
	
	

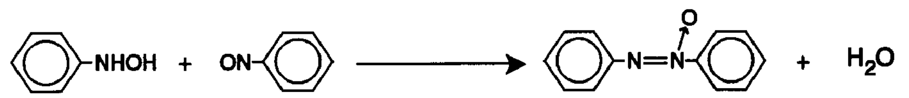
At first, the tertiary amine pyridine, which acts both as ligand for the active copper catalyst and as solvent for the produced azo polymer, was used [95,96,97]. Later, co-solvents, like dimethyl acetamide (dma) [79,88,90,91,94] and dimethyl sulfoxide (DMSO) [92] were used in combination with pyridine to increase the solubility of the formed azo polymer resulting in higher molecular weights. It was also found that N,N-disubstituted amides such as dimethyl acetamide and hexamethyl phosphortriamide (hmpt) can completely take over the function of pyridine [90].

According to Bach [86] every copper-tertiary amine or copper-(N,N-disubstituted amide) complex can be used as long as it is soluble in the reaction medium and capable of existing in the Cu(II) state. The existence of a stable Cu(II) state is based on the idea that the oxidation of the amine monomer is accomplished by intermediate formation of an activated Cu(II) nitrogen base complex that reacts with the amine monomer to regenerate a Cu(I) nitrogen base complex (see Scheme 1.1). A number of Cu(I) salts like copper(I) chloride, copper(I) bromide, copper(I) sulfate, copper(I) tetraamine sulfate, copper(I) acetate, copper(I) propionate, copper(I) palmitate and copper(I) benzoate can be used. Cu(I) salts like copper(I) sulfide, copper(I) cyanide and copper(I) thiocyanate are either not soluble in the nitrogen base or not capable to form a stable Cu(II) salt and are therefore not suitable for the process. According to Bach [86] the use of Cu(II) salts is generally less desirable in the catalyst preparation.

The nitrogen base has to be able to form a stable active Cu(II) nitrogen base complex in the solvent used and must not be oxidized by the catalyst. In order to obtain a high reaction rate and good yield it is necessary that the basicity of the nitrogen base is close to that of the primary aromatic (di)amines (monomers). Generally, aromatic tertiary amines, aliphatic tertiary amines and N,N-disubstituted amides are used. The use of dimethyl acetamide and hexamethyl phosphortriamide as N,N-disubstituted amides is preferred. When aliphatic tertiary amines are used, it is preferred that at least two of the aliphatic groups are straight chain hydrocarbon groups. Mixtures of nitrogen bases can also be used. The nitrogen base can even be used in combination with inert solvents, which do not interfere with the catalyst and are not oxidized to any appreciable extent. E.g. benzene and nitrobenzene can act as a good reaction medium.

The system with copper(I) chloride, pyridine and dioxygen is found to be the best for the oxidative coupling of primary aromatic (di)amines. Terent'ev and Mogilyanskii [109] undertook an initial attempt to unravel the mechanism of the oxidative coupling of aniline to azobenzene for this system in 1961. At that time there were two possible explanations. According to Bamberger and Tschirner [110] the oxidation of primary aromatic amines is expressed by Eq. 1.2. Various products are obtained as a result of branching, condensation and further oxidation. E.g condensation of phenylhydroxylamine with nitrosobenzene gives azoxybenzene (Eq. 1.3) and the formation of azobenzene is explained by the reaction of nitrosobenzene with the unchanged amine (Eq. 1.4). Terent'ev and Mogilyanskii, however, never succeeded in detecting even traces of azoxy compounds among their reaction products. According to Bamberger and Tschirner, this is explained by the fact that the rate of oxidation of phenylhydroxyamine to nitrosobenzene is considerable greater than the rate of reaction of phenylhydroxylamine with nitrosobenzene. As a result nitrosobenzene can react only with aniline resulting in the formation of azobenzene. Terent'ev and Mogilyanskii [108] tested this idea for the copper(I) chloride/pyridine/dioxygen system. During the oxidation of phenylhydroxylamine in this system, dioxygen was absorbed in an amount sufficient for the oxidation of only half the amount of phenylhydroxylamine. The other half of phenylhydroxylamine reacted with the oxidation product, nitrosobenzene, giving azoxybenzene in quantitative yield. Although phenylhydroxylamine is oxidized very rapidly under their conditions (15-20 minutes), reaction with the oxidation product, nitrosobenzene, was faster. Only 15% of the phenylhydroxylamine was oxidized when a reaction mixture of equivalent amounts of nitrosobenzene and phenylhydroxylamine was used. The rest of phenylhydroxylamine reacted directly with nitrosobenzene. Moreover, no azobenzene was formed when a mixture of aniline, nitrosobenzene, pyridine and copper(I) chloride was left under dihydrogen atmosphere for one day. From these experiments Terent'ev and Mogilyanskii [108] concluded that the oxidative coupling of aniline to azobenzene does not involve the formation of the oxidation product phenylhydroxylamine. The supposed mechanism of Bamberger and Tschirner therefore probably does not occur during the oxidative coupling of aniline to azobenzene in the pyridine/copper(I) chloride/dioxygen system.

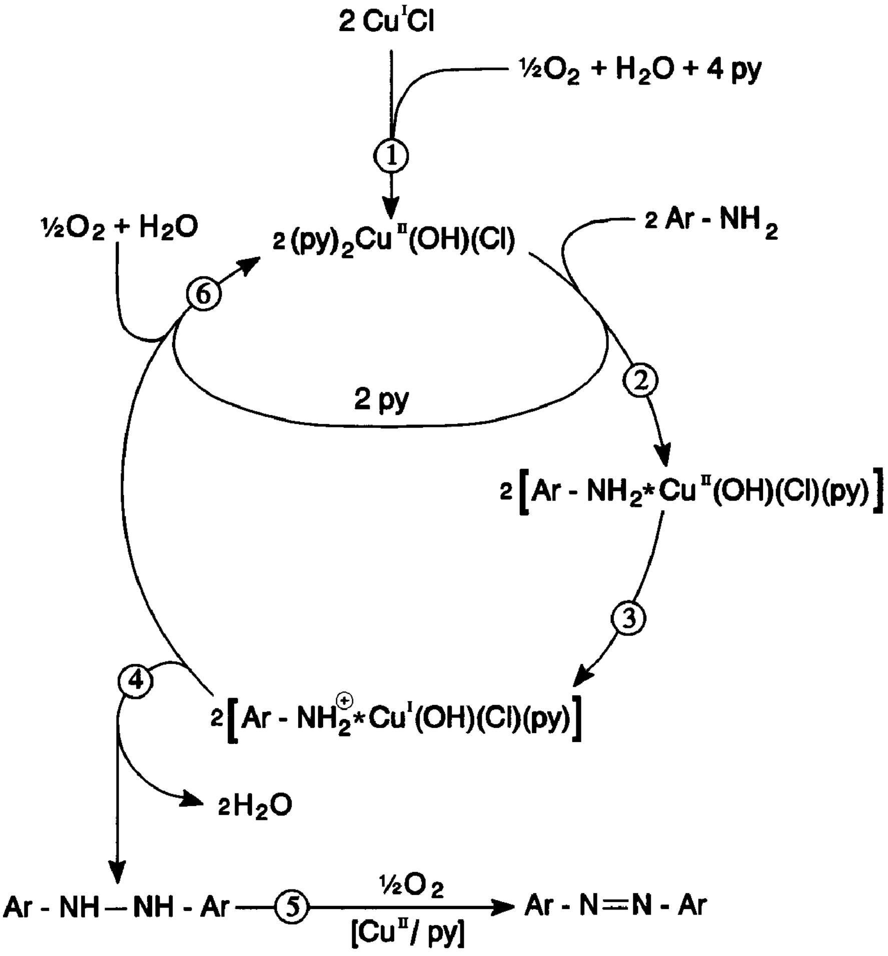
(1.2)



(1.3)

(1.4)

According to Terent'ev and Mogilyanskii another possibility is given by Goldschmidt [111]. He suggested that during the oxidation of primary aromatic amines radicals are formed as a result of dehydrogenation of the amino group. With this in mind Terent'ev and Mogilyanskii [108] suggested that azobenzene and azobenzene derivatives are formed through intermediate radicals, formed by abstraction of one hydrogen atom of the amino group, which dimerize into hydrazine compounds. Subsequently, the hydrazine compound oxidizes very rapidly to the azo compound. Abstraction of the second hydrogen atom from the amino group does not occur, otherwise a number of other reaction products could be expected (phenyl quinone imide, emeraldine, etc.).

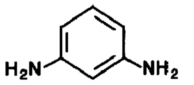
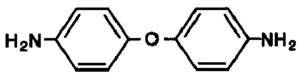
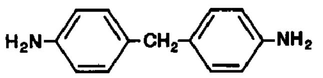
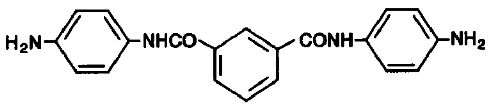
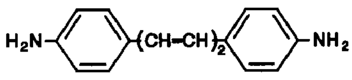
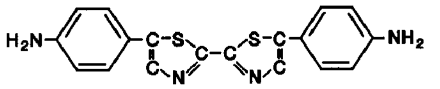
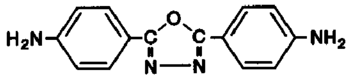


Scheme 1.1

As early as 1966 Bach [95] proposed a reaction mechanism as shown in Scheme 1.1 for a monoamine. According to Bach the catalytically active copper-pyridine complex is probably $(py)_2Cu^{II}(OH)(Cl)$, as proposed also by Finkbeiner et al. [112] for the oxidative coupling of phenols at that time.

After formation of the active catalyst $(py)_2Cu^{II}(OH)(Cl)$ by oxidation of copper(I) chloride (step 1), complexation of the primary aromatic amine and the active catalyst occurs (step 2). The complex formation would involve the displacement of a pyridine ligand by the primary aromatic amine. In 1969 Bach and Black [91] established a correlation between the basicity of the primary aromatic diamine relative to pyridine and the oxidative coupling polymerization rate as measured by the dioxygen absorption (Tab. 1.2).

Table 1.2. *Relation between the relative basicity and the dioxygen consumption rate*

Diamine	Relative Basicity [a]	Rate of dioxygen consumption
	1.068	
	1.015	
	0.927	
	0.926	
	0.875	
	0.808	
	0.665	

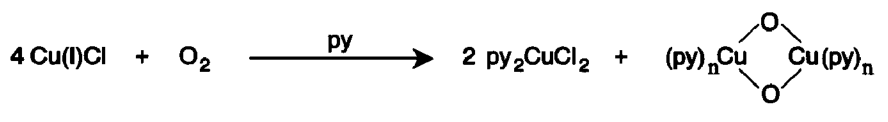
a: determined by titration of the diamine in acetone with perchloric acid; relative basicity of pyridine = 1.0

The rate of oxidative coupling increases with increasing relative basicity of the diamine. The highest coupling rates are obtained with amines having basicities close to that of pyridine. This is a good indication for step 2 as the rate-determining one. After complex formation electron transfer occurs, resulting in the formation of an amine radical-cation, as shown in step 3, or another complex amine radical. Similar to the mechanism of Terent'ev and Mogilyanskii, two amine radical-cations couple after removal of a proton to form the hydrazine linkage (step 4). Dehydrogenation of the hydrazine compound, probably catalysed by the Cu(II)-pyridine complex, results in the formation of the azo compound (step 5). Terent'ev and Mogilyanskii showed that the dehydrogenation of N,N'-diarylhydrazines by the Cu(II)-pyridine complex is substantially faster than the dehydrogenation of the amine [108,109]. After the coupling of the amine radical cations to the hydrazine compound a Cu(I) particle is formed, which is again reoxidized to the active $(py)_2Cu^{II}(OH)(Cl)$ complex (step 6).

A similar reaction mechanism for the formation of the azo linkage, during the oxidative coupling polymerization of primary aromatic diamines, catalyzed by an iron-ethylenediaminetetraacetic acid complex in aqueous solutions, was given by Tsuchida et al. [78].

According to Scheme 1.1 water is needed for the formation of the active copper catalyst. This is, however, not logical because Bach (and also other research groups) never mentioned the addition of water. Moreover, we found that the active catalyst for the oxidative coupling polymerization of primary aromatic diamines could be obtained by using very dry pyridine. Because the structure of the active catalyst postulated by Bach is rather questionable, this thesis will also deal with the structure of the copper complex, which serves as the catalyst for the oxidative coupling polymerization of primary aromatic diamines.

Although a number of studies have dealt with the oxidation of copper(I) chloride in pyridine [113-120], complete identification of all the products formed has never been accomplished. Rogic and Demmin [118] combined some experimental observations in 1978 and concluded that a mixture of bispyridine copper(II) chloride and a di-μ-oxo-bridged copper(II)-pyridine dimer, oligomer or polymer probably is formed (Eq. 1.5).



$$4\,Cu(I)Cl + O_2 \xrightarrow{py} 2\,py_2CuCl_2 + (py)_nCu(\mu\text{-}O)_2Cu(py)_n \qquad (1.5)$$

The fact that the oxygen-oxygen bond in di-μ-oxo-bridged copper(II)-pyridine product has been broken was not determined experimentally by Rogic and Demmin. It may therefore also be possible that the oxygen-oxygen bond still exists. If this is true a structure with a

μ-η^2:η^2 coordinated peroxide ion bridging to two Cu(II) molecules (Fig. 1.1, structure (1)) [121] or a *trans* μ-1,2-peroxide adduct (Fig. 1.1, structure (2)) [122] is, most likely, formed.

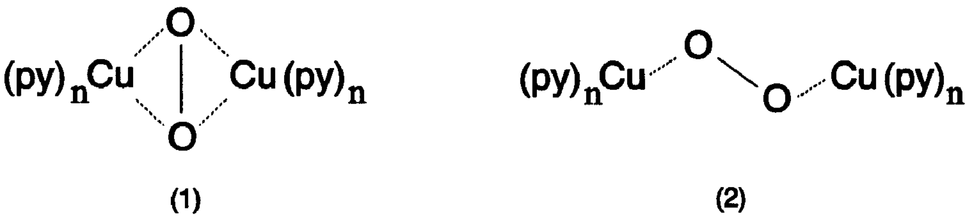


Figure 1.1. *Dioxygen adducts of dinuclear copper complexes.*

Electrical properties of main-chain conjugated aromatic azo polymers

From 1984 onwards the electrical properties of main-chain conjugated aromatic azo polymers, synthesized by oxidative coupling polymerization of primary aromatic diamines by the catalyst prepared from copper(I) chloride, pyridine and dioxygen, have been examined [123,124]. Kuo and Hall prepared films which were cast directly from the reaction mixture or from solutions obtained by dissolving the isolated polymer powder in an acid (trifluoroacetic acid or methanesulfonic acid). The films, n-doped by sodium naphthalide or p-doped by iodine, showed electrical conductivities of 10^{-5} $\Omega^{-1}\cdot cm^{-1}$ to 10^{-4} $\Omega^{-1}\cdot cm^{-1}$.

The electronic structures of neutral and doped poly(*p*-azophenylene) and poly(*p*-phenylenevinylene) were theoretically studied by Yokomichi et al. [125], using the one-dimensional tight-binding SCF-CO (self consistent field-crystal orbital: CNDO/2 CO) method. They concluded that poly(*p*-azophenylene) is expected to have similar features as poly(*p*-phenylenevinylene). In the lightly doped state, however, poly(*p*-azophenylene) tends to make polarons caused by keeping the distance between charges as large as possible and poly(*p*-phenylenevinylene) has the structure suitable for the formation of bipolarons caused by keeping smaller distance between charges than poly(*p*-azophenylene).

The Langmuir-Blodgett technique

During the last few years the Langmuir-Blodgett (LB) technique has been used to prepare thin films of π-conjugated polymers. With the LB technique, it is possible to manipulate surface active molecules into Langmuir monolayer and LB multilayer films with well defined layered structures and ordered molecular organizations. This is usually accomplished by spreading a dilute solution of the surface active molecules onto a purified subphase (mostly water). After evaporation of the solvent the area available for the surface confined molecules is reduced in order to force them into a highly ordered condensed Langmuir monolayer. A stable monolayer, at a fixed temperature and surface pressure, is formed if the area per repeating unit remains constant in time. Multilayer films can be prepared when a solid substrate is dipped many times vertically through the stable monolayer. Roughly, three multilayer film types can be distinguished. Transfer on both the downstroke and upstroke produces a head-to-head/tail-to-tail arrangement known as a Y-type multilayer film. It is possible to have transfer of the monolayer only on the upstroke or downstroke, resulting in a Z-type and X-type multilayer film, respectively. In this way a head-to-tail arrangement is produced. Very rigid films that are not easily transferred using the vertical dipping technique can still be deposited onto a solid substrate by using the horizontal film lifting technique. In this case, a substrate oriented parallel to the Langmuir monolayer is lowered until it just touches this monolayer and is raised again. When this dipping process is repeated a multilayer film with a head-to-tail or head-to-head/tail-to-tail arrangement can be produced. The thickness of a multilayer film can simply be controlled by the number of monolayers transferred.

When water is used as a subphase the surface active molecule mostly consists of a hydrophilic head group for the interaction with the water subphase and a long hydrophobic tail to prevent the molecule from dissolving in the water subphase. In addition, the stability of the Langmuir monolayer is often the result of hydrophobic tail crystallization. Hence, for the processability of an electrically conductive polymer with the LB technique it is necessary to design a surface active π-conjugated polymer.

The successful manipulation of a number of electrically conducting polymers, using the LB technique, has recently been reviewed by Rubner and Skotheim [126].

Outline of the thesis

Because of the failure of most of the main-chain conjugated aromatic azo polymers to dissolve in common organic solvents the processability of these polymers is difficult. The aim of this thesis is to synthesize (processable) main-chain conjugated aromatic azo polymers with interesting properties, by the oxidative coupling polymerization of a primary aromatic diamine in the copper(I) chloride/pyridine/dioxygen system. In addition, a kinetic study was performed to get more insight in the reaction-mechanism of this oxidative coupling polymerization.

In *chapter 2* the oxidative coupling polymerization of octadecyl 3,5-diaminobenzoate by a catalyst prepared from copper(I) chloride, pyridine and dioxygen is described. It will be shown that the oxidative coupling product of octadecyl 3,5-diaminobenzoate is soluble in e.g. chloroform and tetrahydrofuran and consists of a high- and a low-molecular-weight part. It is also shown that the low-molecular-weight part can be separated from the high-molecular-weight part by precipitation in acetone. The characterization of both the high- and the low-molecular-weight parts is reported.

In *chapter 3* the peculiar oxidative coupling polymerization behaviour of octadecyl (alkyl) 3,5-diaminobenzoate(s) and 1,3-diaminobenzene in comparison with 4,4′-ethylenedianiline is discussed.

Chapter 4 will deal with the kinetics of the oxidative coupling polymerization of octadecyl 3,5-diaminobenzoate, 1,12-di(*p*-aminophenoxy)dodecane and 3,3′,5,5′-tetramethylbenzidine.

In *chapter 5* the synthesis, characterization and the properties of a non-conjugated main-chain azo polymer prepared from 1,12-di(*p*-aminophenoxy)dodecane will be discussed.

In *chapter 6* it will be demonstrated that the high-molecular-weight portion of the reaction product obtained from the octadecyl 3,5-diaminobenzoate oxidative coupling polymerization can be processed by means of the Langmuir-Blodgett technique. It will be shown that a multilayer film, prepared by means of the LB technique, has a good alternating layer structure of conjugated material (backbone) and amorphous material (aliphatic side-chains).

Finally, in *chapter 7*, the oxidative coupling in a Langmuir monolayer of octadecyl 3,5-diaminobenzoate at the air-water interface, with and without copper(II) chloride in the water subphase, is discussed.

Parts of this thesis have been published [127, chapter 6] or will be submitted for publication [128-132, chapters 2, 3, 4, 5 and 7, respectively].

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