Acta Chim. Slov. **1998**, *45*(2), pp. 173-183

(Received 29.5.1998)

INFLUENCE OF POLYMERIZATION PARAMETERS ON THE MOLECULAR WEIGHT OF POLYANILINE

Maja Vilčnik, Majda Žigon*, Marko Zupan, Anton Šebenik
Faculty of Chemistry and Chemical Technology, University of Ljubljana, Slovenia
*National Institute of Chemistry, Ljubljana, Slovenia

ABSTRACT

The yield of polymerization and the molecular weight of polyaniline (PAN) were determined in dependence on the ratio of aniline and amoniumperoxodisulphate, temperature, reaction time and pH. It was found that polymerization yield and molecular weight decrease with the increasing ratio oxidant to aniline, pH and temperature. The pH of the reaction mixture rapidly decreases due to the release of proton from 0.80 to 0.35 and during the polymerization slowly increases back to the starting value. The polydispersity is in the wide range and is almost constant with the changing reaction parameters. After the reduction of emeraldine base to leucoemeraldine base, the molecular weight decreases due to the difference in the hydrodinamic volume of quinoid segments in comparision with that of benzenoide, as well as to intermolecular hydrogen bonds between amine and imine groups of benzenoid and quinoide segments of emeraldine base, and the decomposition of the -C-N- bonds after the reduction.

INTRODUCTION

Polyaniline (PAN) has attracted considerable attention since MacDiarmid *et al*. [1] reinvestigated this material as a conducting polymer due to its simple synthesis, good environmental stability, and adequate level of electrical conductivity. Polyaniline is unique among conducting polymers in that its electrical properties can be reversibly controlled

both by charge-transfer doping and by protonation. The wide range of associated electrochemical and optical properties, coupled with good stability, make polyaniline potentially attractive for application as an electronic material. Recent work has shown that polyaniline prepared at room temperature is of fairly low molecular weight [2] and contains defect sites [3]. It is hoped that better-quality polyaniline, with fewer defect sites and higher molecular weight may lead to improvements in its mechanical and electrical properties.

Polyaniline can be synthesized by both electrochemical and chemical oxidative polymerization [5]. Considerable effort has been made to develop relationships between synthesis conditions and properties of polyaniline obtained by electrochemical polymerization [6]. By contrast, relatively little attention has been paid to the chemical polymerization of aniline due to its very complex and undefined structure [7,8,9].

The aim of our work was controlled polymerization of aniline at different reaction conditions using amoniumperoxodisulfate as an oxidant. The course of this reaction was followed by determination of the yield of copolymerization, molecular weight and of its polydispersity in dependence on the reaction parameters. The influence of the reaction parameters on electrical conductivity and energy gap was determined.

EXPERIMENTAL

Materials: Aniline (AN) was a product of Aldrich. Amoniumperoxodisulfate and hydrochloric acid were products of Merck. Phenylhydrazine (Fluka) and 3-chloroperoxybenzoic acid (Aldrich) were used for preparing the leucoemeraldine and the pernigraniline bases. All these and other chemicals in this work were used without further purification. 1-methyl-2-pyrrolidinone (NMP), triethylamine (TEA) and lithium chloride (LiCl) mixture was used as the solvent.

Polymerization: Polymerization of AN (0.0548 mol) was carried out in a reaction vessel at the temperature range from -5 to 10^{o}C. We followed the yield of polymerization in dependence on the ratio of the aniline to amoniumperoxodisulfate and on the concentration of HCl. The oxidant was added after 2 hours and then the reaction continued for 2 additional hours. The dark green polyaniline hydrochlorides were separated, and then washed with 1M HCl and methanol to obtain a colourless solution without any oligomers. The polymers were dried in vacuum to dark green products. The exact reaction conditions are described in Tables 1, 2 and 3. The dark green powders were neutralised with water solution of NH_3 and then were dried. The products which consisted of all three PAN bases, were dissolved in NMP, and then reduced with phenylhydrazine to

leucoemeraldine base [10], or were oxidised with 3-chloroperoxybenzoic acid to pernigraniline base [11].

Molecular weight determination: Before measuring of the molecular weight, the solubility of the PAN was determined. The best solvent for PAN was a mixture of the NMP, TEA and LiCl in the weight ratio of 100:0.5:0.5. The molecular weights were measured by GPC with Ultra-Styragel 10μ columns using mixture of NMP, and LiCl as the eluent in the weight ratio 100:0.5. The flow rate was 0.5 ml/min. Polystyrene and polyvinylpyridine standards were used for calibration. As a detector, the diode array UV detector at 330 nm was used.

Measurements: The structure, sequence monomer distribution, chain end groups, purity and the presence of impurities were followed by NMR spectroscopy of the polymers. The one and two dimensional homo and hetero correlation ^{1}H, and ^{13}C spectra were measured by Varian VXR 300 MHz and INOVA 600 MHz NMR spectrometers. The samples were dissolved in a mixture of NMP, TEA and DMSO-d_6. All signals were quoted on TMS as internal standard. For the determination of individual signals in the NMR spectra and for quantitative measurements of benzenoid and quinoid segments in the polymer, a number of model compounds, their relaxation times, proton coupling and decoupling spectra were taken. For the assignation of ^{13}C NMR spectra, the attached proton test (APT) and model substances were used. FTIR spectra were measured by Perkin Elmer spectrometer using the KBr pallets technique. For resistance measurements, individual films from NMP solution, according to a procedure described elsewhere, were prepared [12]. The impendance spectroscopy with the pellet samples between two carbon wires attached at both sides was used.

RESULTS AND DISCUSSION

Polyanilines are interesting compounds from the point of view of fundamental aspects of the mechanism of charge transport in conducting polymers. The conductivity along the polyaniline backbone can be affected by the degree of oxidation of the polymer (the relative amount of amine and imine groups), the protonation acid and the percentage of protonation [9]. The conductivity is also affected by the degree of water and solvent content, which presumably can affect the charge transport between chains, and also by the morphology and texture of the polymer, the molecular weight and degree of crystallization.

Mechanism of polymerization: The structure of individual polyaniline bases and distribution of the oxidised and reduced units in the chains were determined by ^{13}C and

APT NMR and FTIR spectroscopy (Figure. 1). The spectra of all polyaniline bases are very complex because of many individual distributions of the quinoid and benzenoid rings

Figures available in printed version only

Figure 2: Dependence of the pH on reaction time at 0^{o}C, ratio oxidant/aniline 1.00:1.

in polyaniline chains, different end groups, minor substituents and products of various possible side reactions such as branching, cyclization, crosslinking, conformation effects and reduction in ring symmetry. The simplest is the spectrum of the leucoemeraldine base with two main signals of benzenoid rings which represent 1-4 substitution and a number of small signals of end groups. The general assignation of individual signals is marked on the spectra.

Although there is still some uncertainty regarding the exact mechanism of aniline polymerization, it is likely that radical cation species are produced as a result of oxidative attack on the aniline monomer. These then condense with the loss of protons to give the protonated semi-oxidised emeraldine form of polyaniline as the reaction product [4]. The following scheme of polymerization can be predicted (Scheme 1).

Cationic chain polymerization is usually carried out at low polymerization temperatures, which favour propagation over competition with side reactions. Solvents with a high

dielectric constant favour both initiation and propagation leading to high molecular weight products [8]. One of the characteristics of step-growth polymerization is that the molecular weight of the polyaniline rises steadily throughout the reaction, and therefore long reaction time is essential to obtain high molecular weight products.

Solubility of PAN: The formed nonprotonated emeraldine base is soluble in NMP but the macromolecules produce aggregates. This was seen from the light scattering measurements of the particle size of polyaniline solutions in NMP. The -NH- protons on the polymer backbone are partly blocked with inter and intra molecular hydrogen bonding. The aggregates are formed due to interactions such as physical entanglements or hydrogen bonding with the size up to 15μm [13]. Triethylamine increases the solubility of polyaniline and, in combination of LiCl, it breaks the aggregates to the dissolved macromolecules and the fictive high molecular weight decreases to the real value. The presence of TEA acts as a dedoping agent, being a proton-acceptor with his lone electron pair on nitrogen.

Determination of molecular weight: Determination of the molecular weight by GPC is questionable due to the presence of aggregates in NMP, formed by hydrogen bonds between the amine and imine segments and also due to possible interaction between the solute and the stationary phase. The NMP and TEA changes the characteristics of the columns. In the case of emeraldine base, the -NH- and =N- groups produce a stronger interaction between individual macromolecules as in the case of leucoemeraldine base, where only interactions between -NH- groups are possible. For this reason, individual electrolites can reduce the interactions. We tried different contents of LiCl and TEA. LiCl hinders lone electron pairs of nitrogen and prevents hydrogen bonds. The presence of triethylamine increases the solubility of polyaniline, but the column is not stable due to additional interactions. This is evident from GPC chromatograms, which have multimodal molecular weight distribution with a high portion of fictive high molecular weight fractions. The multimodal molecular weight distribution disappeared by the addition of LiCl, which also prevents the interaction of solute to the mobile and stationary phase [3]. The optimal content was determined from the dependence of the retention time on the content of LiCl, when the molecular weight reached the minimal value. The chromatograms with unimodal distribution were obtained using NMP with LiCl as solvent in the weight ratio 100:0.5. The size of aggregates is about 50 times higher than the observed molecular weight. This proves that the inter and intramolecular electrostatic interactions between polymer chains are disrupted by the addition of LiCl [3,14].

Influence of the temperature: Molecular weight of polyaniline rapidly decreases with increasing reaction temperature due to the condensation of radical cation species which

lose protons to give the protonated emeraldine form (Table 3). Cationic chain polymerization is usually carried out at low polymerization temperatures in the solvents with a high dielectric constant, which favours both initiation and propagation leading to high molecular weight [4,8]. The low temperature increases the dipole moment and this favours the production of high molecular weight polyaniline compared to materials prepared at room temperature. The ^{13}C NMR spectra shows that the polyaniline synthesized at lower temperatures consists of almost para-substituted phenylene rings linked by amine groups with a few small signals which indicate defect sites on the benzene ring [14-17]. The fact that the yield and molecular weight increase linearly with decreasing reaction temperature, confirms the cationic step-growth mechanism of the polymerization.

The influence of the oxidant: Molecular weight decreases linearly with the increasing content of the amoniumperoxodisulphate due to the partial oxidation of individual segments, which are not further reactive for cataionic step-growth polymerization (Table 1). The same holds for the increase of the content of hydrochloric acid (Table 2). Higher concentration of hydrochloric acid decreases the propagation of cationic spices. In accordance with the reaction mechanisms the acidity of the reaction mixture increases during polymerization due to the release of a proton [18]. The pH of the reaction mixture rapidly decreases from 0.80 to 0.35 and during polymerization slowly increases back to the starting value (Figure 2). Due to the decreasing pH, the reaction equlibria favour the termination of macrocations, which leads to a lower molecular weight of polyaniline.

Influence of the reduction: In all cases the molecular weight of emeraldine base decreases after the reduction to leucoemeraldine base. There are however several reasons. The hydrodynamic volume of rigid quinoid segments is bigger than that of benzenoid. Secondly, the intermolecular hydrogen bonds between amine and imine groups of benzenoid and quinoid segments of emeraldine base decompose after the reduction of quinoid structures. The third reason is the decomposition of some -C-N- bonds after the reduction.

Electrical conductivity: Polyaniline acts as an electrically conductive material only in the protonation form of emeraldine salt. Its electrical conductivity is about $6.7 \cdot 10^{-2}$ S/cm, due to the doping of emeraldine base by hydrochloric acid. The conductivity rapidly decreases with the reduction of emeraldine base to leucoemeraldine base to the value of $8.5 \cdot 10^{-10}$ S/cm. After the oxidation of emeraldine base to pernigraniline base, electrical conductivity decrease to $4.1 \cdot 10^{-9}$ S/cm. In the case of emeraldine salt, quinoid rings with hybridised π orbitals which are resonance stabilised, enable charge transport between chains, although the three other rings of polyaniline are in nonconductive benzenoid form. In the case of fully reduced leucoemeraldine base, all rings are in benzenoid form, each isolated one from

other by -NH- groups and each macromolecule is in nondoping form. There is no charge transport nor along single macromolecules neither between macromolecules. Electrical conductivity decreases for 10^8 for emeraldine base and 10^7 times for leucoemeradine base. The electrical conductivity and mechanical properties of polyaniline increase with the decreasing reaction temperature and are optimal almost at stechiometrical ratio between the oxidant, hydrochloric acid and aniline. The formed films are compact with good mechanical properties. The conductivity of polyaniline does not depend on the temperature of surroundings which indicates a small energy gap.

CONCLUSION

The highest molecular weight and yield of polymerization of polyaniline were obtained at a low temperature and at an equivalent ratio between aniline oxidant and hydrochloric acid. The formed films are compact with good mechanical properties.

ACKNOWLEDGEMENT

This work was financed by the Ministry of Science and Technology of the Republic of Slovenia. The financial support of the Ministry is fully acknowledged.

REFERENCES

[1]. A.G. MacDiarmid, J.C. Chiang, M. Halpern, W.S. Huang, S.L. Mu, N.L. Somasiri, W. Wu and S.I. Yaniger, *Mol. Cryst. Liq. Cryst.*, **1985**, 121, 173
[2]. P.N. Adams, D.C. Apperley and A.P. Monkman, *Polymer*, **1993**, 34, 328
[3]. A.M. Kenwright, W.J. Feast, P.N. Adams, A.J. Milton, A.P. Monkman and B.J. Say, *Polymer*, **1992**, 33, 4292
[4]. P.N. Adams, P.J. Laughlin, A.P. Monkman and A.M. Kenwright, *Polymer*, **1996**, 37, 3411
[5]. J.C. Chiang and A.G. MacDiarmid, *Synth. Met.*, **1986**, 13, 193
[6]. W.S. Huang, B.D. Humphrey and A.G. MacDiarmid, *J. Chem. Soc. Faraday Trans.*, **1986**, 82, 2385
[7]. C.H. Ong, S.H. Goh and H.S.O. Chan, *Polym. Bull.*, **1997**, 39, 627
[8]. P.N. Adams, P.J. Laughlin, A.P. Monkman, *Synth. Met.*, **1996**, 76, 157
[9]. G. Boara and M. Sparpaglione, *Synth. Met.*, **1995**, 72, 135
[10]. Y. Wei, K. F. Hsueh, G. W. Jang, *Macromolecules*, **1994**, 27, 519
[11]. Y. Sun, A. G. MacDiarmid, A. J. Epstein, *J. Chem. Soc., Chem. Commun.*, **1990**, 529
[12]. M. Angelopoulos, G. E. Asturias, S. P. Ermer, A. Ray, E. M. Scherr, A. G. MacDiarmid, *Mol. Cryst. Liq. Cryst.*, **1988**, 160, 151

[13]. M. Angelopoulos, Y.H. Liao, B. Furman, T. Graham, *Mat. Res. Soc. Symp. Proc.*, **1996**, 413, 637
[14]. S. Ni, J. Tang, F. Wang, L. Shen, *Polymer*, **1992**, 33, 3607
[15]. T. Hagiwara, M. Yamaura, K. Iwata, *Synth. Met.*, **1998**, 26, 195
[16]. A.C. Kolbert, S. Cardarelli, K.F. Thier, N.S. Sariciftci, Y. Cao A.J. Heeger, *Physic. Rev.*, **1995**, 51, 1541
[17]. A.M. Kenwright, W.J. Feast, P. Adams, A.J. Milton, A.P. Monkman, B.J. Say, *Synth. Met.*, **1993**, 55-57, 666
[18]. J. Stejskal, P. Kratochvil, A.D. Jenkins, *Polymer*, **1996**, 37, 367

POVZETEK

Določili smo vpliv razmerja med anilinom in amonperoksidisulfatom, temperature, časa reakcije in pH na izkoristek polimerizacije in molsko maso polianilina (PAN). Izkoristek polimerizacije in molska masa padata z rastočim razmerjem med oksidantom in anilinom, pH in temperaturo. Na začetku pH reakcijske zmesi intenzivno pade od 0,80 do 0,35 zaradi odcepa protonov in med reakcijo počasi raste na začetno vrednost. Polidisperznost je v širokem območju in je neodvisna od reakcijskih parametrov. Po redukciji emeraldine v leukoemeraldino bazo molska masa pade zaradi razlike hidrodinamskih volumnov benzenoidnih in kinoidnih segmentov, kot tudi zaradi intermolekularnih vodikovih vezi med aminskimi in iminskimi skupinami benzenoidnih in kinoidnih segmentov emeraldine baze ter zaradi razpada -C-N- vezi pri redukciji.