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Polymerization of anilines by the use of copper(II) perchlorate as an oxidative coupling agent

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SUMMARY

Polyaniline and polyalkylaniline perchlorates were prepared by oxidative coupling polymerization of anilines by the use of copper(II) perchlorate in acetonitrile as an oxidant. The corresponding polymer bases obtained by treating the perchlorates with alkaline solution were soluble in dimethylsulfoxide and partly soluble in tetrahydrofuran. The molecular weights of the THF-soluble components were 2000-6000. The charge transport of the perchlorates is influenced by the chain length and the steric effect of alkyl substituents.

INTRODUCTION

Electroconducting polyaniline has attracted a great deal of attention, because it exhibits interesting charge transport properties and has many potential uses in electric and electronic devices (1). Polyaniline has been prepared by either electrochemical or chemical polymerization of aniline. For the chemical method, ammonium persulfate is commonly used as an oxidative coupling agent (1,2). The physical properties including electrical conductivity and solubility in organic solvents are sensitively dependent on a synthetic method employed (1). Usually, conducting polymers are insoluble in common organic solvents. This insolubility makes it difficult to characterize the structure of the polymer chains. It is important, therefore, to develop new synthetic methods that provide highly electroconductive materials with a high solubility in solvents. Recently, we have reported that aniline can be polymerized by the use of copper(II) perchlorate as an oxidant (3). The resulting polyaniline perchlorate is highly electroconductive and soluble in organic solvents; it has been well characterized by solution electronic spectra and X-ray photoelectron spectra (3,4), although the molecular weight has not been determined. In the present study, the polymerization of aniline has been carried out in different conditions and the products have been characterized by molecular weight measurements; the charge transport is expected to have a correlation with polymer chain length. This new synthetic method has been applied for the polymerization of some alkylanilines; obtained polymers have been characterized by molecular weight and electrical conductivity measurements.

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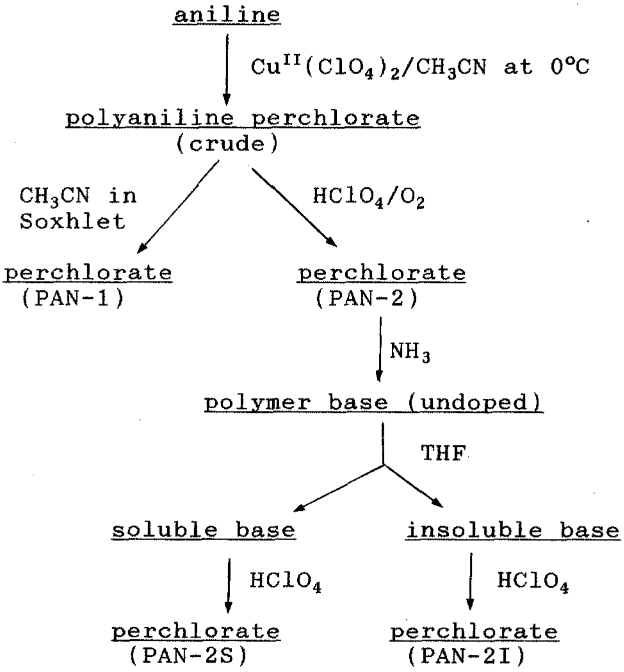
RESULTS AND DISCUSSION

The polymerization of aniline was carried out by the use of copper(II) perchlorate as an oxidant at 0, 25 and 80 °C. The obtained polyaniline perchlorate was washed with acetonitrile in a Soxhlet extractor to remove copper(I) perchlorate. The material obtained at 0 °C (referred to as PAN-1) exhibited a higher electrical conductivity (6 S cm^{-1} at room temperature) than others obtained at 25 °C (3 S cm^{-1}) and 80 °C (2 S cm^{-1}). Therefore, materials prepared at 0 °C were used for further experiments shown in Scheme I. In order to avoid possible effects of heating in a Soxhlet extractor, polyaniline perchlorate was washed with perchloric acid at room temperature (Scheme I). The resulting perchlorate (referred as to PAN-2) showed an identical electrical property with that of PAN-1. When PAN-2 was deprotonated by a treatment with ammoniacal solution, an undoped polymer base was obtained, which was soluble in dimethylsulfoxide and partly soluble in tetrahydrofuran (THF). The quantity of this THF-soluble component was much larger than that of a polymer base prepared from PAN-1. The polymer base obtained from PAN-2 was, therefore, partitioned to a THF-soluble component and a THF-insoluble component, each of which was successively treated with perchloric acid, and the perchlorates, PAN-2S and PAN-2I, were obtained. The dopant concentration of every polyaniline perchlorate obtained was approximately equal to 0.5 of the so-called polyemeraldine salts (Table 1).

Figure 1 shows the electrical conductivities σ as functions



Scheme I

Table 1. Electrical data of perchlorates of polyaniline and alkyl derivatives, $[(-C_6H_3\cdot R\cdot NH-)(ClO_4)_m\cdot nH_2O]_x$: conductivity σ/S cm^{-1} at room temperature and activation energy E/eV for electrical conduction at high temperatures.

Polymer	R	*m*	*n*	MW[a]	σ	*E*
PAN-1	H	0.45	0.8	(6000)[b]	6	0.04
PAN-2	H	0.35	0.8	---	6	0.04
PAN-2S	H	0.4	0.7	2000	0.3	0.08
PAN-2I	H	0.55	1.2	---	3	0.04
P2etAN	C_2H_5	0.75	1.3	3000	$1x10^{-4}$	0.2
P3etAN	C_2H_5	0.50	0.7	3000	$2x10^{-6}$	0.2
P2prAN	C_3H_7	0.80	1.4	4000	$6x10^{-4}$	0.1

[a] Molecular weight of a polymer base corresponding to each perchlorate.
[b] MW of the THF-soluble component.

of temperature. At high temperatures, the temperature dependence of every perchlorate can be explained with the semiconducting property given by:

$$\sigma = \sigma_\infty \exp(-E/kT) \qquad (1)$$

with the activation energy E that is shown in Table 1. At low temperatures, the conductivity deviates from eq. 1, and may be explained by the variable-range hopping conduction model (5).

The molecular weight was determined to be ca. 2000 for the THF-soluble polymer base, from which the perchlorate, PAN-2S was prepared (Table 1). This polymer perchlorate exhibited a high electrical conductivity of 0.3 S cm^{-1} at 300 K, although each chain contained only ca. 20 aniline units on the average. PAN-2I obtained from the THF-insoluble base is expected to have a larger molecular weight than that of PAN-2S. The electrical conductivity of the former perchlorate was significantly higher than that of the latter, although the dopant concentrations of the two perchlorates were almost identical with each other. This is an example demonstrating that the molecular weight (or chain length) of a conducting polymer is an important factor that controls charge transport. In a polymer base obtained from PAN-1, the quantity of the THF-soluble component was smaller than that in PAN-2, and the molecular weight of the former was significantly larger than that of the latter (Table 1); in PAN-1 oligomer components were removed by treatment in a Soxhlet extractor, whereas oligomers remained in PAN-2 which were purified with perchloric acid. These two perchlorates showed electrical properties identical with each other (Fig. 1). This suggests that molecular-weight distribution is not an important controlling factor for charge transport. This is supported by the fact that the conductivity of PAN-2 showed no significant difference from that of PAN-2I; the latter was obtained by removing the soluble (i.e., low molecular weight) component from PAN-2 by solvent extraction.

Since polyalkylaniline perchlorates were highly soluble in hot acetonitrile, they were purified with perchloric acid;

purification with acetonitrile in a Soxhlet extractor could not be performed for these polymers. The treatment of the perchlorates with ammoniacal solution yielded the corresponding polymer bases, which were thoroughly dissolved in THF. The molecular weights of these polymer bases were 3000-4000 (Table 1). The electrical conductivities of these perchlorates were well explained by eq. 1 at temperatures above 200 K. The activation energies and the room-temperature conductivities are shown in Table 1. The molecular weights of polyalkylaniline

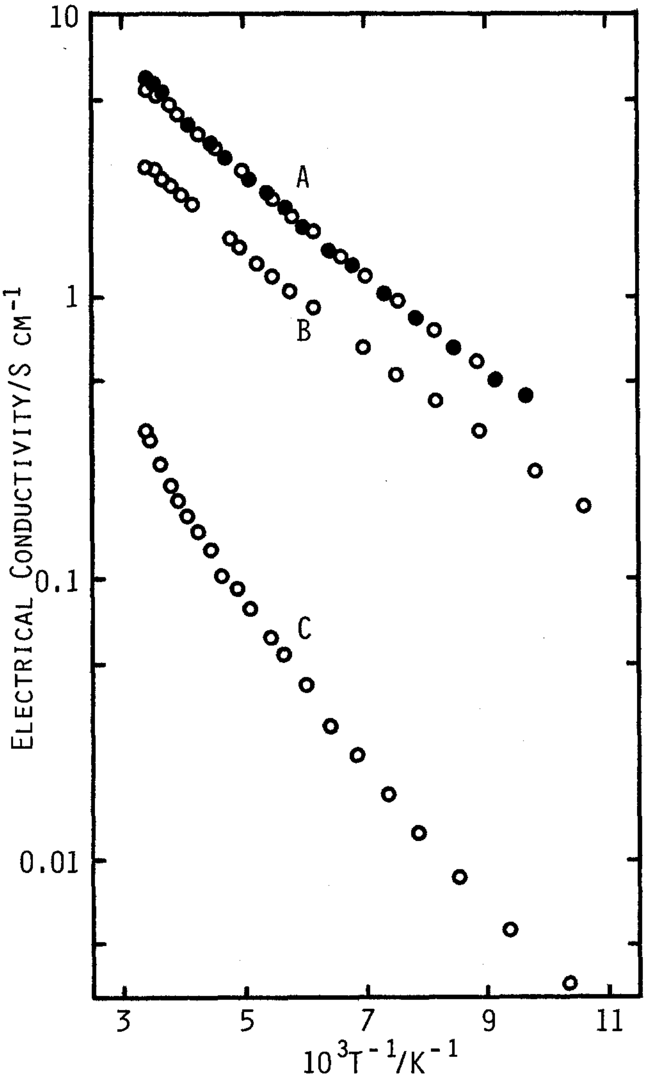


Fig. 1. Temperature dependence of the electrical conductivities of polyaniline perchlorates: PAN-1 (A,●); PAN-2 (A,o); PAN-2S (B); PAN-2I (C).

bases had the same order of magnitude as the molecular weight of the soluble polyaniline base corresponding to PAN-2S. The polyalkylaniline perchlorates, however, were much less conductive than the soluble polyaniline perchlorate, PAN-2S. This difference between the electrical properties is related to the steric effect of the alkyl substituents (6). In polyaniline chains, the molecular planes of neighboring aniline units are twisted with each other, and the twist angle is expected to markedly influence the charge transport along a polymer chain (7). The steric effect of the alkyl substituent increases the twist angle and results in the decrease of electrical conductance.

In summary, copper(II) perchlorate functions as a good coupling agent for the preparation of polyaniline: the product is highly conductive in spite of the low molecular weight.

EXPERIMENTAL

Preparation of Materials. The polymerization at 25 °C was carried out by essentially the same method as reported previously (3). To freshly distilled aniline (0.63 g, 6.8 mmol) in acetonitrile (20 ml) was added dropwise an acetonitrile solution (10 ml) containing copper(II) perchlorate hexahydrate (5.2 g, 14 mmol) with stirring in a nitrogen atmosphere. A deep green powder were precipitated immediately. The resulting reaction mixture was stirred for 1 h to complete the reaction. The products were washed with acetonitrile in a Soxhlet extractor until the extracting solvent was colorless. The polymerization was carried out also at 0 and 80 °C. Since the product at 0 °C (PAN-1) exhibited a higher electrical conductivity than other products, it was used for further experiments. The composition determined by elemental analyses for PAN-1 was $[(-C_6H_4NH-)(ClO_4)_{0.45}\cdot 0.8H_2O]_x$ (Anal. Found: C, 48.04; H, 4.92; N, 9.39; Cl, 10.99. Calcd.: C, 47.96; H, 4.43; N, 9.32, Cl, 10.62).

Polyaniline perchlorate freshly prepared at 0 °C was suspended in 3 M perchloric acid. Into the resulting mixture, air was bubbled for 24 h, and then the powder was separated by filtration. In the course of this treatment, copper(I) perchlorate involved in the product as a contaminant was oxidized by air to the corresponding Cu(II) compound, which was highly soluble in water. After washed repeatedly until the filtrate contained no copper, the product was filtered off, washed with a dilute perchloric acid and dried in vacuum. The composition of this polymer (PAN-2) was $[(-C_6H_4NH-)(ClO_4)_{0.35}-0.8H_2O]_x$ (Anal. Found: C, 51.33; H, 4.78; N, 9.26; Cl, 9.76%. Calcd.: C, 51.35; H, 4.74; N, 9.98, Cl, 8.84%).

Deprotonation of PAN-2 was performed by treatment with 4 M ammonia for 24 h. The resulting undoped polymer base was suspended in tetrahydrofuran for ca. 10 min at room temperature, and was partitioned to THF-soluble and THF-insoluble components. These two components were treated individually with 4 M perchloric acid for 3 h, and two different polymer perchlorates were obtained: PAN-2S obtained from the THF-soluble component and PAN-2I form the THF-insoluble component. The compositions determined by elemental analyses were: $[(-C_6H_4NH-)(ClO_4)_{0.4}-0.7H_2O]_x$ for PAN-2S (Anal. Found: C, 50.50; H, 4.50; N, 9.21;

Cl, 9.54%. Calcd.: C, 50.22; H, 4.50; N, 9.76, Cl, 9.88%); $[(-C_6H_4NH-)(ClO_4)_{0.55}-1.2H_2O]_x$ for PAN-2I (Anal. Found: C, 42.99; H, 4.39; N, 8.46; Cl, 11.57%. Calcd.: C, 43.04; H, 4.45; N, 8.37, Cl, 11.65%).

The polymerization of 2-ethylaniline, 3-ethylaniline and 2-propylaniline was performed by essentially the same method as for aniline at 0 °C by the use of an appropriate monomer. The products were purified with perchloric acid in the same procedure as for the polyaniline perchlorate. The compositions of the polymers were: $[(-C_8H_8NH-)(ClO_4)_{0.75} \cdot 1.3H_2O]_x$ for poly(2-ethylaniline) perchlorate (P2etAN in Table 1) (Anal. Found: C, 44.18; H, 5.32; N, 6.15; Cl, 12.14%. Calcd.: C, 44.24; H, 5.38; N, 6.45, Cl, 12.24%; $[(-C_8H_8NH-)(ClO_4)_{0.5} \cdot 0.7H_2O]_x$ for poly(3-ethylaniline) perchlorate (P3etAN) (Anal. Found: C, 53.20; H, 5.88; N, 6.34; Cl, 10.42%. Calcd.: C, 52.94; H, 5.78; N, 7.72, Cl, 9.77%; $[(-C_9H_{10}NH-)(ClO_4)_{0.8} \cdot 1.4H_2O]_x$ for poly(2-propylaniline) perchlorate (P2prAN) (Anal. Found: C, 44.85; H, 5.34; N, 5.91; Cl, 10.46%. Calcd.: C, 45.42; H, 5.84; N, 5.89, Cl, 11.92%).

The electron spin resonance spectra of the materials studied showed no copper(II) signal; copper was not involved as a contaminant. The elemental analyses were performed by Huffman Laboratories, Golden CO. U.S.A.

Warning note: the polymer perchlorates may be explosive, when dehydrated.

Physical Measurements. The electrical conductivity was determined on compressed pellets by van der Pauw's four-probe method or by the standard two-probe method. The molecular weight was determined for polymer bases with the aid of a gel-permeation chromatograph consisting of a Varian 2510 HPLC pump and a Perkin-Elmer Lambda 2 UV/VIS detector at a wavelength of 320 nm. The calibrant was polystyrene and the eluent was THF.

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REFERENCES

1. Geniès E M, Boyle A, Lapkowski M and Tsintavis C (1990) Synth Met 36: 139, and references therein.
2. MacDiarmid A G, Chiang J C, Richter A F and Epstein A J (1987) Synth Met 18: 285, and references therein.
3. Inoue M, Navarro R E and Inoue M B (1989) Synth Met 30: 199.
4. Inoue M B, Nebesny K W, Fernando Q and Inoue M (1991) J Mater Chem, in press.
5. Zuo F, Angelopoulos M, MacDiarmid A G and Epstein A J (1989) Phys Rev B 39: 3570.
6. MacDiarmid A G and Epstein A J (1989) Faraday Discuss Chem Soc 88: 317.
7. Tanaka K, Wang S and Yamabe T (1990) Synth Met 36: 129.

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