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Motomichi Inoue[a]; M. Monica Castillo-Ortega[a]; Michiko B. Inoue[a]
[a] CIPM, Universidad de Sonora Apdo Postal, Hermosillo Sonora, Mexico

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POLYANILINE TOLUENESULFONATES: X-RAY DIFFRACTION AND ELECTRICAL CONDUCTIVITY

Motomichi Inoue,* M. Monica Castillo-Ortega, and Michiko B. Inoue
CIPM, Universidad de Sonora
Apdo Postal 130, Hermosillo
Sonora, Mexico

ABSTRACT

Two polyaniline toluenesulfonates with different crystallinities were synthesized by using iron(III) and copper(II) toluenesulfonates, respectively, as oxidative coupling agents. The toluenesulfonate obtained with the iron(III) salt showed well-defined X-ray powder diffraction peaks; the other toluenesulfonate showed a diffuse pattern. When the toluenesulfonate with the higher crystallinity was neutralized and then doped again with HCl, the resulting polyaniline chloride showed an X-ray pattern closely resembling that of the original toluenesulfonate. The diffraction patterns of the toluenesulfonate and the chloride can be interpreted by assuming an essentially identical crystal packing in the unit cell. Since the cell volumes of the two salts are almost identical, the counteranion with a larger molecular size has a closer contact with a polyaniline chain; the close intermolecular contact may enhance interchain diffusion of charge carriers.

INTRODUCTION

Charge carriers in electroconductive polyaniline salts are polarons (anilinium ions) and/or bipolarons (quinolinium ions), which induce electrical conduction along the polymer chain [1,2]. Magnetic resonance studies of polyaniline have demonstrated that interchain spin diffusion occurs in addition to intrachain spin diffusion, suggesting that an interchain charge transport may have a significant contribution to the electrical conductivities [3,4]. The interchain interaction is probably dependent on properties of a counteranion in a polyaniline salt as well as on conformation and crystal packing of the polymer chains. When an aromatic anion such as a toluenesulfonate ion is incorporated as a counteranion, a strong intermolecular interaction is expected to be operative between polyaniline and counteranion molecules. In this work, we synthesized a polyaniline toluenesulfonate that showed a well-defined X-ray powder diffraction pattern, and studied its structural and charge-transport properties.

EXPERIMENTAL

Polyaniline toluenesulfonate (abbreviated as PA-TS1) was synthesized by oxidation of aniline with iron(III) toluenesulfonate as follows. Iron(III) toluenesulfonate was obtained as a hygroscopic crystalline solid by concentration of an aqueous solution containing toluenesulfonic acid (2.62 g) and $FeCl_3.6H_2O$ (1.25 g). 2.4 g of this iron(III) salt was dissolved in 10 ml of water. The resulting solution was added dropwise to freshly distilled aniline (0.135 g) in water (10 ml) with stirring under a nitrogen atmosphere. After the reaction mixture was stirred for 2 hours, the reaction product was collected on a filter, washed with water and dried in vacuum. The most probable composition determined on the basis of the elemental analyses was $[(-C_6H_4NH-)(C_7H_7SO_3^-)_{0.33}{\cdot}0.8H_2O]_n$. Anal., Found (Calc.): C, 62.22 (61.60); H, 5.72 (5.55); N, 8.63 (8.65); S, 6.55 (6.53); Cl^- was not detected. Another polyaniline toluenesulfonate (PA-TS2), $[(-C_6H_4NH(C_7H_7SO_3^-)_{0.4}{\cdot}0.7H_2O]_n$, was prepared by the method reported previously by using copper(II) toluenesulfonate as an oxidant in acetonitrile [5].

The electrical conductivity was determined on the compressed pellets of the powder materials by van der Pauw's four-probe method [6] at temperatures between 100 and 300 K. The X-ray powder diffraction patterns were obtained on a Rigaku Geigerflex diffractometer operated with Cu Kα (λ = 1.542 Å) radiation and a Ni filter.

RESULTS AND DISCUSSION

The powder electrical conductivity σ of PA-TS1 was 0.2 S cm^{-1} at 300 K. The activation energy for electrical conduction at the high temperature limit, E_∞, was

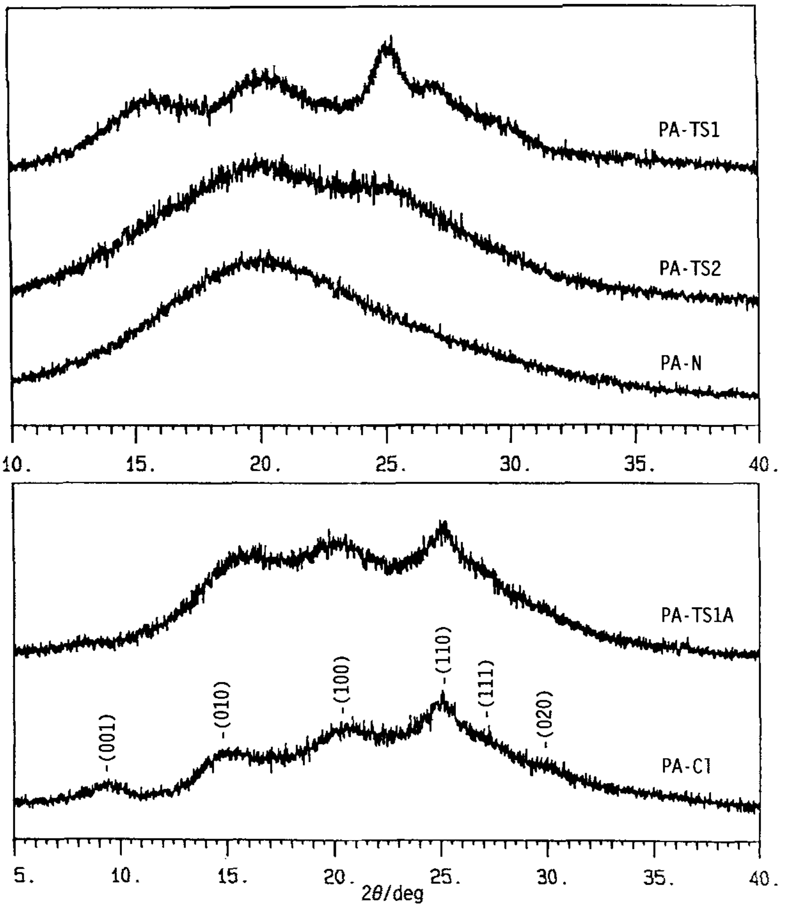

Figure 1. X-ray powder diffraction patterns of polyaniline salts.

0.07 eV; the temperature dependence deviated from the Arrhenius equation at low temperatures. PA-TS2 showed a higher conductivity, probably due to the higher dopant concentration: 10 S cm^{-1} (300 K); $E_\infty = 0.02$ eV.

Figure 1 shows X-ray powder diffraction patterns observed for the toluenesulfonates. PA-TS1 synthesized by using the iron(III) salt as an oxidant showed some well-defined diffraction peaks, in contrast to PA-TS2 synthesized with the copper(II) salt. When PA-TS1 was neutralized with 3 M NH_3, the resulting neutral polyaniline, PA-N, exhibited a very broad peak centered at 20° (Figure 1), which was characteristic of an amorphous material [7]. When PA-N was doped again with 4 M toluenesulfonic acid, the resulting toluenesulfonate PA-TS1A showed an X-ray pattern essentially identical with that of PA-TS1, although the diffraction peaks were

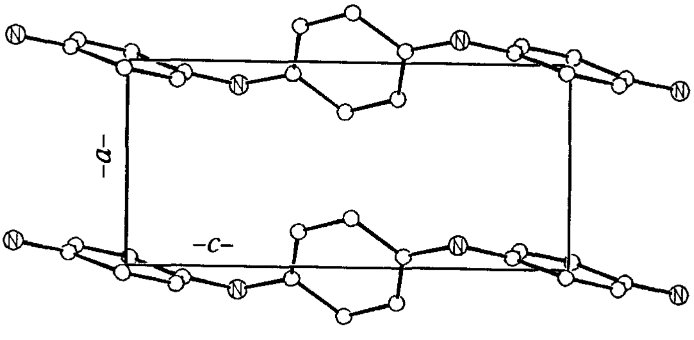

Figure 2. Packing diagram of polyaniline chains.

slightly broader than the corresponding peaks of PA-TS1 (Figure 1). When the same neutral polyaniline was acidified with HCl instead of toluenesulfonic acid, the resulting chloride PA-Cl exhibited a well-defined X-ray powder diffraction pattern which closely resembled that of the original PA-TS1 (Figure 1). PA-TS2 synthesized by using the copper(II) salt as an oxidant showed a diffuse X-ray pattern (Figure 1). When a neutral polymer obtained from PA-TS2 was doped again with toluenesulfonic acid, the X-ray powder pattern of the resulting salt was identical with that of the original PA-TS2. The local structures of polyaniline chains in the toluenesulfonates are maintained in the neutral polyanilines derived from the polymer salts, and ordered, upon redoping, in the same manner as in the original salts; namely, the original structure of each salt is memorized in its neutral polymer. Pouget, et al [7] have determined structure of a polyaniline chloride classified as ES-I assuming a pseudo-orthorhombic unit cell. The diffraction patterns of PA-TS1 and PA-Cl closely resemble the pattern of ES-I. The crystal packing of polyaniline chains in PA-TS1 and PA-Cl is, therefore, essentially identical with that of ES-I. On the basis of the crystal data reported for ES-I, the diffraction peaks observed for PA-Cl were indexed with $a = 4.3_5$ Å, $b = 5.9_1$ Å and $c = 9.4_0$ Å (Figure 1). The proposed crystal packing in the unit cell is illustrated in Figure 2. A polyaniline chain is placed parallel to the c axis in such a way that the phenyl rings are centered at 000 and $00^1/_2$ and the N atoms are located at $xy^1/_4$ and $xy^3/_4$ The phenyl rings in a polyaniline chain are rotated alternately about the N–(C_6H_4)–N axis, which is inclined from the c axis. A chloride ion occupies a space formed by polyaniline chains. Essentially identical structure is formed in PA-TS1 (and also in PA-TS1A), because its X-ray powder pattern closely resembles that of PA-Cl except that the peak at $2\theta \approx 10°$ in the former pattern is almost buried in the noise level. The cell dimensions of PA-TS1 were determined as $a = 4.4_4$, $b = 5.6_7$ and $c = 10.0$ Å. The cell volume is approximately 250 Å^3, which is close to 240 Å^3 of PA-Cl. Since the cell volumes of the two salts are almost identical, the counteranion with a larger molecular size has a closer contact with polyaniline chains. Each crystal unit cell accommodates an NH–(C_6H_4)–NH–(C_6H_4) unit. Since the analytical data shows that three TS anions are involved per ten aniline units, three anions are distributed statistically in five unit cells. It is reasonable that the phenyl plane of a toluenesulfonate ion is almost parallel to the molecular planes of the adjacent aniline groups resulting in formation of an alternating face-to-face stack of aniline and counteranion rings along the [110] direction. The face-to-face distance between the polymer and the organic anion is approximately 3.5 Å, which is close to 3.4 Å predicted for the van der Waals contact. This contact may enhance charge transport in the conducting polymer.

REFERENCES

[1] S. M. Geniès, A. Boyle, M. Lapkowski, and C. Tsintavis, *Synth. Met.*, *16*, 139 (1990).

[2] A. G. MacDiarmid, J. C. Chiang, A. F. Richter, and A. J. Epstein, *Synth. Met.*, *18*, 285 (1987).

[3] K. Mizoguchi, M. Nechtschein, J. P. Travers, and C. Menardo, *Synth. Met.*, *29*, E417 (1989).

[4] M. Iida, T. Asaji, R. Ikeda, M. B. Inoue, M. Inoue, and D. Nakamura, *J. Mater. Chem.*, *2*, 257 (1992).

[5] M. Inoue, F. Medrano, M. M. Castillo-Ortega, K. Asano, and M. Nakamura, *Synth. Met.*, *55-57*, 1057 (1993).

[6] J. L. van der Pauw, *Phillips Res. Rep.*, *13*, 1 (1958).

[7] J. P. Pouget, M. E. Józefowicz, A. J. Epstein, X. Tang, and A. G. MacDiarmid, *Macromol.*, *24*, 779 (1991); M. E. Józefowicz, R. Laversanne, H. H. S. Javadi, A. J. Epstein, J. P. Pouget, X. Tang, and A. G. MacDiarmid, *Phys. Rev.*, *B*, *39*, 12958 (1989).