Polyaniline Co-Doped with Camphor Sulfonic and Hydrochloric Acids by Chemical Oxidation in Aqueous Solution

ELI RUCKENSTEIN, WUSHENG YIN

Department of Chemical Engineering, State University of New York at Buffalo, Buffalo, New York 14260

ABSTRACT: A co-doped polyaniline was prepared from aniline camphorsulfonate (ANICSA) and aniline hydrochloride (ANIHCl), which was soluble in common organic solvents, such as *m*-cresol. Without any additional doping, it possessed a higher conductivity (2 S/cm) than those prepared from ANICSA or ANIHCl alone (0.4 S/cm). In other words, a synergistic effect arose through the chemical oxidative polymerization of a mixture of ANICSA and ANIHCl. The mole ratio of (CSA + HCl)/aniline was 1; if additional HCl was introduced, the conductivity reached a value as high as 7.9 S/cm. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 80–85, 2001

Key words: polyaniline; aniline camphorsulfonate; aniline hydrochloride; co-doping; chemical oxidative polymerization

INTRODUCTION

Among the methods proposed[1–7] to improve the solubility, hence the processiblity of polyanilne, that involving the doping of the insulating emeraldine base with dodecyl benzenesulfonic or camphor sulfonic acid has attracted attention because of the high conductivity of 10^2 S/cm achieved.[1,2] The emeraldine base was obtained by preparing first polyaniline via the chemical polymerization of aniline in an 1*M* HCl aqueous solution using ammonium persulfate as initiator. After filtration, the polyaniline (PANI) was washed with an 1*M* HCl aqueous solution and distilled water, and finally was treated with a NH_4OH solution. The emeraldine thus obtained was dissolved in an organic solvent (*m*-cresol) and doped with camphorsulfonic acid (CSA). The CSA-doped PANI exhibited a large conductivity of 400 S/cm, which can be attributed to the conformational change of the polymeric chains, the so-called secondary doping. A soluble polyaniline doped with camphorsulfonic acid was also synthesized by the electrochemical oxidative polymerization of aniline in an 1*M* camphorsulfonic acid aqueous solution.[8] Its conductivity was 1 S/cm, but its cost was high because of the large amount of expensive camphorsulfonic acid needed.

In a previous paper,[9] the suspension polymerization was employed to prepare a soluble polyaniline via the chemical oxidative polymerization of a mixture of aniline dodecyl benzenesulfonate (ANIDBSA) and aniline hydrochloride (ANIHCl) in an aqueous solution, without passing through the emeraldine base stage. The aniline dodecyl benzenesulfonate moieties of the polymer enhanced its solubility, hence its processibility, while the aniline hydrochloride moieties provided the conductive structure of the co-doped polymer. In the present paper, other sulfonic acids, such as the CSA or toluene sulfonic acid (TSA) were selected for the enhancement of the solubility of the

resulting co-doped polymer. Because CSA and TSA are much more water soluble than dodecyl benzene sulfonic acid (DBSA), the solution polymerization could be employed to prepare the doped polymer. While the emphasis of the paper is on the effect of CSA, the results obtained with TSA as co-dopant are also provided at the end of the paper.

EXPERIMENTAL

Chemicals

Aniline (ANI, Aldrich, 99%) was purified by distillation under reduced pressure prior to use. Hydrochloric acid (Aldrich, 37%), 10-camphorsulfonic acid (CSA0, Aldrich), CSA (Aldrich, 98%), TSA (Aldrich, 98%), ammonium persulfate (APS, Aldrich, 99%), methanol (Aldrich, 99%), and m-cresol were used as received. The water was double distilled and deionized.

Polymer (PANI Co-Doped with CSA and HCl) Preparation

Aniline (1.86 g) was introduced with stirring in a conical flask, containing 70 g of water and CSA and HCl in selected amounts [moles (CSA + HCl)/ moles ANI = 1], located in an ice bath. A solution of ammonium persulfate (1.2 g) in 10 g deionized water was added slowly to the aniline solution, with stirring. The reaction was allowed to take place with stirring for 1.5 h at a controlled temperature of $0 \pm 1°C$ and for 2.5 h at room temperature. After being precipitated with methanol, the polymer was washed with distilled water several times, dried in a vacuum of 10 mm Hg for more than 12 h, and then was weighed for the determination of the yield.

Determination of the Electrical Conductivity

The polymer was ground, pressed under 5.7×10^5 psi at 80°C for 1–2 min, the obtained sheet was cut in a rectangular shape, and the electrical conductivity measured at room temperature by the standard four-point method.

Fourier Transform Infrared (FTIR), UV-vis and Energy Dispersive Spectroscopy (EDX) Analyses

The powders of the product and KBr were ground into a fine powder and pressed into a pellet. The FTIR analysis was performed with a Perkin-Elmer (Model 1760×) instrument. The product powder was dissolved in m-cresol, and the UV spectrum obtained using a Shimadzu UV-210A spectrophotometer. The EDX analysis was performed with a PGT/TMIX field emission microscopy instrument.

RESULTS AND DISCUSSION

During the aqueous solution polymerization of ANICSA and ANIHCl, the initial color of the solution varied from green to blue and finally to dark green with increasing HCl/CSA mole ratio. The polymer could be dissolved in m-cresol. Table I lists the characteristic Fourier transform infrared (FTIR) peaks of the undoped emeraldine PANI and the resulting co-doped polymers. Compared to PANI, the characteristic peak at 1590 cm^{-1}, which can be assigned to the C=C of the quinoid ring, shifted to 1566, 1570, and 1566 cm^{-1} for the co-doped polymers R01, R37, and R46; the C$_{aromatic}$–N stretching vibration shifted from 1313 to 1303 cm^{-1} for R01, and 1306 cm^{-1} for R37 and R46 (see Table I for the meaning of Rmn). The shifting was caused by the *in situ* co-doping polymerization of ANIHCl and ANICSA.

The UV-vis absorption spectra of the synthesized copolymers R28 and R46 are presented in Figure 1. The maximum at about 900 nm can be assigned to a localized polaron, characteristic for the co-doped PANI. The free-carrier tail (starting at 1100 nm) is due to the electron delocalization in the polaron band, probably caused by the secondary co-doping. The latter effect occurs because the strong interactions between m-cresol and PANI change the conformation of the chains from a coil to an extended one.[1,10] The peak at about 350 nm caused by the π—π^* transition of the

Table I   FTIR Peaks of the As-Synthesized Co-Doped Polymers and PANI Base

Code[a]	C=C (quinoid ring) (cm^{-1})	C$_{aromatic}$—N (cm^{-1})
PANI	1590	1313
R01	1566	1303
R37	1570	1306
R46	1566	1306

[a] ANIHCl/ANIDCSA (mole ratio): R01 (0:1), R37 (3:7), and R46 (4:6) The other polymerization conditions are described in the experimental section.
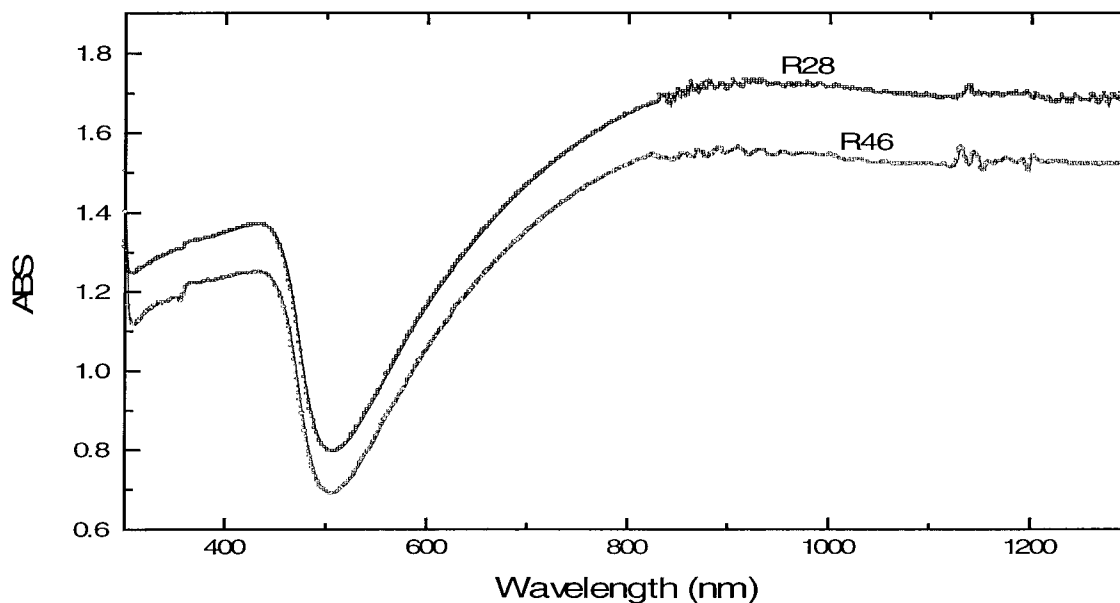
Figure 1 UV spectra of the doped polymers R28 and R46 (R28: ANIHCl/ANIDBSA = 2:8).

benzenoid ring could not be detected, being overlapped by the broad peak at about 430 nm of the polaron band.

The effects of the ANIHCl/ANICSA mole ratio in the feed on the conductivity and yield of the resulting polymer is presented in Figure 2 when no additional HCl is introduced. With increasing ANIHCl/ANICSA mole ratio, both the conductivity and yield first increase and then decrease, passing through a maximum conductivity of 2 S/cm and a maximum yield of 19 wt % at a mole ratio of 4/6.

As noted above, at low ANIHCl/ANICSA mole ratios, the solution acquired from the beginning a green color. This indicates that the polymer was
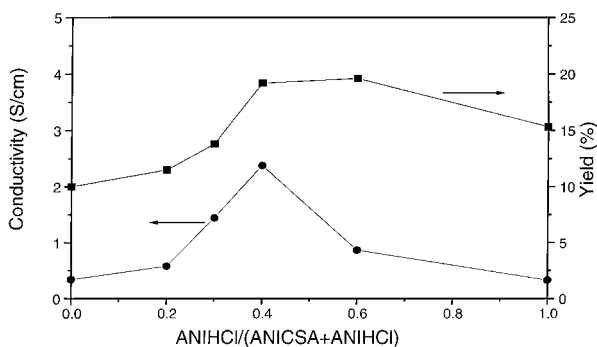

Figure 2 Effect of ANIHCl/(ANICSA + ANIHCl) mole fraction on the conductivity and yield of the doped polymer.

doped once formed, because the green color characterizes a solution containing doped PANI. With increasing ANIHCl/ANICSA mole ratio, the initial color of the solution gradually changed from green to blue (undoped PANI) and, finally, to dark green. This change in color indicates that at low and large ratios, a doped PANI was generated and that at intermediary ratios PANI was only partially doped.

The EDX spectra of copolymers R28 and R37 shown in Figure 3 reveal that (1) only the sulfur peak is present in the copolymer R28 and (2) both the chlorine and sulfur peaks are present in the copolymer R37 with a Cl/S atomic ratio of 19/81, which is lower than the feeding ratio (30/70). Consequently, when the ratio HCl/CSA is small, the molecules are doped by CSA, while at sufficiently large ratios by HCl. Water is not a good solvent for either of these doped macromolecules, and as a result, they acquire a coiled conformation. Because of the bulky tridimensional structure of CSA, the steric repulsion makes the CSA-doped macromolecules less coiled. The steric repulsion due to the CSA groups reduces, however, the rate of polymerization and the molecular weight of the macromolecules generated. Hence at low ratios, both the yield and the molecular weight are low. At the other extreme, PANI doped only with HCl, the conformation is coiled, but the yield and molecular weight are again low because the reactive
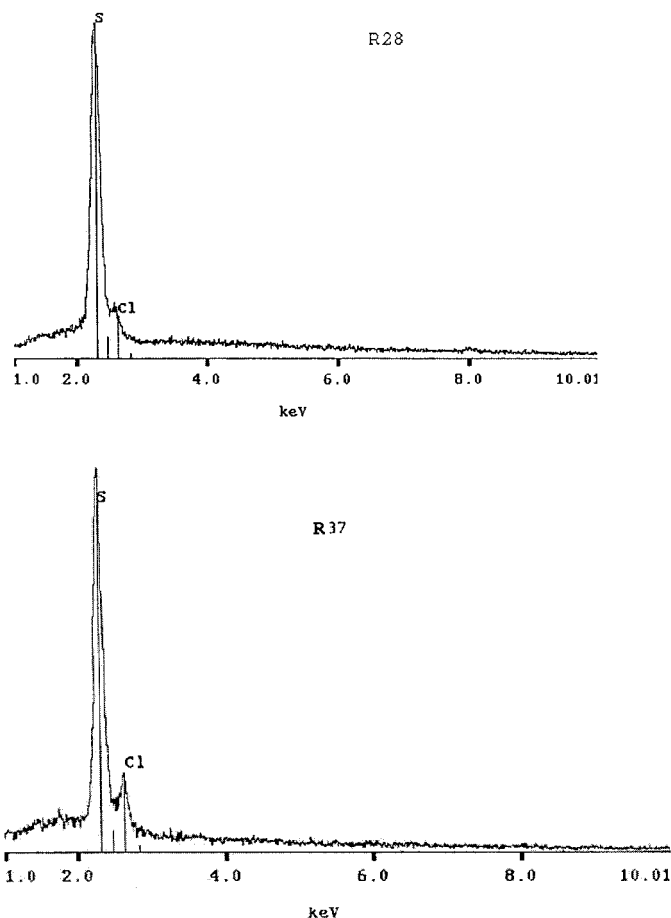
Figure 3 EDX spectra of R28 and R37 of Table I.

site is not enough exposed. At intermediary ratios, the molecules will be less coiled because of the presence of CSA, but enough reactive because they are more exposed and contain HCl-doped units which react more easily. The above considerations explain why the yield and the conductivity pass through a maximum (the conductivity passes through a maximum because the larger molecules are expected to provide a higher conductivity).

Comparing the present results to those regarding the co-doped polymers P(ANIHCl-co-PANIDBSA),[9] one can conclude that the Cl/S atomic ratio is strongly dependent on the structure of the functional group (R—) of the R—SO_3H acid employed. Table II presents a comparison between the Cl/S atomic ratio in the resulting polymers. For an ANIHCl/ANICSA(DBSA) mole feed ratio of 20/80, chlorine was hardly found in the two conducting polymers, while for a ratio of 30/70, the Cl/S atomic ratio was 20/80 for ANIHCl/ANICSA, but still negligible for ANIHCl/ANIDBSA. This occurs

because the camphorsulfonic acid is much more compatible with water than DBSA.

Figure 4 presents the effect of additional HCl in the solution on the conductivity and yield of the

Table II   The Cl/S Atomic Ratio of Doped Polymers Obtained from ANIHCl/ANICSA and from ANIHCl/ANIDBSA

Code[a]	ANIHCl/ANICSA(DBSA) Feed Ratio (molar)	Cl/S Atomic Ratio[b]
R28	20/80	0/100
R37	30/70	20/80
DR28	20/80	0/100
DR37	30/70	0/100
DR46	40/60	8/92

[a] R represents the ANIHCl/ANICSA system; and DR the ANIHCl/ANIDBSA system. The preparation conditions for DR28, DR37, and DR46: 1.86 g ANI, 100 g H_2O, 1.2 g APS; reaction times 1.5 h at 0°C followed by 2.5 h at room temperature.
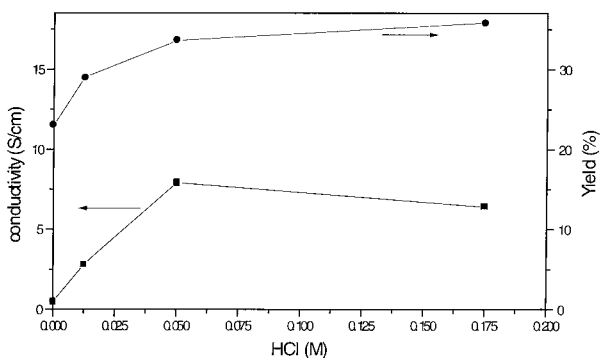[b] Determined by EDX.

Figure 4   Effect of the additional HCl on the conductivity and yield of the co-doped polymer for an ANIHCl/ANICSA mol ratio in the feed of 2/8.

resulting copolymer for an ANIHCl/ANICSA mole ratio of 2/8. When the additional concentration was increased from 0 to 0.05M, the conductivity and yield increased from 0.48 to 7.9 S/cm, and from 11.5 to 16.8%, respectively. With a further increase to 0.175M, the conductivity exhibited a small decrease to 6.8 S/cm, while the yield continued to increase to 17.9%. The maximum conductivity was 7.9 S/cm at 0.05M HCl solution, which is higher than that achieved via electrochemical polymerization (1 S/cm).[8] The conductivity decreases at high additional HCl concentrations, probably because some chlorine substituted PANI was formed.[11]

The effect of the amount of oxidant, ammonium persulfate, on the conductivity and yield of the polymer for an ANIHCl/ANICSA mole ratio of 2/8 is presented in Fig. 5. When $(NH_4)_2S_2O_8$ increased from 1.2 to 2.0 g, the conductivity increased from 0.48 to 2.0 S/cm, and the yield increased from 11.5 to 27.3%. When the amount of oxidant was not too large, the yield of emeraldine and its molecular weight increased with increasing amount of oxidant. At large amounts of oxidant (outside the range of the present experiments), side reactions are expected to take place and the amount of emeraldine and its molecular weight are expected to decrease with increasing amount of oxidant.

Figure 6 shows that the conductivity of the co-doped polymers are strongly affected by the reaction temperature. Indeed, for an increase of the reaction temperature of the first stage from 0 to 5°C, the conductivity increased from 0.48 to 1.5 S/cm but the yield decreased somewhat. With a further increase to 23°C (room temperature), the conductivity decreased to 0.98 S/cm and the yield exhibited a small decrease. This happened because the overoxidative and the reverse hydrolysis side reactions are stimulated by higher temperatures.

Figure 7 presents the conductivities of the resulting co-doped polymer prepared using ANIHCl and various aniline-substituted sulfonates. The conductivity of the resulting polymer was in the sequence TSA > CSA0 > DBSA > CSA. The conductivity, when TSA was employed, was as high as 6.8 S/cm.

Figure 6   Effect of reaction temperature on the conductivity and yield of the co-doped polymer for an ANIHCl/ANICSA mole ratio in the feed of 2/8.

CONCLUSION

A conductive co-doped polymer based on ANICSA and ANIHCl, which is soluble in organic solvents, could be prepared by the *in situ* doping chemical polymerization. A synergistic effect was observed
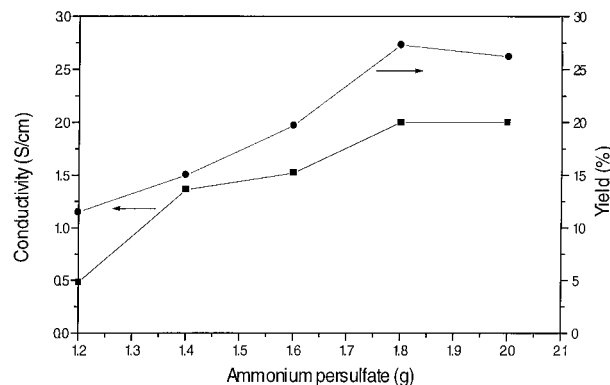

Figure 5   Effect of the amount of ammonium persulfate on the conductivity and yield of the co-doped polymer for an ANIHCl/ANICSA mol ratio in the feed of 2/8.
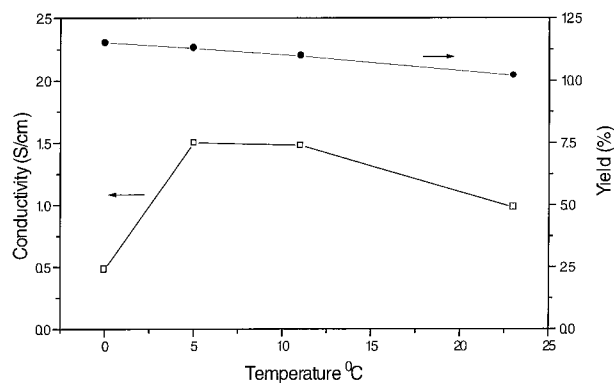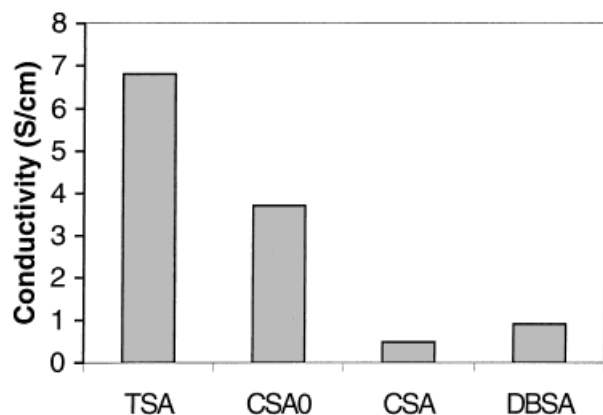
Figure 7 Effect of various sulfonic acids on the conductivity of the co-doped polymer for a mole ratio of HCl/R—SO_3H of 2/8.

regarding the conductivity and the yield of the co-doped polymers, which were higher than those achieved from either ANIHCl or ANICSA. At an ANIHCl/ANICSA mole ratio of 4/6 in the feed, the co-doped polymer exhibited a maximum conductivity of 2 S/cm and a maximum yield of 19.2%. The conductivity reached a value as large as 7.9 S/cm when additional HCl was introduced in the feed. An exclusively CSA-doped conductive polymer could be also obtained via chemical polymerization with a conductivity higher than that prepared via electrochemical polymerization. A comparison is made among various co-doped polymers prepared using ANIHCl and various aniline-substituted sulfonates.

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