

SYNTHESIS AND PROPERTIES OF ANILINE AND *o*-AMINOBENZENESULFONIC ACID COPOLYMER*

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Abstract Poly(aniline-*co-o*-aminobenzenesulfonic acid) (PAOABSA) as a water soluble conducting polymer was synthesized by chemical polymerization. The productivity and the room-temperature conductivity of the copolymer were measured as a function of the reaction conditions, such as reaction temperature, the ratio of oxidant to monomer and the degree of sulfonation defined as the ratio of sulfur to nitrogen atoms(S/N). The main results obtained are summarized as follows: (1) lower reaction temperature (at about 0°C) is favorable for the enhancement of the room-temperature conductivity of the copolymer; (2) higher content of oxidant is unfavorable for increasing the room-temperature conductivity of the copolymer; (3) both productivity and room-temperature conductivity of the copolymer decrease with increase of the degree of sulfonation which was always lower than 0.5 even an excess of *o*-aminobenzenesulfonic acid was added, probably because the reactivity ratio of aniline ($\gamma_1=2.99 \pm 0.05$) is much higher than that of *o*-aminobenzenesulfonic acid ($\gamma_2=0.06 \pm 0.02$) estimated by using Fineman-Ross method and least square method.

Keywords Watersoluble polyaniline, Reactivity ratio, Copolymer

INTRODUCTION

Polyaniline (PANI) as a typical conducting polymer has attracted considerable attention because of its varied structure, stability in air, special doping mechanism and attractive application in technology. Unfortunately, the insolubility and infusibility of polyaniline make it difficult for utilization. Therefore, synthesis of soluble conducting polyaniline has attracted great consideration and significant progress has been made in recent years^[1-6]. Among the soluble conducting polyanilines, water-soluble conducting polyanilines are of particular importance because of its self-doping characteristics and environmental preponderance. A series of papers concerning water-soluble conducting polyaniline with varied conductivity have been published in the literature^[7-14]. The first water-soluble conducting polyaniline is the sulfonated polyaniline(SPAN) reported by Yue, et al.^[9], which has higher room temperature conductivity than other water soluble polyaniline derivatives. Moreover, the degree of sulfonation which is defined as the ratio of sulfur to nitrogen atoms as high as 0.75 of SPAN (LEB-SPAN) has been synthesized by Wei et al.^[15], using the full reduced form of PANI, leucoemeraldine base form of PANI as starting material. Recently, a fully sulfonated degree of SPAN has been reported by Shimizu et al.^[16] by using *m*-aminobenzene-sulfonic acid derivative as the starting materials. However, the degree of sulfonation of water-soluble polyaniline mentioned in the literature is fixed. In fact, it is expected that the degree of sulfonation is an important parameter to monitor the composition and physical properties of water soluble conducting polyaniline^[17, 18]. In our laboratory, a new type of water-soluble conducting

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polyaniline derivative, i.e. PAOABSA, having an adjustable degree of sulfonation, was synthesized directly from aniline and *o*-aminobenzenesulfonic acid^[19, 20]. Moreover, it has been demonstrated that the electrical and magnetic properties of the copolymer strongly depend on its degree of sulfonation^[21].

In this article, the productivity and the conductivity of the copolymer at room temperature were measured as a function of reaction conditions, such as reaction temperature, the ratio of aniline monomer to oxidant, and the degree of sulfonation. The lower degree of sulfonation (<0.5) observed for the copolymer is discussed by a term of reactivity ratio of aniline and *o*-aminobenzenesulfonic acid in the copolymer estimated by using Fineman-Ross method^[16] (FR-method) and least square method.

EXPERIMENTAL

Copolymerization of aniline and *o*-aminobenzenesulfonic acid was carried out in 1.2 mol/L HCl solution employing ammonium persulfate as oxidant and a modified literature procedure^[11]. A series of experiments were performed for the optimization of reaction conditions. The ratio of oxidant to monomer was changed from 0.5 to 1.5 and the mole fraction of aniline in the reaction mixture was changed from 0.66 to 0.25. The copolymerization was controlled at different reaction temperatures ($-15^{\circ}\text{C} \sim 60^{\circ}\text{C}$). It was found that poly(*o*-aminobenzene sulfonic acid) cannot be polymerized. Room temperature conductivity of the copolymer was measured by the standard four-probe method using the Keithley 19b SYSTEM DMM Digital Multimeter and ADVENTIST Rb142 programmable DC voltage/current generator as the current source.

RESULTS AND DISCUSSION

Effect of Reaction Conditions on the Productivity and the Room Temperature Conductivity

It was found that the productivity and the conductivity of the copolymer strongly depend on the reaction conditions, such as reaction temperature, the ratio of oxidant to comonomer, and the degree of sulfonation in the copolymer.

The reaction temperature

In order to find a favorable reaction temperature for the copolymerization, the reactions were carried out under different temperatures from -15°C to 60°C , while the ratios of aniline to *o*-aminobenzenesulfonic acid (1:1) and the ratio of comonomer to oxidant (1:1) were kept constant. The productivity and the room temperature conductivity of the copolymer synthesized at different reaction temperatures are given in Table 1. As one can see, the room temperature conductivity of the copolymer increased from 0.009 S/cm to 2.2 S/cm and the productivity of the copolymerization was also enhanced accordingly when the reaction temperature decreased from 60°C to -15°C . Moreover, it was noted that a straight line was obtained on the plot of $\lg \sigma$ versus T , as shown in Fig. 1. Therefore, copolymerization was conducted at 0°C (with ice bath) in favor of higher room temperature conductivity (0.56 S/cm) and higher productivity ($\sim 55\%$) of the copolymer.

Table 1. Effect of reaction conditions on the productivity and room-temperature conductivity of PAOABSA copolymer

Reaction temperature ($^{\circ}\text{C}$)	Monomer/Oxidant (mol:mol)	Productivity (%)	Room-temperature conductivity (S/cm)
-15	1:1	49	2.2×10^0
0	1:1	55	5.6×10^{-1}
27	1:1	43	3.3×10^{-1}
47	1:1	36	5.0×10^{-2}
60	1:1	29	9.0×10^{-3}
0	2:1	31	4.5×10^{-1}
0	3:2	52	2.0×10^{-1}

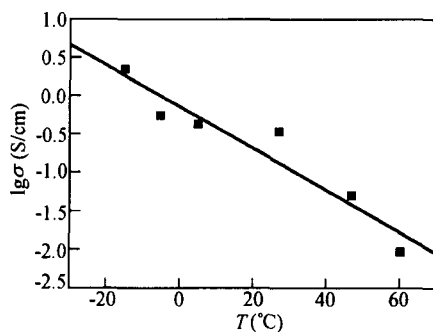


Fig. 1 Effect of reaction temperature on the room-temperature conductivity of PAOABSA copolymer

The ratio of monomer to oxidant

Three different ratios of comonomer to oxidant were chosen to optimize the favorable oxidant content. From Table 1, one can see that the best ratio of monomer to oxidant is 1:1 to favor the higher room-temperature conductivity of the PAOABSA copolymer. Lower content of ammonium persulfate will affect the productivity though the room-temperature conductivity of PAOABSA copolymer is similar to that of copolymer synthesized at 1:1 ratio of monomer to oxidant. However, higher content of ammonium persulfate results in lower room-temperature conductivity of PAOABSA copolymer.

The degree of sulfonation

The degree of sulfonation of the copolymers can be adjusted by controlling the mole fractions of the feed. The PAOABSA copolymers with different degrees of sulfonation were synthesized at 0°C with 1:1 ratio of monomer to oxidant. The elemental analysis, productivity and room temperature conductivity of the copolymers are summarized in Table 2. Parameter f_1 is defined as the mole fraction of *o*-aminobenzenesulfonic acid in the reaction mixture, whereas, F_1 is defined as the mole fraction of *o*-aminobenzenesulfonic acid in the copolymer, which corresponds to the degree of sulfonation in the copolymer measured by elemental analysis. As shown in Table 2, the fraction of F_1 for all samples is lower than that of f_1 . Moreover, the productivity of the PAOABSA copolymer decreases with the increase in degree of sulfonation; accordingly, the room-temperature conductivity of the PAOABSA copolymers decreases with the increase in degree of sulfonation. The results of structural characterization of the copolymer^[20] show that the room-temperature conductivity of the copolymer decreases with the increase of the degree in sulfonation is presumably due to the steric effects of *o*-aminobenzenesulfonic acid substituents which produce torsional twists and shorten the conjugation lengths in the copolymer.

Table 2. Composition, elemental analysis and room-temperature conductivity of PAOABSA copolymers

PAOABSA		Elemental composition (wt%)			Degree of sulfonation (S/N)	Productivity (%)	Conductivity (S/cm)
f_1	F_1	N	S	Cl			
0	0	11.64		13.72	0	84	6.9
0.25	0.15	10.29	3.54	7.67	0.15	77	3.37
0.33	0.21	10.52	5.11	5.25	0.21	66	1.2
0.5	0.30	10.04	6.88	4.07	0.30	53	0.50
0.66	0.34	9.40	7.20	1.94	0.34	34	0.34
0.75	0.36	9.22	7.47	1.83	0.36	29	0.15

f_1 = Mole fraction of *o*-aminobenzenesulfonic acid in the reaction mixture;

F_1 = Mole fraction of *o*-aminobenzenesulfonic acid in the copolymer

The interesting thing is that although more than 50% mole fractions of *o*-aminobenzenesulfonic acid was added to the reaction mixture, the degree of sulfonation of the copolymer was less than 0.5, which means that the content of *o*-aminobenzenesulfonic acid units in the PAOABSA copolymer was lower than that of aniline units. In other words, the reactivity of *o*-aminobenzenesulfonic acid in the copolymerization was lower than that of aniline. This may be a reason why poly(*o*-aminobenzenesulfonic acid) cannot be polymerized, which will be discussed in detail in the next paragraph.

Calculation of Reactivity Ratio of Monomers in the Copolymerization

In general, the Fineman-Ross method (FR-method)^[22] can be used to determine the reactivity of monomers in the copolymerization, provided the conversion of the copolymerization is very low (less than 10%). Thus, in order to keep the conversions to less than 10%, the reaction mixture was filtered immediately when the reaction solution turned green, and then washed with 1.2 mol/L HCl and followed by washing with methanol until the filtrate became colorless. The resulting precipitate was dried under vacuum for 24h.

Based on the FR-method, the copolymerization composition equation of the two monomers is expressed as:

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left(\gamma_1 \frac{[M_1]}{[M_1] + \gamma_2 [M_2]} \right) \quad (1)$$

where $d[M_1]$ and $d[M_2]$ are the mole fraction of aniline and *o*-aminobenzenesulfonic acid in the copolymer; γ_1 and γ_2 are the reactivity ratio of aniline and *o*-aminobenzenesulfonic acid in the copolymerization respectively. There are several methods to obtain the copolymer composition, such as elemental analysis as used in this work, IR spectroscopy, UV-Vis spectroscopy and NMR. For low conversion, $[M_1]$ and $[M_2]$ correspond to the mole fraction of the two units in the feed. However, it was found that the fraction of *o*-aminobenzenesulfonic acid in the copolymer is lower than that in the feed, as shown in Fig. 2, in which F_2 defined as the mole fraction of *o*-aminobenzenesulfonic acid in the copolymer, while f_2 corresponds to the mole fraction of *o*-aminobenzenesulfonic acid in the feed. This result indicates that it is difficult to get the copolymer of PAOABSA with high degree of sulfonation. Typical data of $[M_1]$, $[M_2]$, $d[M_1]$ and $d[M_2]$ for the PAOABSA copolymer with different conversion degrees are given in Table 3, in which M_1 and $d[M_1]$ are the mole fraction of aniline in starting materials and the copolymers respectively, while M_2 and $d[M_2]$ are the mole fraction of *o*-aminobenzenesulfonic acid in starting materials and the copolymers respectively.

Table 3. Reaction parameters determined for the reactivity ratios in the copolymerization of aniline(M_1) with *o*-aminobenzenesulfonic acid(M_2)

Mole fraction of two monomers feed		Conversion degree (%)	Mole fraction of two units in the copolymer	
M_1	M_2		$d[M_1]$	$d[M_2]$
0.66	0.33	7.5	0.87	0.13
0.60	0.40	6.8	0.85	0.15
0.50	0.50	2.6	0.76	0.24
0.33	0.66	8.9	0.69	0.31
0.25	0.75	6.4	0.65	0.34

If let $x = M_1/M_2$, $y = d[M_1]/d[M_2]$, the composition Eq. (1) can be rewritten as:

$$(y-1) \frac{x}{y} = \gamma_1 \left(\frac{x^2}{y} \right) - \gamma_2 \quad (2)$$

Thus, a linear line should be obtained if x^2/y was plotted against $(y-1) x/y$ as shown in Fig. 3, and γ_1 and γ_2 can be calculated from the slope and the intercept of the straight line, respectively. Therefore, the reactivity ratio for aniline (γ_1) and *o*-aminobenzenesulfonic acid (γ_2) (at 1~5°C) was calculated to be 2.99 ± 0.05 and 0.06 ± 0.02 , respectively.

Since the experimental data are unequally weighted by the FR equations, the data obtained under extreme experimental conditions (in Eq. 2 at rather low M_2 comonomer concentration) have the greatest influence on the slope of a line; accordingly, the calculated γ_1 and γ_2 values depend on arbitrary factors, such as which monomer is selected as M_1 . Thus, the resulting γ_1 and γ_2 were verified by using the least square method (LSC-method).

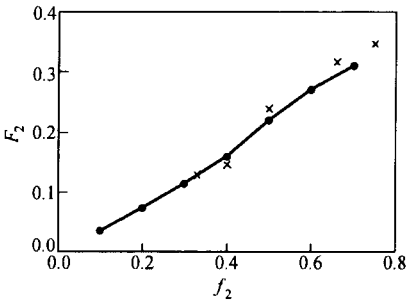


Fig. 2 Curve of copolymer composition F_2 versus monomer composition f_2 of PAOABSA
-•- From copolymerization composition equation using γ_1 and γ_2 , -x- from $[M_2]$ and $d[M_2]$ data

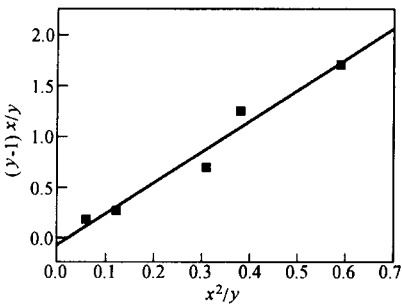


Fig. 3 Fineman-ross plot for polymerization of PAOABSA copolymers

Applying Eq. (2) and the LSC-method, the following equations will be obtained:

$$\gamma_1 A_1 - \gamma_2 n = C_1 \tag{3}$$

$$-\gamma_1 n + \gamma_2 A_2 = C_2 \tag{4}$$

where

$$A_1 = \sum_{i=1}^n \frac{x_i^2}{y_i}; \quad A_2 = \sum_{i=1}^n \frac{y_i}{x_i^2}; \quad C_1 = \sum_{i=1}^n x_i \left(1 - \frac{1}{y_i}\right); \quad C_2 = \sum_{i=1}^n \frac{y_i}{x_i} \left(\frac{1}{y_i} - 1\right)$$

and n is the experimental point which was equal to 5. According to Eqs. (3) and (4), γ_1 and γ_2 can be expressed as

$$\gamma_1 = \frac{A_2 C_1 + n C_2}{A_1 A_2 - n^2} \tag{5}$$

$$\gamma_1 = \frac{A_1 C_2 + n C_1}{A_1 A_2 - n^2} \tag{6}$$

Based on the data given in Table 4, A_1 , A_2 , C_1 and C_2 were calculated. Then, γ_1 and γ_2 were found to be 2.90 and 0.03 from Eqs. (5) and (6), which is consistent with the results calculated by the FR-method.

Table 4. Calculation of monomer reactivity ratios of the copolymer using LSC- method

x	y	x^2/y	$(y-1)x/y$	y/x^2	$(1/y-1)y/x$
2.00	6.75	0.59	1.70	1.68	-2.87
1.50	5.85	0.38	1.24	2.6	-3.23
1.00	3.2	0.31	0.69	3.2	-2.2
0.50	2.17	0.12	0.27	8.68	-2.34
0.33	1.89	0.06	0.16	17.36	-2.70

The reactivity ratio of *o*-aminobenzenesulfonic acid (γ_2) is not equal to zero, indicating the homopolymerization of *o*-aminobenzenesulfonic acid is not entirely impossible. This result is consistent with the experimental observation, i.e. the reaction solution turned from colorless to red without the formation of precipitate, indicating the oligomers formed were very small. On the other hand, it can copolymerize with aniline to form copolymer (PAOABSA). The result that γ_1 is far

higher than γ_2 implies that aniline is more reactive than *o*-aminobenzenesulfonic acid inducing more aniline units in the copolymer chains. This causes the copolymerization to become a non-ideal one. Moreover, the lower γ_2 suggests that it is impossible to synthesize copolymer with high degree of sulfonation.

A comparison of the calculated curve of F_2 versus f_2 with the experimental curve as shown in Fig. 2, the values denoted by the sign $\bullet$ were obtained by calculation of the copolymerization composition equation of the two monomers using γ_1 and γ_2 values, and the values denoted by the sign $\times$ were taken from $[M_2]$ and $d[M_2]$ data in Table 3 corresponding to f_2 and F_2 , respectively. As one can see, there are no distinctive differences in the curve trends between the experimental and the calculated curves. This indicates that the calculated results of γ_1 and γ_2 values are reliable. However, from the curve trends, we can imagine that it is very difficult to obtain copolymers with a degree of sulfonation higher than 50%, which is also consistent with our experimental results.

CONCLUSIONS

A new type of water soluble conducting polyaniline copolymer, poly(aniline-*co*-*o*-aminobenzenesulfonic acid) (PAOABSA) was synthesized by one step polymerization. The productivity and the conductivity of the copolymer at room temperature were measured as a function of the reaction conditions, such as reaction temperature, the mole fraction of monomers, and the ratio of monomer to oxidant. It was found that decrease in the reaction temperature (at about 0°C) and the mole fraction of *o*-aminobenzenesulfonic acid is favorable for increasing the productivity and room temperature conductivity of the copolymers. Moreover, the monomer reactivity ratios of aniline and *o*-aminobenzenesulfonic acid were calculated using FR and LSC methods. The reactivity ratio of aniline ($\gamma_1 = 2.99 \pm 0.05$) is much higher than that of *o*-aminobenzenesulfonic acid ($\gamma_2 = 0.06 \pm 0.02$) at 0~5°C. This is consistent with the experimental fact that the lower degree of sulfonation (<0.5) in the copolymer was observed, and the lower reactivity ratio of the *o*-aminobenzenesulfonic acid may be a reason why that the copolymer has lower sulfonated degree although *o*-aminobenzenesulfonic acid was added in excess.

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