Preparation and Characterization of Sulfonated Poly(phenylene oxide)**

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ABSTRACT: Sulfonated poly(2,6-dimethyl phenylene oxide) (SPPO) has been prepared through the reaction of PPO and fuming sulfuric acid in the media of chloroform. The effect of the amount of sulfuric acid on sulfonation contents has also been discussed. The structure of SPPO was characterized by using FT-IR, ^1H NMR, ^{13}C NMR and other analysis methods. Conductimetric titration, elemental analysis and ^1H NMR were used to determine the sulfonation contents of SPPO, *i.e.*, the percentage of sulfonated units.

KEY WORDS Poly(2,6-dimethyl phenylene oxide) / Sulfonation / Sulfonation contents /

Poly(2,6-dimethyl phenylene oxide) is a novel excellent engineering plastics, whose modification has been actively studied to acquire some special functional properties during the past few years.¹⁻³ Sulfonated poly(phenylene oxide) (PPO) has been reported to be used as composite film material to purify waste water.⁴ With its $P_{\text{H}_2\text{O}}/P_{\text{N}_2}$ as high as 2×10^4 , it is also a wonderful material for gas dehumidity.⁵ SPPO has been applied as matrix of single ion conducting polymer solid electrolytes.⁶ Huang *et al.*³ prepared sulfonated PPO by using chlorosulfonic acid as sulfonating agent, in which the reaction was so violent and strict that the sulfonating contents were difficult to control. Moreover, it was hard to acquire highly-sulfonated PPO by this method.

In the present paper, a better sulfonating way has been investigated, where reaction fuming sulfuric acid is employed as sulfonating agent in the media of chloroform. With simple condition and easily-controlled reaction

process, the reaction can reach a sulfonation content of 70%. Conductimetric titration, ^1H NMR, and elemental analysis were used to determine the sulfonation contents. FT-IR, ^1H NMR and ^{13}C NMR were also applied to characterize its structure.

EXPERIMENTAL

Materials

Poly(2,6-dimethyl phenylene oxide) (PPO), obtained from the Beijing Institute of Chemical Engineering, was used to make SPPO after purified. Chloroform, fuming sulfuric acid, methanol and tetrahydrofuran (THF) were all A.R. grade.

Preparation of SPPO

PPO was added to chloroform and dissolved to form a 10% (w/v) solution by stirring for half an hour at a constant temperature. Then fuming sulfuric acid in an additional funnel was added slowly with vigorous stirring. The

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reaction lasted for 3–4 hours. Sulfonation products were immersed in deionized water to eliminate excess acid. Finally, the sulfonated samples were dried at vacuum oven.

Characterization and Determination of Sulfonation Contents of SPPO

FTIR. PPO was dissolved in chloroform, while SPPO in methanol. The tested samples were prepared as cast film over NaCl discs and measured by Analect RFX-65A FTIR.

¹H NMR. PPO was dissolved in CDCl₃, observe frequency 90 MHz. SPPO was dissolved in CD₃OD, observe frequency 400 MHz, using a pulse width equivalent to a flip angle of 90°C, pulse delay of 2.6 s, recycle 32 times, solvent CD₃OD as inner standard.

¹³C NMR. Observe frequency 100 MHz,

using a pulse width equivalent to a flip angle of 90°C, pulse delay of 1.6 s, recycle 21632 times. Solvent CD₃OD as inner standard. Operating at room temperature.

Conductimetric Titration. SPPO was dissolved to form an about 0.05% (wt.) solution. Then 0.1 N NaOH aqueous solution was added to it. The change of conductivity with the volume of base solution was recorded by a DDS-11A type conductimeter.

Elemental Analysis. Sulfur contents were analyzed by oxygen bottle combustion method.

RESULTS AND DISCUSSION

The sulfonation reaction of PPO and fuming sulfuric acid, which is reversible, can be divided into two steps⁷:

K_1 , K_2 , X_1 , and X_2 are the equilibrium constants of the first and the second step, the initiative concentrations of structural units for PPO and $\text{H}_3\text{S}_2\text{O}_7^+$, respectively. From the two equilibria above, the concentration of sulfonated units can be deducted:

$Y =$

$$\frac{B(X_1 + X_2) - \sqrt{B^2(X_1 - X_2)^2 + 4X_1 \cdot X_2 / (K_1 \cdot K_2)}}{2[B^2 - 1/(K_1 \cdot K_2)]}$$

$$\left(B = \frac{1}{\sqrt{K_2}} + 1 \right)$$

as $K_1 \cdot K_2 \gg 1$

$$Y \approx \frac{X_1 + X_2 - |X_1 - X_2|}{2B} \quad \frac{X_1 > X_2}{X_2/B} \quad (1)$$

As the initiative concentration of $\text{H}_3\text{S}_2\text{O}_7^+$, X_2 is in direct proportion to the amount of the fuming sulfuric acid. So we can assume $X_2 = m \cdot N$ (N is the volume fraction of fuming

sulfuric acid, while m is a constant). Meanwhile, sulfonation contents is also in direct proportion to the concentration of SPPO, we can obtain $Y = n \cdot s$ (s was sulfonation contents, n as a constant). Figure 1 shows the dependence of sulfonation contents on the amount of sulfuric acid. In the graph, the dots are the experimental results, while the line is obtained according to eq 1 and the conductimetric titration result of Sample no. 1.

From Figure 1, it can be seen that the relation between the sulfonation contents and the volume fraction of fuming sulfuric acid, especially when the volume of sulfuric acid is large, deviate from linear type. This phenomenon shows the complicity of the reaction. When fuming sulfuric acid is more, there will be more species of sulfonating agent, such as $\text{H}_2\text{S}_2\text{O}_7$, H_3SO_4^+ etc., to take part in sulfonation. When the concentration of fuming sulfuric acid is low, the comparatively weak sulfonation agents are difficult to work effec-

tively. For this reason, the sulfonation contents deviated higher from linear curve when the concentration of sulfuric acid is high.

Comparison is made between SPPO and the original sample PPO by FT-IR and NMR.

As shown in Figure 2, the typical peaks are the absorption at 1378 cm^{-1} , 1190 cm^{-1} , and 857 cm^{-1} . The strong bands at the frequency of 1190 cm^{-1} can be ascribed to the sym-

metry stretch vibration for C–O–C of aromatic ether. The mid-strong absorption bands at the frequency of 857 cm^{-1} and 1378 cm^{-1} are the deformation vibration peaks for the insulated hydrogen on the aromatic ring and the methyl groups, respectively. The mid-strong peaks at 670 cm^{-1} and 1066 cm^{-1} appear after PPO is sulfonated. This can be assigned to the vibration of the $-\text{SO}_3\text{H}$ group. In a general way, the group of $-\text{SO}_3\text{H}$ has another strong absorption between $1210\text{--}1150\text{ cm}^{-1}$, but here it is verllapped by the stronger band of the C–O–C symmetry vibration of polyether.

Figure 3 shows the ^1H NMR spectra of PPO and SPPO. In the spectrum of SPPO (B in the Figure 3), peak a (at 6.60 ppm) and peak b (at 6.32 ppm) belong to the hydrogen on sulfonated and un-sulfonated aromatic ring, respectively. Meanwhile the two peaks at high field (peak c, 2.62 ppm and peak d, 2.18 ppm) are assigned to the protons of methyl groups on sulfonated and un-sulfonated aromatic ring, respectively. From the spectra, it is obvious

Figure 1. Dependence of sulfonation contents on the amount of sulfuric acid.

Figure 2. FTIR spectra of PPO and SPPO.

that the chemical shift of the aromatic hydrogen moves to low field much by the strong inducing action of $-\text{SO}_3\text{H}$, which indicates that the sulfonated groups are attached to the aromatic ring of PPO. It is further confirmed by the ^{13}C NMR spectrum of SPPO in Figure 4.

The chemical shifts for various aromatic carbon of SPPO can be calculated according to Grant's empirical formula.⁸ The calculated results are in good agreement with the experimental results (in Figure 4).

Figure 3. ^1H NMR spectra of PPO and SPPO. A, PPO in CDCl_3 ; B, SPPO in CD_3OD .

As SPPO solution shows light orange color, it is difficult to determine accurate end point with indicator. The study of using conductimetric titration gets rather satisfactory results.

Two different types of titration curve have been obtained from the conductimetric titration to SPPO solution of tetrahydrofuran (THF) and methanol (as shown in Figures 5 and 6), which can be explained as follows: In the solution of SPPO, two equilibria which are the ionization equilibria of H_2O and SPPO are affected when the base titrant is added. Dissociation equilibrium is related to the dielectric constant of the system. As SPPO dissociates little in the solution of THF (the dielectric constant of THF is only 7.6), few H^+ are neutralized at the beginning that the NaOH solution is added. On the other hand, the dielectric constant of the SPPO solution system is increased by the adding of NaOH solution which causes much more SPPO's ionization. For this reason, the conductivity of the system rises at firsts. The dielectric constant of the system increases with the amount of the NaOH solution added, then SPPO becomes easier to ionized. The effect of OH^- neutrali-

Figure 4. ^{13}C NMR spectrum of SPPO (in CD_3OD).

Figure 5. Conductimetric titration curve of SPPO in THF solution.

Figure 6. Conductimetric titration curve of SPPO in CH₃OH solution.

zation with H⁺ which decreases the conductivity looms large. The titration curve at the stage declines. After the equal stoichiometric point, as the H⁺ in the system are all neutralized, the excess NaOH solution increases the conductivity. The case is different as to the SPPO solution of methanol. The dielectric constant of methanol solution is relatively high (the dielectric constant of methanol is 39.2), so SPPO ionized much in it. The effect of neutralization which decreases the conductivity plays an important role from the beginning of titration, while the effect of increasing the dielectric constant is comparatively weak. After the equal stoichiometric point, the conductivity augments with the adding of excess base solution. This curve is simple and similar to the conductimetric

Figure 7. Conductimetric titration curve of SPPO in CH₃OH solution as free acid is not eliminated completely.

Table I. Sulfonation contents of SPPO

Sample no.	1	2	3	4	5	6
Titr. result/%	26.8	29.3	34.7	41.0	53.5	68.6
EA result/%	26.3	31.0	38.0	39.3	54.4	72.5

titration curve in aqueous solution.

The conductimetric titration curve will show an obvious slope transition when the excess sulfuric acid isn't washed out completely (as shown in Figure 7). As being easier to dissociate, free sulfuric acid is prior to SPPO to be neutralized. When the free sulfuric acid is neutralized at first, as it's easy to ionize, the conductivity decreases fast. After the slope transition which appears when the free sulfuric acid has been all titrated, the conductivity changes more slowly with the adding of base solution for the reason that SPPO's ionization is not so easy.

The sulfonation contents determined by conductimetric titration and elemental analysis are listed in Table I. The two results are close by and large.

The sulfonation contents can also be determined by ¹H NMR spectrum. According to the assignment of the peaks in Figure 3, the sulfonation contents, *i.e.*, the percentage of sulfonated units can be calculated from the density of peak a and peak b. The B in Figure 3 is the ¹H NMR spectrum of the sample No.

6. The sulfonation content is 71.8%, which is calculated from integrating the peak area in the ^1H NMR spectrum, while the results from conductimetric titration and elemental analysis are 68.6% and 72.5%, respectively. The three results are in agree with one another generally. But after all, the method of conductimetric titration is convenient, accurate and reliable.

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