EFFECT OF SOLVENT COMPOSITION ON THE SULFONATION DEGREE OF POLY(PHENYLENE OXIDE) (PPO)[*]

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Abstract This paper investigates the possibility of attaining sulphonated poly(phenylene oxide) (SPPO) with a relatively higher sulfonation degree. To achieve this aim, the approach we adopt is to improve the solubility of the final product in the mixed solvent so that the sulfonation may take place between the bulk solutions and PPO powders even at higher sulfonation degree. It is shown that the addition of a proper amount of dimethyl formide (DMF) to the conventional PPO-chloroform system can actually enhance the sulfonation effect. The solvent composition is then correlated with the sulfonation degree based on the solubility parameters. It is interesting to find that solubility parameters between the mixed solvent and the precipitated products keep an approximately unchanged value at about 4.9, which is just equal to that when pure chloroform is used, though the solubility parameters of both solvents increase with the content of DMF in solution. This may be the main reason why the addition of DMF can reduce the precipitation and improve the ion exchange capacity (IEC) of SPPO polymer.

Keywords Poly(phenylene oxide), Sulfonation, Solubility parameter

INTRODUCTION

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) is a versatile and well-known polymer with high glass transition temperature (T_g)[1–5]. The applications of its membrane shape have already been proven to be an attractive material with excellent mechanical properties and resistant to a number of chemical agents[2, 6, 7]. Unfortunately, PPO has a relatively low selectivity for gases and much lower solubility in most dipolar solvents due to its hydrophobicity, which limits its uses as an attractive membrane material in many conventional applications, for example, gas separation, pervaporation, especially for ion exchange membrane and bipolar membranes which have been reported in recent years. To improve these properties, PPO was subjected to many modifications by various electrophilic substitutions including bromination, carboxylation and methyl esterified carboxylation[8–11], sulfonylation and acylation[8–10] and by introduction of trialkyl-silyl, hydroxyethylene and ethyleneoxytrialkyl-silyl groups in the polymer backbone[12].

In addition, sulfonation is another important chemical modification of PPO[1, 5, 7, 13, 14]. Medium-sulfonated PPO (SPPO) was considered as a potential material for reverse osmosis membranes[14–16] as well as for improving gas selectivity[13, 17]; while for a relatively high sulfonation degree, SPPO is an attractive material for charged membrane, pervaporation membrane, ion exchange membrane and bipolar membrane which are the bases for various membrane processes, such as nanofiltration, diffusion dialysis, electrodialysis and water cleavage technology, *etc.*[18–20]. Therefore, SPPO with a higher sulfonation degree is actually required. However,

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this aim is not easily attained for a conventional sulfonation process due to the limited solubility of the final product, SPPO, in chloroform, which in many cases is used as the solvent. It was reported that the highest attainable sulfonation degree of the product is about 9.5% using sulfuric acid as the sulfonating agent[5, 21]. Though the sulfonation degree could be raised by using chlorosulfonic acid as the agent, the degree could also hardly exceed 40% no matter how high the molecule weight of the used PPO[5, 13−16, 22]. SPPO with higher degree than this value will be obtained in this paper. Our approach is to improve the solubility of the products in the mixed solvent in order to make the sulfonation reaction take place in the bulk solutions and not at the interface between sulfonating agent and PPO. The solvent composition is then correlated with the sulfonation degree based on the solubility parameters. The applications of these highly sulfonated polymers in bipolar membranes will be reported later.

EXPERIMENTAL

Materials

Poly(phenylene oxide) (PPO) with $[\eta] = 0.53$ dL $\bullet$ g^{-1} in chloroform at 25℃ was obtained from Asashi Co., Japan. Solvents, chloroform and dimethyl formide (DMF) of analytical grade were used as received.

Sulfonation Procedure[15, 22]

PPO was stirred at room temperature for 0.5−1.0 h with mixed solvents of chloroform and DMF to form an 8% solution. Volumetric proportions of DMF in solution ranged from 0 (pure chloroform) to 16.7%. Prior to PPO sulfonation, a small quantity of sulfonable materials (ethanol and water) in the solution was determined and removed by neutralization with additional chlorosulfonic acid. The PPO batches were then sulfonated by enough of chlorosulfonic acid until the product is precipitated from the solution. Then, it was filtered, washed with distilled water and dried at room temperature. If sodium form is preferred, SPPO of hydrogen form is allowed to contact with an aqueous salt, preferably a basic solution such as sodium or a potassium hydroxide solution. After equilibrating the polymer with the solution, the solid was rinsed with distilled water to remove the excess electrolytes and dried in use.

Determination of Sulfonation Degree of SPPO

Sulfonation degree (x) was calculated from the ion exchange capacity (IEC) measurements*. The IEC of SPPO was determined by the acid-base back titration method with phenolphthalein as the indicator. For more precise determination, the sulfonation degree was also determined by proton nuclear magnetic resonance (^{1}H-NMR) techniques. The spectra were acquired on Bruker AMX-400 Spectrometer using a deuterated DMF solvent.

RESULTS AND DISCUSSION

^{1}H-NMR spectra

The presence of sulfonic group in the PPO repeat unit results in a shift of the signal from protons attached to methyl group in *ortho* position to the sulfonic group, and that from the aromatic proton of the substituted unit. Therefore, the ^{1}H-NMR spectrum of SPPO shows two extra signals at about $\delta = 2.4$ and 3.4 in addition to those of PPO. The degree of sulfonation was calculated from the intensities of the additional signals. The results are shown in Table 1.

Sulfonation

In conventional sulfonation processes, an obvious feature is that the products are easily precipitated from the reaction solutions, if a designated amount of sulfonating agent is added due to the limited solubility of the products in the solvent. Thus, there is a problem of maximum amount of sulfonating agent (SA). For example, if pure chloroform is used as the solvent, 3.5 mL chlorosulfonic will be enough to sulfonate 120 g PPO. So the

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* $x = \text{IEC}/1000/((1-M_{\text{SPPO}} \times \text{IEC}/1000)/M_{\text{PPO}} + \text{IEC}/1000)$, where IEC is in unit: meg/g dry hydrogen polymer and M_{SPPO} and M_{PPO} denote the molecular weight of SPPO (H form) and PPO, respectively.

IEC of the products can hardly exceed about 1.8−2.0 meq/g (Na form), because if additional chlorosulfonic acid is added, the products will precipitate from the solution (stirring is then impossible) and PPO powders are wrapped inwards, and a further sulfonation will be restricted to the interface between the solution and the precipitated polymer. Of course, such sulfonation can not bring about an appreciable increase in IEC and also SPPO may not have a uniform distribution of sulfonic groups within the polymer batch. If we call the reactant ratio (molar ratio of ClSO$_3$H to PPO) at which the product is just precipitated the critical ratio R_c, it will be interesting to find that this value can be raised by adding some polar solvents *e.g.*, DMF, to the reactant solution. Thus it is favorable to homogenize the reaction and increase the IEC. The R_c values with different solvent ratio of DMF to chloroform are listed in Table 1.
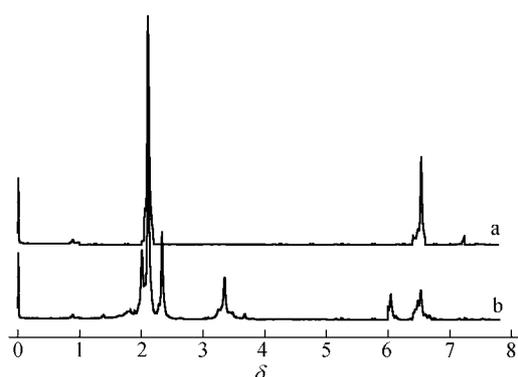

Fig. 1 ^{1}H-NMR spectra of (a) PPO, and (b) SPPO (H form)

Table 1. IEC, R_c values and other characteristic parameters in sulfonation system with different solvent ratio

Volumetric - ratio for DMF (%)	R_c (Molar ratio)	Target IEC (meq/g) (Sodium form)	Actual IEC (meq/g) (Sodium form)	Actual sulfonation degree, x		δ_{12} [b] based on Eq. (3)	δ_p [b, c] based on Eqs. (1) and (2)	$(\delta_p - \delta_{12})$ [b]
				Titration	^{1}H-NMR			
0	0.29	3.027	2.0	0.302	0.304	19.03	23.96	4.93
0.833	0.58	4.626	2.2	0.340	0.333	19.07	24.08	5.01
2.50	0.67	4.953	2.27	0.354	0.348	19.17	24.12	4.95
4.17	1.0	5.932	2.52	0.407	0.412	19.27	24.31	5.03
8.33	1.67	6.173[a]	2.80	0.470	0.472	19.50	24.49	4.99
16.67	3.08	6.173[a]	3.21	0.573	0.570	19.99	24.82	4.83

[a] The maximum value for theoretical IEC (at this time x is assumed to be 2.0)
[b] The solubility parameters are in unit: J$^{1/2} \cdot$ cm$^{-3/2}$
[c] Calculated from Eq. (2) and based on titration measurements

Table 2. $E_{coh, i}$ and V_i values of the structural units in SPPO polymers[24]

	Phenyl(tetra-substitution)	Phenyl(penta-substitution)	$-CH_3$	$-O-$	$-SO_3H$
$E_{coh, i}$ (J $\cdot$ mol^{-1})	31946.8	31946.8	4710.4	3349.6	18841.5
V_i (cm$^3 \cdot$ mol^{-1})	14.4	−4.6	33.5	3.8	27.6

Obviously, with the increasing content of DMF in solution, R_c values increase, and products with higher sulfonation degree will be produced, as shown in Table 1. An increase in IEC due to the change of solvent compositions can be explained by the theory of solubility parameters. As we know, the solubility parameter of a polymer can be calculated from the contributions of the groups that are contained therein[23]:

$$\delta_p = \sqrt{\frac{\sum E_{coh,i}}{\sum V_i}} \qquad (1)$$

where $E_{coh,i}$ and V_i are respectively the inward aggregating energy and the molar volume of group i. The group contributions to solubility parameters of SPPO polymer are summarized in Table 2.

Substituting $E_{coh,i}$ and V_i values in Eq. (1) yields the following equation for calculating the solubility parameters of SPPO with different sulfonation degree,

$$\delta_p = \sqrt{\frac{44717.2 + 18841.5x}{85.2 + 8.6x}} \qquad (2)$$

In this equation, the value of x can be taken from the results of either titration measurements or ^{1}H-NMR measurements because they are very close to each other as shown in Table 1. In our case, the substituted x values are based on titration measurements. The solubility parameters for SPPO with different x are summarized in Table 1. It is evident that δ_p values increase with IEC, that is, the polarity of SPPO increases with IEC. Therefore, it can no longer be dissolved in non-polar pure solvents such as chloroform when the IEC attains a designated value based on the solubility rules[23]. However, the polarity of non-polar solvent may be improved by the addition of some polar solvent. According to the mixed rule, the solubility parameter of a mixed solvent can be calculated from that of the corresponding pure solvents times their volumetric fractions:

$$\delta_{12} = \delta_1 U_1 + \delta_2 U_2 \qquad (3)$$

δ_{12}, δ_1, δ_2 are the solubility parameters of mixed solvent, pure solvent 1 and solvent 2, and U_1 and U_2 denote the volumetric fractions. The results are also tabulated in Table 1. It is interesting to find that solubility parameters between the mixed solvent and the precipitated products keep approximately unchanged (*i.e.*, ~4.9) which is just equal to that when pure chloroform is used, though the solubility parameters of both solvents increase with the content of DMF in solution. This may be the main reason why the addition of DMF can reduce the precipitation and improve IEC. It is well known that the necessary condition for a polymer to homogeneously dissolve in a solvent is that the difference between their solubility parameters should lie within 3.5–4.1 $J^{1/2} \cdot cm^{-3/2}$ as described in most textbooks and manuals[23–26]. Our result deviates from this range and thus it conforms with this rule. Our results also imply that if $(\delta_p - \delta_{12})$ attains a value of 4.9, the products will easily be precipitated and further reaction is difficult.

The measured IEC and x values of the products from both titration and ^{1}H-NMR methods as reported in Table 1 verify the fact that we actually obtain SPPO by using mixed solvents and by changing the compositions. However, by comparing the practical IEC with the sulfonating agent added in the system, it is easy to find that not all the sulfonating agent takes part in the reaction. Most sulfonating agent are not reacted with PPO, especially in the cases of high DMF content. These un-reacted parts are probably combined with DMF to form a soft sulfonating agent, DMF-SO$_3$H. Therefore, DMF possibly has two actions to improve the sulfonation process: one is the enhancement of the solubility parameter in the solution and the other is its combination with the excess amount of sulfonating agent to form a soft agent and thus homogenize the reaction. Further studies will be conducted to clarify the latter effect.

CONCLUSIONS

The higher achievable degree of sulfonation of PPO was obtained by using mixture of solvents, chloroform and DMF. The sulfonation degree of the products was measured by using both titration and ^{1}H-NMR techniques. A critical reactant ratio R_c is defined in this paper and it increases with the content of DMF in solution. Addition of DMF prevents the precipitation of products from the solution and further sulfonation can be further conducted uniformly between the solution and PPO even in the presence of a large excess of chlorosulfonic acid. It is not unusual for the products to achieve a sulfonation degree as high as 3.21 meq/g which is far beyond the value reported in literature[5, 13–16, 22]. An increase in IEC due to the change of solvent compositions is explained by the theory of solubility parameters. The solubility parameters of both mixed solvents and SPPO were calculated and compared with each other. It is interesting to find that the solubility parameters between them remains

approximately unchanged at about 4.9 which is just equal to the value when pure chloroform is used, though their respective solubility parameter increases with the content of DMF in solution. This may be the main reason that the addition of DMF can reduce the precipitation and improve IEC.

Sulfonation degrees obtained from titration measurements showed more consistency with those from ^{1}H-NMR measurements. However, both are far away from the target values, especially in the case of high DMF content. It shows that not all the sulfonating agents take part in the reaction, most sulfonating agent do not react with PPO even in the case of no addition of DMF. These un-reacted parts are probably combined with DMF to form a soft sulfonating agent, DMF-SO$_3$H. This may be another reason for addition of suitable DMF to cause an increase in IEC of the products. Further studies will be conducted to clarify this effect.

REFERENCES

1   Xu, T.W., Yang, W.H. and He, B.L., Chinese J. Chem. Eng., 1998, 6: 283

2   Toi, K., Morel, G. and Paul, D.R., J. Appl. Polym. Sci., 1982, 27: 2997

3   Xu, T.W. and Yang, W.H., J. Membrane Sci., 2001, 183: 193

4   Pan, C.Y. and Wang, J.J., Chinese J. Polym. Sci., 2001, 19(2): U3

5   Fu, H.Y., Jia, L.D. and Xu, J.P., J. Appl. Polym. Sci.,1994, 51: 1399

6   Plate, N.A. and Yampol'skii, Y., in: "Polymer Gas Separation Membranes", ed. by Paul, D.R. and Yampo'skii, Y., CRC Press, London, 1994, p.156

7   Hnulbe, K.C., Matsuura, T. and Noh. S.H., J. Membrane Sci, 1998, 145: 243

8   Mahajan, S.S., Polym.-Plast. Tecn. Eng., 1991, 30: 27

9   Chern, R.T., Sheu, F.R. and Jia, L., J. Membr. Sci., 1987, 35: 103

10 Percec, S., J. Appl. Polym. Sci., 1987, 33: 191

11 Story, B.J. and Koros, W.J., J. Membr. Sci., 1992, 67: 191

12 Pedretti, U., Gandini, A. and Roggero, A., 1992, U.S. Pat., 5,169,416

13 Kruczek, B. and Matsuura, T., J. Membr. Sci., 1998, 146: 263

14 Huang, R.Y.M. and Kim, J.J., J. Appl. Polym. Sci.,1984, 29: 4029

15 Plummer, C.W., Kimura, G. and Laconti, A. B., "Development of SPPO membranes for reverse osmosis", in: "Office of Saline Water Research and Development Progress Report No. 551", General Electric, Lynn Mass., 1970, p.53

16 Hamza, A., Chowdhury, G. and Matsuura, T., J. Appl. Polym. Sci., 1995, 58: 613

17 Jia, L.D., Sheu, F.R., Chern, R.T. and Hopfenberg, H.B., Chinese J. Polym. Sci.,1989, 7(4): 306

18 Xu, T.W., Xu, X.G., Yang, W.H. and Qu, Q.S., Chinese J Membrane Sci., 2000, 20: 57

19 Xu, T.W. and Yang, W.H., J. Membrane Sci., 2001, 183: 193

20 Xu, T.W. and Yang, W.H., J. Membrane Sci., 2001, 190: 159

21 Schauer, J., Loour, P. and Vacik, J., J. Membrane Sci., 1986, 29: 169

22 Huang, R.Y.M. and Kim, J.J., J. Appl. Polym. Sci., 1984, 29: 4017

23 Van Krevelen, D.W., "Properties of Polymers", Elsevier, Amsterdam, 1976

24 Hanson, C.M. and Beerbower, A., "Encyclopedia of Chemical Technology, Supplement Volume", Wiley, New York, 1971, p.889-910

25 Zhao, C.T., Hou, J.N., Zhang, X., Zhu, W. and Xu, M., Chinese J. Polym. Sci., 1996, 14(4): 376

26 Fan, J.H., Wan, M.X. and Zhu, D.B., Chinese J. Polym. Sci., 1999, 17(2): 165