Preparation of Sulfonated Novel Poly(bis[4-(3-aminophenoxy) phenyl]sulfone pyromellite)imide Derivatives by Heterogeneous Sulfonation

JONG-YOUNG JEON, BOMG-SEOB SHIM

Department of Textile Engineering, Sangju National University, 711-744, Sangju. Kyeongbuk, Korea

ABSTRACT: Sulfonated poly(bis[4-(3-aminophenoxy)phenyl]sulfone pyromellite)imide derivatives with various ion-exchange capacities were prepared by heterogeneous sulfonation with chlorosulfonic acid. The effects of sulfonating agent concentration, reaction temperature, and reaction time were investigated. The mechanical and thermal properties, contact angle, change of polydispersity, and solubility were calculated for studying change of their properties. The reactions were effective, when the temperature is <10 °C and the concentration of chlorosulfonic acid is between 0.05 and 0.1 M. The value of ion-exchange capacity was increased with reaction time, reaction temperature, and concentration of sulfonating reagent. Thermal and mechanical properties were nearly unchanged according to the degree of sulfonation, but the hydrophilicity indirectly measuring contact angle was increased with increasing the value of ion-exchange capacity. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 1881–1887, 2002

Key words: contact angle; chlorosulfonic acid; heterogeneous sulfonation; hydrophilicity

INTRODUCTION

Polyimide derivatives have a large number of applications in modern industry because they have excellent mechanical properties and high thermal and chemical resistance. Many of those, however, are difficult to fabricate because of their infusibility and insolubility in common organic solvents.[1–5] We have reported earlier the preparation of polyimide derivatives that are soluble in organic solvents. Those, however, are hydrophobic materials.[6]

In this study, I have focused on the preparation of sulfonated polyimide. The sulfonation of polymer is a common procedure to change the properties from hydrophobic to hydrophilic.[7–10] Modified polyimides with hydrophilic properties are desirable for many diversified applications. In this article, polyimide derivatives were prepared according to the method used in earlier research.[6] The sulfonated polyimides were then prepared by a heterogeneous method with chlorosulfonic acid in solution.

EXPERIMENTAL

Reagents

The polyimide derivative used for chemical modification was synthesized by a one-step method that was reported earlier.[6] It was dissolved in N-methyl-2-pyrrolidome (NMP), filtered off, and then poured into a large quantity of methanol. The precipitate was filtered off, washed repeatedly with methanol, and dried in vacuo at 110 °C

before using. Chlorosulfonic acid (CSA, Aldrich Chemical Co.) was used without further purification. Tetrachloromethane (CCl₄, Aldrich Chemical Co.) was purified with concentrated H_2SO_4, washed with water, then dried with $CaCl_2$, and distilled before using. Other laboratory-grade reagents were used without further purification.

Measurements

The viscosity of polymer solution was measured with an Ubbelohde viscometer in 0.5 g/dL NMP at 30 °C. The molecular weight distribution was obtained by gel permeation chromatography (GPC, Water 150C). The infrared (IR) spectrum was recorded on film with a Hartman & Braun model BOMEN DA 8.16. The thermal properties were measured by differential scanning calorimetry (DSC, Dupont 2100) and thermogravimetric analysis (TGA, Perkin-Elmer TGA7). The mechanical properties and solubility were measured by the same methods as in the previous paper.[6] The contact angle was obtained at 25 °C and RH of 65% with a contact angle analyzer (Enama G1).

Ion exchange capacity (IEC) was calculated according to Fisher's method:[10]

$$IEC \text{ (meq/g)} = (50 \times N_{NaOH} - Y \times N_{HCl})$$
$$\div \text{ polymer weight (g)} \quad (1)$$

where Y is the amount of HCl consumed and N_{NaOH} and N_{HCl} are normal concentration of NaOH and HCl, respectively.

Sulfonation of Polyimide Derivatives with CSA

A four-necked 250-mL round-bottomed flask equipped with a seal Teflon stirrer, nitrogen gas inlet tube, thermometer, and addition funnel with pressure equalization arm, was charged with polyamide (PI) and CCl₄. CSA was dissolved in dichloroethane in the addition funnel. The concentration of CSA is 0.01–0.1 M in dichloroethane. Under nitrogen conditions, CSA was slowly added into the flask with vigorous stirring, and the funnel was exchanged with a reflux condenser with $CaCl_2$ guard tube. The reaction mixture was kept at this condition to obtain sulfonated PI (SPI). When the reaction was completed, SPI was filtered off, washed free of used solvents by repeated use of methanol and water, and dried in vacuo at 120 °C.

RESULTS AND DISCUSSION

The IR spectra of PI and SPI are shown in Figure 1. The absorption peaks of identified PI exhibited
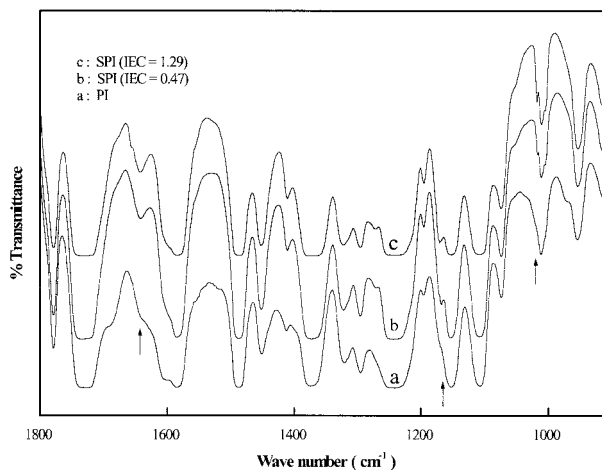

Figure 1 Fourier transforem infrared (FTIR) spectra of PI and SPI.

strong bands at ~1780 and 1710 cm⁻¹, which are assigned to the stretch vibration of the C—O linkage of the cyclic imide, and a band at 1370 cm⁻¹, which is due the C—N stretch vibration of cyclic imide groups.[1–6] On the other hand, in the spectra of SPI, new absorption peaks, as marked on the IR chart, appeared at ~1020 and 1170 cm⁻¹. These peaks are peculiar to symmetric stretching and asymmetric vibration of —SO₃H introducing sulfonation,[11, 122] respectively. In addition, peaks are exhibited at ~1660–1670 and 1200 cm⁻¹ with an IEC of >1.0. The former relate to amide peaks, which could be degradation of imide ring in the concentrated sulfonating condition, and the latter are assigned to the chemical shift of asymmetric peak of the —SO₃H group, having a strong hydrogen bond. It could be deduced from the spectra that the products sulfonated with CSA were SPI.
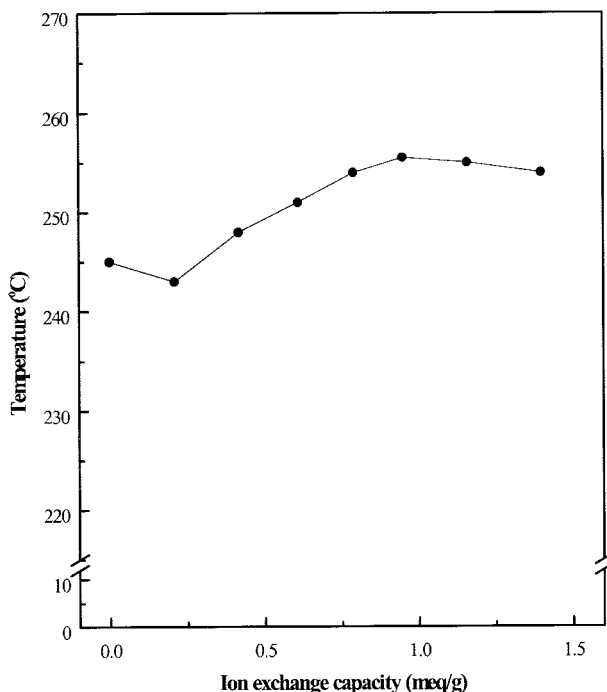
The IEC consequence of SPI as a function of reaction temperature and concentration of CSA is shown in Figure 2. The influence of reaction temperature was determined over a temperature range from −10 to 40 ° in the sulfonating reaction. The temperature was limited to the temperature at which the reaction mixture could not make a lump together. As a result, the IEC value of the polymers increased with increasing sulfonating reagent content up to 0.1 M CSA, where a limiting value apparently was reached. Although, the IEC value increased with increasing concentration at the aforementioned content, the reaction mixture was held together and the reaction could not proceed.

The degree of sulfonation was also increased with increasing reaction temperature. When the
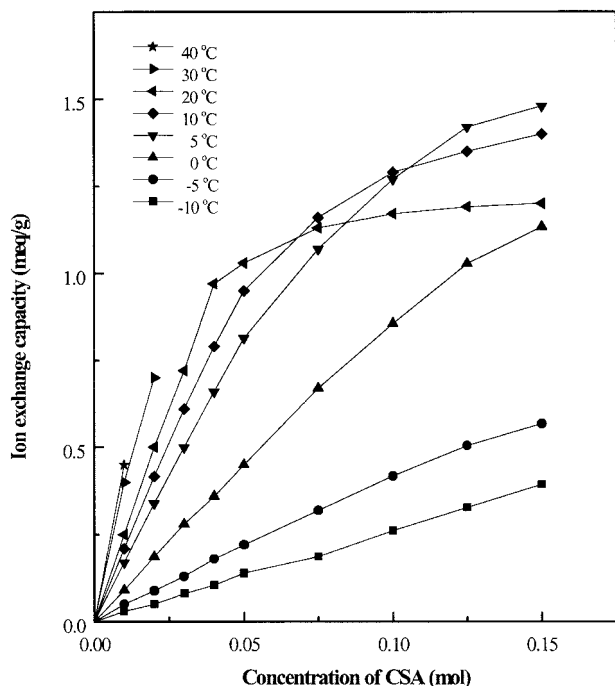
Figure 2 IEC as a function of CSA concentration and reaction temperature. Reaction was carried out for 8 h under N_2.

Figure 4 Evaluation of T_g versus IEC in the SPI.

reaction was carried out at >30 °, it did not proceed smoothly and the result was not satisfactory. The polymer treated at >30 °C was clustered in

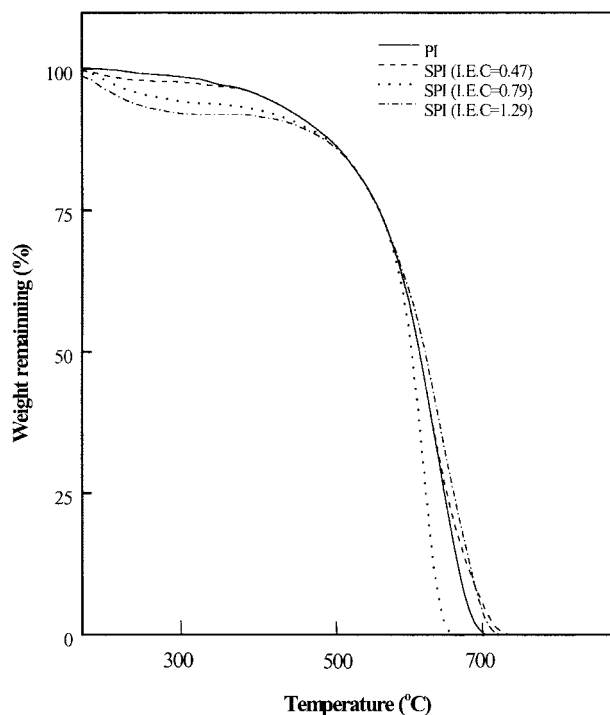the reaction mixture. On the other hand, below that temperature, the IEC value increased with increasing reaction temperature. These results might be explained by the reactivity of reagents
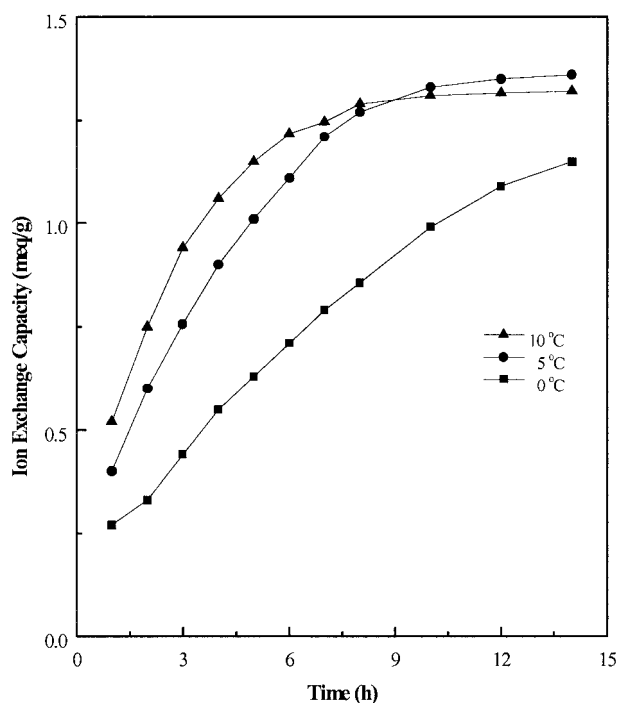
Figure 3 IEC as the function of reaction time.

Figure 5 TGA traces of PI and SPI.

Table I   Thermal Behavior of PI and SPI Derivatives in TGA Traces[a]

No.	T_i (°C)[b]	T_{10} (°C)[c]	T_{max} (°C)[d]	T_f (°C)[e]
PI[f]	400 ± 10	470 ± 5	600 ± 5	700 ± 5
SPI (IEC = 0.41)	150 ± 10	470 ± 5	600 ± 5	730 ± 5
SPI (IEC = 0.79)	150 ± 10	441 ± 5	607 ± 5	694 ± 5
SPI (IEC = 1.29)	120 ± 10	429 ± 5	610 ± 5	710 ± 5

[a] Measured at a heating rate of 20°C/min in nitrogen.
[b] Initial decomposition temperature.
[c] 10% weight loss temperature.
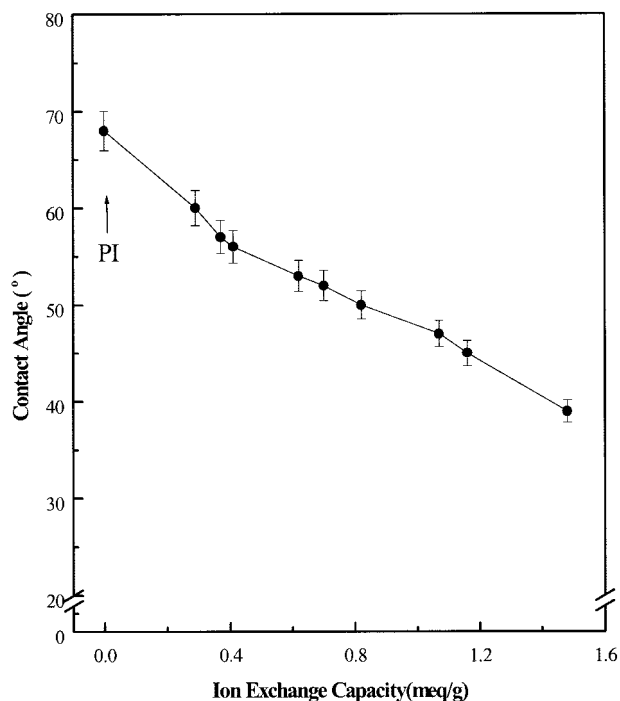[d] Temperature of maximum rate of weight loss.
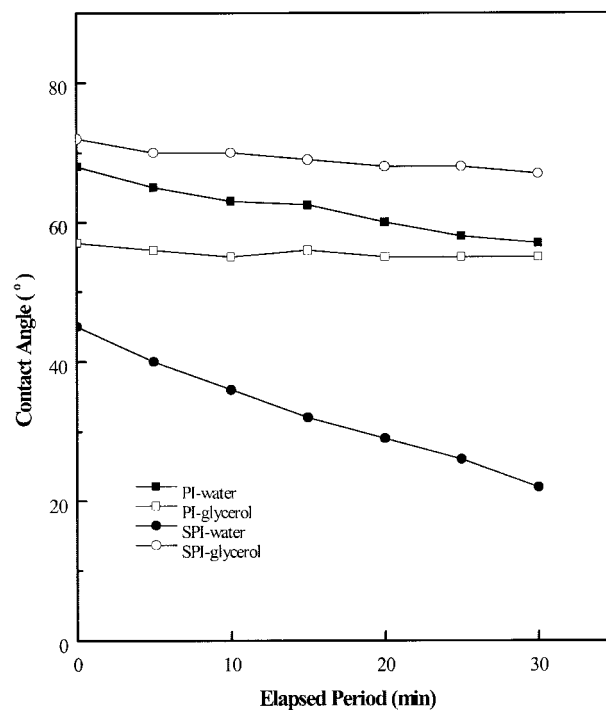[e] Final decomposition temperature.
[f] Reference 6.

and the solubility of used polymer surface.[13, 14] Both the probability of impingement and the amount of exothermic heat increased with the increase in content of the reagent and reaction temperature. Although the probability of contact between polymer and sulfonating agent increased, the generated heat probably disturbs the substituted reaction because this is a vigorous exothermic reaction. The solubility of polymer surface increased in proportion to the increasing IEC value. When this value was increased, it was probably easy to lump together because interaction between sulfonated polymers increases. Generally, the sulfonating substitution reaction is performed below room temperature because the sulfonating reaction is a vigorously exothermic reaction:[12–14]

The influence of the reaction time on the IEC value of SPI is shown in Figure 3. The extent of sulfonating reaction increased rapidly until a reaction time of 4 h. However, after that time, the IEC value gradually increased and was maintained at the increased level until the completion of the reaction. These results might relate to the equilibrium between reactants (PI and sulfonating agent) and products (SPI and byproduct).[13, 14]

Figure 6 The contact angle of water on the SPI films as function of IEC.

Figure 7 Contact angle changes of water and glycerol on the PI and SPI (IEC = 1.29) films.
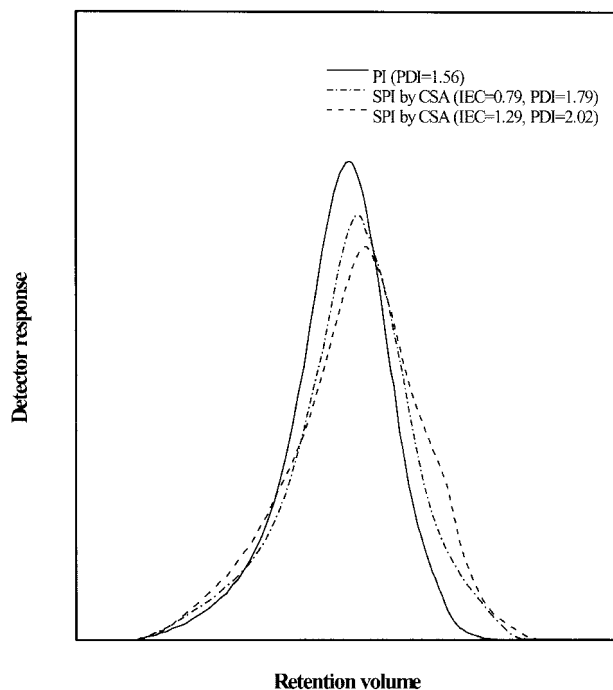
Figure 8 GPC of PI and SPI.

Table III Tensile Strength and Elongation of PI and SPI[a]

No.	Tensile Strength (kg/mm^2)	Elongation (%)
PI[b]	7.2 ± 0.2	7.7 ± 0.5
SPI (IEC = 0.79)	7.4 ± 0.2	7.4 ± 0.5
SPI (IEC = 1.29)	7.4 ± 0.2	7.2 ± 0.5
Ultem-1000[c]	5.6 ± 0.2	6.7 ± 0.5

[a] Measured at room temperature.
[b] Reference 6.
[c] Purchased from General Electric Specialty Plastics.

to the degree of sulfonation. These results were probably due to increased inter-/intramolecular association between the polar sulfonated sites and also to the increased molecular bulkiness.[15, 16] The rotation of the mainchain was hindered due to the introduction of —SO$_3$H groups along the backbone, and inter-/intramolecular force associating with the introduced polar groups was also increased by the newly conformed hydrogen bond, and so on.

The TGA curves of PI and SPI as a function of IEC value are shown in Figure 5. To assess the relative thermal stability, the initial decomposition temperature, T_i; 10% weight loss temperature, T_{10}; the maximum rate of weight loss temperature, T_{max}; and complete decomposition temperature, T_f, for each step were noted. The temperature of maximum rate of weight loss was confirmed by the DTG trace. These results are summarized in Table I. All the samples with different IEC value degraded with a similar TGA pattern in air. The weight loss up to 300 °C might be due to the loss of either absorbed moisture or residual solvents or due to the decomposition of the lower molecular weight chain degraded in the sulfonation reaction and residual reagent. The T_{max} was observed in the range of 580–610 °C. The thermal behavior was mostly similar to the DSC results, so it can also be explained in the same way as in the previous DSC case.

The enhancement of hydrophilicity yielded by the sulfonated polyimide derivatives is illustrated by the water–polymer film contact angle data represent in Figure 6. The contact angle of water–SPI film became diminished in proportion to the IEC value. The results of water–glycerol–polymer film contact angle data as a function of elapsed period are shown in Figure 7. The contact angle of water–SPI was decreased with treatment time.

Polyimide + Sulfonating agent $\rightleftharpoons$

Sulfonated polyimide + Byproduct

When the rate of reaction and inverse reaction became equal, the value was maintained after that state. The sulfonating reaction, a substitution reaction, went step by step, and the degree of sulfonation gradually increased as time went by, creating an equilibrium state.[14] From the results, the substitution reaction gradually went on with the reaction time to reach a limited IEC value; after that state, the reaction did not proceed.

The evaluation of glass transition temperature (T_g) versus the IEC value is shown in Figure 4. The values were calculated from the DSC thermograms. The slight increase in T_g was proportional

Table II Viscosity and Yield of PI and SPI[a]

No.	Viscosity (dL/g)	Yield (%)
PI[b]	0.79	>98
SPI (IEC = 0.79)	0.80	>95
SPI (IEC = 1.29)	0.86	>95

[a] Measured at room temperature.
[b] Reference 6.

Table IV Solubility of PI and SPI[a]

Solvent	δd	δp	δh	δt	Solubility[b] PI	SPI
Acetic acid	7.1	3.9	6.6	10.5	IS	IS
Acetic anhydride	7.8	5.7	5.0	10.9	IS	IS
Acetone	7.6	5.1	3.4	9.8	IS	IS
Chloroform	8.7	1.5	2.8	9.3	IS	IS
m-Cresol	8.8	2.5	6.3	11.1	S	IS
Diethyl ether	7.1	1.4	2.5	7.7	IS	IS
N,N-Dimethylacetamide	8.2	5.6	5.0	11.1	S	S
N,N-Dimethylformamide	8.5	6.7	5.5	12.1	S	S
Dimethylsulfoxide	9.0	8.0	5.0	13.0	S	S
1,4-Dioxane	9.3	0.9	3.6	10.0	IS	IS
Formamide	8.4	12.8	9.3	17.9	IS	IS
Formic acid	7.0	5.8	8.1	12.2	SW	IS
Glycerol	8.5	5.9	14.3	17.6	IS	IS
Methanol	7.4	6.0	10.9	14.5	IS	IS
N-Methyl-2-pyrrolidone	8.8	6.0	3.5	11.2	S	S
Nitrobenzene	9.8	4.2	2.0	10.9	S	PS
1-Propanol	7.8	3.3	8.5	12.0	IS	IS
Pyridine	9.3	4.3	2.9	10.7	SW	PS
Tetrahydrofuran	8.2	2.8	3.9	9.5	IS	IS
Toluene	8.8	0.7	1.0	9.1	IS	IS

[a] Besides continuously at 25°C for 7 days, when the sample was partial soluble in the solvent, that was heated at 70°C for 24 h.
[b] Where S is soluble, PS is partial soluble, SW is swell, and IS is insoluble in solvent.

Comparing between water and glycerol, the contact angle of glycerol–PI was lower than that of water–PI. The reason for this result could be explained by the fact that the surface tension of glycerol is less than that of water.[17, 18] On the other hand, the contact angle of glycerol–SPI was larger than that of water–SPI. The reason for the observed behavior could be that the enhanced hydrophilicity of SPI, with the introduced polar —SO₃H groups, would tend to pull water molecules into the interior of the SPI film by virtue of its hydrophilic attraction.[19] Therefore, the contact angle of water–SPI was less than that of glycerol–SPI.

The GPC results for PI and SPI are shown in Figure 8. Although a direct comparison of the molecular weight distribution of polymer was not possible because the molecular structure changed from PI to SPI, the influence of reaction conditions on molecular weight distribution was possible to investigate. As a result, the peak of the lower molecular weight as SPI was shown as a weak shoulder, and the maximum intensity of those peaks was slightly shifted to the lower molecular weight range. It can be deduced from these chromatograms that the degradation of

polymer and the hydrogen bond between the introduced —SO₃H groups might have occurred for the sulfonating reaction.[20] The viscosity of the polymer with various IEC values is shown in Table II. The viscosity value of polymers became slightly diminished in proportion to the increasing IEC value. Those results might be related to the degradation of polymer mainchain as in the previous GPC case.

The effect of degree of sulfonation on mechanical properties of SPI shows in Table III. Both tensile strength and elongation were slightly decreased with increasing degree of sulfonation.

The typical solubility of PI and SPI is listed in Table IV. All the polymers were dissolved well in some aprotic polar solvents, such as DMAc, NMP, DMF, and DMSO. However, SPI with a relatively higher IEC value was not dissolved in nitrobenzene and m-cresol. These results might be due to the change of solubility parameter as a consequence of introducing —SO₃H groups.[17, 18, 20]

CONCLUSION

Sulfonated polyimides were synthesized by CSA. The thermal and mechanical properties of SPI

were slightly dependent on degree of sulfonation. However, the solubility changed as a consequence of introducing —SO_3H groups. Hydrophilicity, as determined by water–film contact angle, could be varied over a wide ranged by controlling the degree of sulfonation. The degradation of mainchain during sulfonation reaction might have occurred and that was confirmed by GPC and changed viscosity. The overall properties of SPI were consistent with those of PI.

REFERENCES

1. Sroog, C.E.; Endrey, A.L.; Abramo, S.V.; Berr, C.E.; Edwards, W.M.; Olivier, K.L. Polymer 1965, 3, 1373.
2. Bessonov, M.I.; Koton, M.M.; Kudryatsev, V.V.; Laius, L.A. Thermally Stable Polymers. Consultants Bureau. (Plenum: New York, 1987.
3. Boutevin, B.; Ikada, Y.; Irie, M.; Tabata, Y.; Takekoshi, T. New Polymer Materials, L deritz & Bauer: Berlin, 1990.
4. Critchley, J.P.; Knight, G.J.; Wright, W.W. Heat Resistant Polymers. Plenum: New York, 1983.
5. Conly, R.T. Thermal Stability of Polymer. Marcel Dekker: New York, 1970.
6. Jeon, J-Y.; Tak, T-M. J Appl Polym Sci 1996, 60, 1921; 60, 2353; 61, 371; and 61, 529.
7. Fisher, D.; Eysel, H.H. J Appl Polym Sci 1994, 52, 545.
8. Goethals, E.J. Encyclopedia of Polymer Science and Technology; John Wiley & Sons: New York, 1970.
9. Goldstein, S.; Schmuckler, G. Ion Exchange Membr 1972, 1, 63.
10. Fisher, S.; Kumin, R. Anal Chem 1951, 27, 1191.
11. Johnson, B.C.; Yilgör, I.; Tran, C.; Iqbal, M.; Wightman, J.P.; Lloyd, D.R.; Mcgrath, J.E. J Polym Sci, Polym Chem Ed 1984, 22, 721 (1984).
12. Lee, J.; Marvel, C.S. J Polym Sci, Polym Chem Ed 1984, 22, 295.
13. Odian, G. Principle of Polymerization, 2nd ed.;, John Wiley & Sons, Inc.: New York, 1981.
14. Solomones, T.W. Fundamentals of Organic Chemistry; John Wiley & Sons, Inc.: New York, 1982.
15. Bunn, A.; Rose, J.B. Polymer 1993, 34, 1114.
16. Attwood, T.E.; Cinderery, M.B.; Rose, J.B. Polymer 1993, 34, 1322.
17. Othmer, K. Encyclopedia of Chemical Technology, 3rd ed.; John Wiley & Sons Inc.New York, 1984.
18. Kricheldrof, H.R. Handbook of Polymer Synthesis; Marcel Dekker: New York, 1992.
19. Moore, W.J. Physical Chemistry, 5th ed.; Longman: London, 1972.
20. Hinke, E.; Staude, E. J Appl Polym Sci 1991, 42, 2951.