Available online at www.sciencedirect.com

ScienceDirect

Polymer 48 (2007) 6210–6214

polymer

www.elsevier.com/locate/polymer

Polymer Communication

Water resistant sulfonated polyimides based on 4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BNTDA) for proton exchange membranes

Jingling Yan, Changpeng Liu, Zhen Wang, Wei Xing, Mengxian Ding*

Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China

Received 5 May 2007; received in revised form 7 July 2007; accepted 10 July 2007
Available online 18 July 2007

Abstract

A series of sulfonated polyimides (SPIs) were synthesized in *m*-cresol from 4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BNTDA), 4,4′-diaminodiphenylether-2,2-disulfonicacid (ODADS), and 4,4′-diamino-diphenyl ether (ODA) in the presence of triethylamine and benzoic acid. The resulted polyimides showed much better water resistance than the corresponding sulfonated polyimides from 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTDA) and ODADS, which is contributed to the higher electron density in the carbonyl carbon atoms of BNTDA. Copolyimides S-75 and S-50 maintained their mechanical properties and proton conductivities after aging in water at 100 °C for 800 h. The proton conductivity of these SPIs was 0.0250–0.3565 S/cm at 20 °C and 100% relative humidity (RH), and increased to 0.1149–0.9470 S/cm at 80 °C and 100% RH. The methanol permeability values of these SPIs were in the range of 0.99–2.36 $\times 10^{-7}$ cm^2/s, which are much lower than that of Nafion 117 (2×10^{-6} cm^2/s).

Keywords: 4,4′-Binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BNTDA); Sulfonated polyimides; Water resistance

1. Introduction

Recently, considerable attentions have been paid to proton exchange membrane fuel cells (PEMFCs) as a clean electric source for automobile, stationary, and portable power applications due to their lower weight, high efficiency, and low poison emission [1–3]. Proton exchange membrane (PEM) is a critical component in PEMFC. Perfluorosulfonate ionomers, such as Nafion, are the state-of-art membrane materials with features of high conductivity and excellent chemical stability [4–6]. However, because of their high cost, low operational temperature below 80 °C, and large gas crossover, many efforts have been made to develop alternative PEMs, especially sulfonated aromatic polymers [7–9].

Sulfonated polyimides have been studied by several groups as potential PEM materials [10–18]. Water resistance (including hydrolytic stability and solubility or swelling in water) of SPIs is an important factor that affects the fuel cell performance since the imide groups are relatively susceptible to decomposition due to the nucleophilic attack by water. The influence of the diamine structures on the hydrolytic stability of SPIs has been well investigated. It is known that SPIs derived from the diamine with higher basicity showed better hydrolytic stability. The separation of sulfonic acid groups from the aminophenyl rings and the introduction of aliphatic segments in both the main and the side chains are effective approaches to enhance the basicity of diamines [10–18]. Watanabe et al. [15,16] prepared SPIs from 1,4,5,8-naphthalene-tetracarboxylic dianhydride (NTDA), 3,3′-bis(sulfopropoxy)-4,4′-diaminobiphenyl (BSPA), and 10-decamethylenediamine (DMDA). Impressively, these SPI membranes showed comparable performance to Nafion in fuel cell at 80 °C and were durable for 5000 h without distinct degradation.

---

* Corresponding author.
E-mail address: mxding@ciac.jl.cn (M. Ding).

0032-3861/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2007.07.026

By far, most widely used six-membered dianhydride for SPIs is NTDA, except for 4,4′-ketone dinaphthalene 1,1′,8,8′-tetracarboxylic dianhydride (KDNTDA) recently employed by Okamoto et al. [19]. The hydrolysis of imide groups was mainly resulted from the nucleophilic attack of the water molecule on the carbonyl carbon atoms; the dianhydrides with higher electron density in carbonyl carbon atoms should produce polyimides with higher hydrolytic stability. The electron density of the carbonyl carbon atoms can be characterized by their electron affinity (E_a), and the lower the absolute values of E_a is, the higher the electron density is in carbonyl carbon atoms [20]. It has been reported that 4,4′-binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BNTDA) has a lower electron affinity, i.e. 3.7790 vs 4.0102 eV, than NTDA [21]. Therefore, in this paper, we present the synthesis of SPIs on the basis of BNTDA, 4,4′-diaminodiphenylether-2,2-disulfonic-acid (ODADS), and 4,4′-diamino-diphenyl ether (ODA). Furthermore, the SPIs based on BNTDA showed enhanced water resistance compared with the corresponding polymers from NTDA.

2. Experimental

2.1. Materials

4,4′-Binaphthyl-1,1′,8,8′-tetracarboxylic dianhydride (BNTDA) [22] and 4,4′-diaminodiphenylether-2,2-disulfonic-acid (ODADS) [12] were prepared according to the reported procedures. The other reagents used in this study were purchased from Shanghai Chemical Reagent Plant. 4,4′-Diamino-diphenyl ether (ODA) was purified by sublimation in vacuum. Triethylamine (Et_3N) and *m*-cresol were used after distillation. Other reagents were of analytical grade and used as received.

2.2. Synthesis of sulfonated polyimides based on BNTDA

A representative polymerization procedure is described as follows: 0.5400 g (1.5 mmol) of ODADS, 0.3004 g (1.5 mmol) of ODA, 0.8040 g (3.0 mmol) of BNTDA, 0.51 g (4.2 mmol) of benzoic acid, 0.36 g (3.6 mmol) of triethylamine, and 15 mL of *m*-cresol were placed in a three-necked, 100 mL round-bottom flask equipped with a mechanical stirrer, nitrogen inlet and outlet. The mixture was stirred at room temperature for 10 min and then heated at 80 °C for 2 h and then at 180 °C for 10 h. After cooling to 100 °C, 10 mL *m*-cresol was added to dilute the viscous solution. Then it was poured into 100 mL of ethanol with stirring. The fiberlike precipitate was collected by filtration and extracted with ethanol in a Soxhlet extractor for 24 h, and then dried in vacuum for 4 h to afford powder of sulfonated polyimide with the yield of 95%.

2.3. Membrane preparation and proton exchange

SPI films (in triethylammonium salt form) were prepared by casting their *m*-cresol solution (5%) at 100 °C for 8 h. Then the film was soaked in methanol for 24 h to remove the residual solvent and dried at 120 °C for 8 h in vacuum. The proton exchange was performed by boiling the films in 0.5 mol/L H_2SO_4 for 3 h and then immersing them in 2 mol/L H_2SO_4 at room temperature for 2 weeks. The films in proton form were thoroughly washed with deionized water.

2.4. Measurements

Fourier transform infrared (FT-IR) spectra were determined with a Bio-Red Digilab Division FTS-80 spectrometer. ^1H NMR (tetramethylsilane as an internal standard) spectra were recorded on a Varian Unity spectrometer at 400 Hz. Inherent viscosities were determined at 30 °C with an Ubbelohde viscometer, and the concentration was 0.5 dL/g in *m*-cresol. Thermogravimetric analysis (TGA) was performed with a Perkin–Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C/min in air. The films were dried at 120 °C or 3 h in vacuum and then balanced at 50% relative humidity for 2 days before measurements. The tensile measurements were carried out on an Instron model 1122 at room temperature at a rate of 5 mm/min. The relative humidity when testing was also 50%.

2.5. Proton conductivity

Proton conductivity of membranes was measured by a four-electrode AC impedance method from 0.1 Hz to 100 KHz, 10 mV ac perturbation and 0.0 V dc rest voltage. Impedance spectra were recorded using a Princeton Applied Research Model 273A Potentiostat (Model 5210 Frequency Response Detector, EG&G PARC, Princeton, NJ). The membranes were fixed in a measuring cell made of two outer gold wires to feed current to the sample and two inner gold wires to measure the voltage drops. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in water. The proton conductivity (σ) of the membranes was calculated using the following equation:

$$\sigma = \frac{L}{RA} \qquad (1)$$

where L, R, and A denote the distance between the two inner gold wires, the resistance of the membrane, and the cross-sectional area of the membrane, respectively.

2.6. Water uptake

Water uptake was measured by immersing an SPI sample into water at 80 °C for 6 h. Then the sample was taken out, wiped with tissue paper very quickly, and weighed on a microbalance. Water uptake was calculated from the following equation:

$$S = (W_s - W_d)/W_d \times 100\% \qquad (2)$$

where W_d and W_s are the weights of dry and corresponding water-swollen membranes, respectively.

2.7. Water resistance tests

Water resistance tests were performed by aging membrane sheets of SPIs in proton form in water at 100 °C for 200–800 h. After aging, the membrane sheets were dried at 120 °C for 3 h and then subjected to the characterizations, such as mechanical properties and proton conductivities.

3. Results and discussions

3.1. Synthesis of polymers

As shown in Scheme 1, a series of SPIs were synthesized in *m*-cresol from BNTDA, ODADS, and ODA in the presence of triethylamine and benzoic acid. The percent of ODADS in the diamines was 100, 75 and 50, and the polymers were coded as S-100, S-75, and S-50, respectively. Their inherent viscosity (in triethylammonium salt form) was in the range of 1.60–2.20 dL/g in *m*-cresol. The polyimides were proton-exchanged with 0.5 mol/L H_2SO_4 in boiling condition for 3 h and then with 2 mol/L H_2SO_4 at room temperature for 2 weeks [14]. The completion of proton exchange was confirmed by the disappearance of the peaks assigned for triethylamine in ^{1}H NMR spectra. The structures of polymers were further confirmed by FT-IR and the results are shown in Fig. 1. The absorption bands near 1707 cm^{-1} (asym C=O str), 1660 cm^{-1} (sym C=O str), and 1367 cm^{-1} (C–N str) were assigned to the characteristic absorption of imide ring groups and the bands near 1084 (asym S=O str) and 1026 cm^{-1} (sym S=O str) were assigned to the sulfonic acid groups. Furthermore, the intensities of the bands at around 1026 and 1084 cm^{-1} increased with the degree of sulfonation. BNTDA-based SPIs (in proton form) were soluble in DMSO and *m*-cresol at room temperature, as well as in DMAc and NMP on heating.

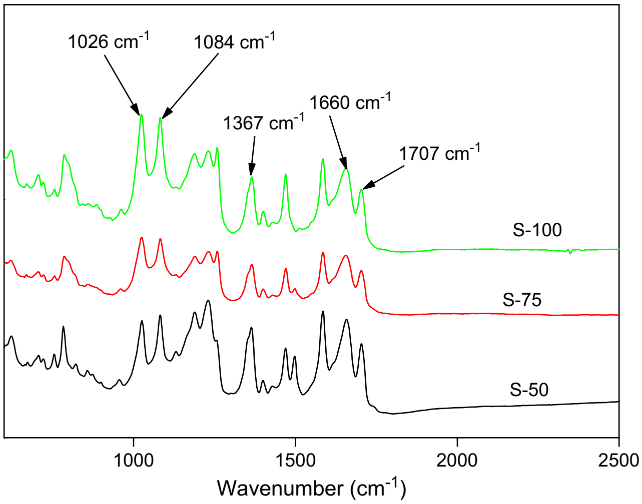
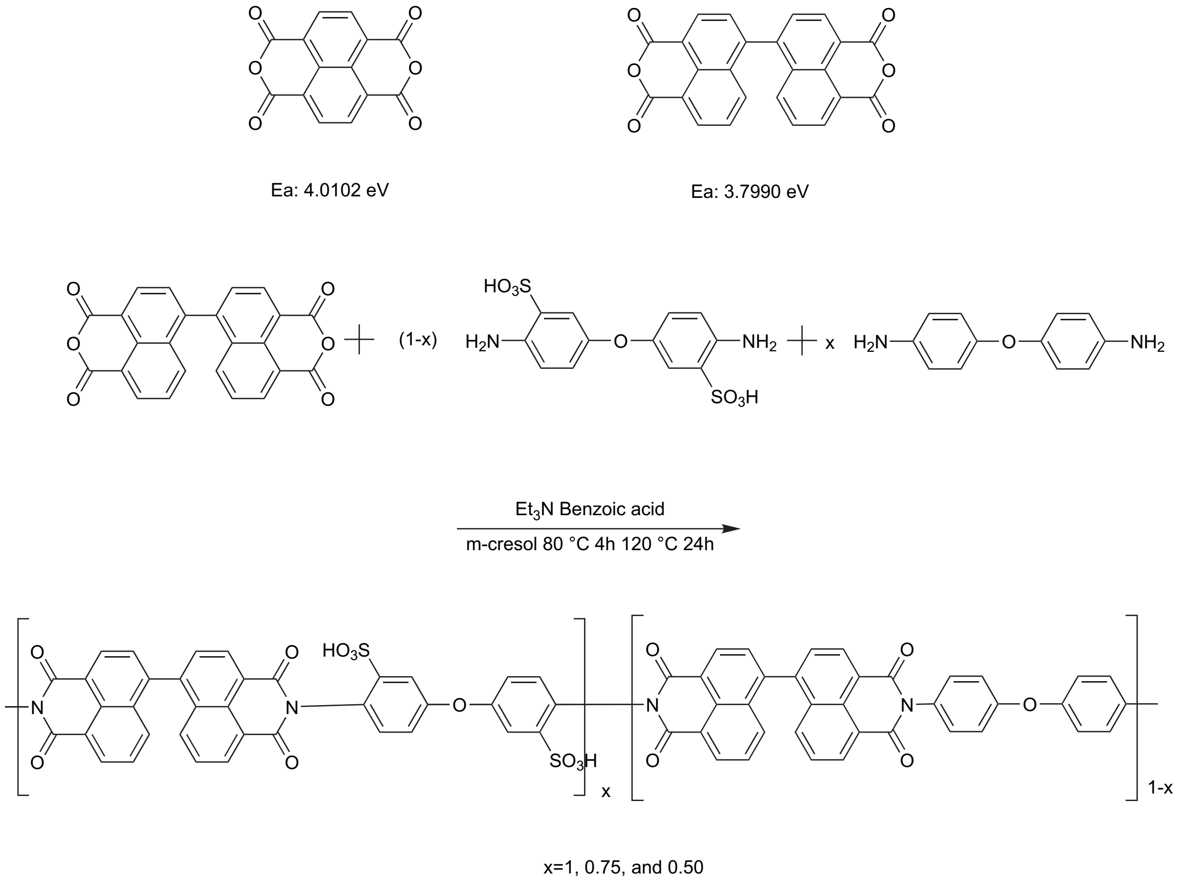


Fig. 1. FT-IR spectra of SPIs based on BNTDA.



Scheme 1. The electron affinity of NTDA and BNTDA and the synthesis of sulfonated polyimides derived from BNTDA.

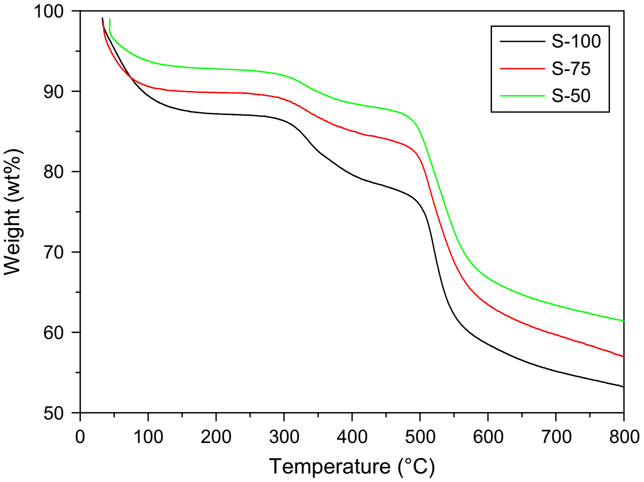


Fig. 2. TGA curves of SPIs based on BNTDA.

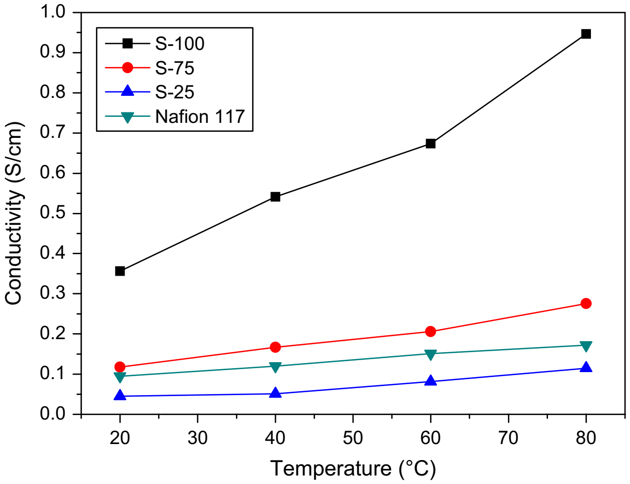


Fig. 3. Temperature dependence of the proton conductivity of BNTDA-based SPIs and Nafion 117 at 100% RH.

Thermal stability of BNTDA-based SPIs was investigated by TGA measurement. The TGA curves of SPIs are illustrated in Fig. 2. All SPIs showed three-step weight loss: the first from room temperature to 170 °C due to the loss of absorbed water, the second starting from 280 °C due to the degradation of sulfonic acid groups, and the third at around 500 °C due to the decomposition of polyimide backbones. The thermal stability of BNTDA-based SPIs was similar to that of SPIs from NTDA and ODADS [12].

3.2. Water uptake, proton conductivity, and methanol permeability

The ion exchange capacity (IEC), water uptake, and proton conductivity of BNTDA-based SPIs are listed in Table 1. Proton conductivity of the membranes (about 30 μm) of BNTDA-based SPIs was measured at 100% relative humidity (RH). The proton conductivity of these SPIs at 100% RH is a function of temperature, and increased linearly in general as the temperature increases (Fig. 3). Though all BNTDA-based SPIs have much higher IEC values compared with Nafion 117, their proton conductivity is in the same magnitude or even slightly lower (S-50) than those of Nafion 117. This is due to the strong acidity and unique phase-separation structure of Nafion, which is favorable for proton transport. Furthermore, the proton conductivity of BNTDA-based SPIs greatly depended on their IEC and water uptake. Higher IEC and water uptake led to higher proton conductivity.

The values of water uptake and the numbers of water molecules per sulfonic acid group (λ) were in the range of 38–83%, and 13–16, respectively. The homopolymers showed highest water uptake among these SPIs because of its highest IEC value. The water uptake values of BNTDA-based SPIs were lower than those of the corresponding polyimides from NTDA with an equal IEC value [12]. It can be rationalized in terms of the introduction of bulky, hydrophobic binaphthyl group.

The methanol permeability of BNTDA-based SPIs was investigated at 20 °C by the method in the literature [23] and the results are listed in Table 1. The methanol permeability values of SPIs were about one order of magnitude lower than that of Nafion. These properties will reduce the crossover of water and methanol, which is useful to enhance the performance of direct methanol fuel cells.

3.3. Water resistance

The water resistance of BNTDA-based SPIs was tested by aging their membrane sheets at 100 °C in water. After aging, the membrane sheets were dried in vacuum at 120 °C for 3 h, and then subjected to the characterizations such as mechanical properties and proton conductivities. After aging at

Table 1
The inherent viscosity, IEC, water uptake, and conductivity of BNTDA-based sulfonated polyimides

Polymer	η_{inh}[a] (dL/g)	IEC[b] (meq/g)	P_M (10^{-7} cm^2/s)	Water uptake (%)	λ (H_2O/SO_3^-)	Conductivity[c] (S/cm)			
						20 °C	40 °C	60 °C	80 °C
S-100	2.20	2.78	2.36	83	16	0.3565	0.5411	0.6734	0.9470
S-75	1.72	2.21	2.25	53	13	0.1174	0.1667	0.2058	0.2755
S-50	1.60	1.57	0.99	38	13	0.0450	0.0511	0.0811	0.1149
Nafion 117	–	0.91	20	40	24	0.0952	0.1231	0.1512	0.1720

[a] Inherent viscosity measured with 0.5 dL/g at 30 °C in *m*-cresol.
[b] Calculated values.
[c] At 100% relative humidity.

Table 2
Properties of BNTDA-based SPI membranes before and after aging in water at 100 °C

Polymer	Aging time (h)	Conductivity[a] (S/cm) 20 °C	Conductivity[a] (S/cm) 80 °C	Tensile strength (MPa)	Modulus (GPa)	Elongation (%)
S-75	0	0.1174	0.2755	101	1.46	35
S-75	250	0.1131	0.2710	97	1.33	23
S-75	400	–	–	97	1.26	22
S-75	800	0.1089	0.2602	95	1.22	16
S-50	0	0.0450	0.1149	110	1.35	40
S-50	200	0.0390	0.1053	108	1.33	30
S-50	400	–	–	103	1.26	26
S-50	800	0.0372	0.1012	94	1.03	22

[a] At 100% relative humidity.

Table 3
The water resistance comparison of SPIs based on NTDA/ODADS and BNTDA/ODADS

Polymer	IEC (meq/g)	Temperature aged (°C)	Time[a] (h)	Ref.
S-100	2.78	100	150	This study
S-75	2.21	100	>800	This study
S-50	1.57	100	>800	This study
NTDA–ODADS	3.37	50	0.17	[12]
NTDA–ODADS/ODA (1:1)	1.95	80	25	[12]
NTDA–ODADS/BAPB (1:1)	1.68	80	200	[12]
NTDA–ODADS/BAPHF (1:1)	1.73	80	11	[12]
NTDA–ODADS/BAPF (1:1)	1.71	80	13	[12]

[a] The time when the membranes lost their mechanical properties.

100 °C for 150 h, S-100 became brittle, whereas the membranes of S-75 and S-50 were not broken when they were folded to zero degree and then folded back after aging both at 100 °C for 800 h. The comparison of the properties of S-75 and S-50 before and after aging is listed in Table 2. S-75 and S-50 maintained their mechanical properties after aging at 100 °C for 800 h with a small decrease in tensile strength, modulus, and elongation. Furthermore, no appreciable difference was observed on proton conductivity values of S-75 and S-50 after aging.

The hydrolytic stability of SPIs from NTDA and BNTDA is compared in Table 3. It can be concluded that the usage of BNTDA improved greatly the hydrolytic stability of sulfonated polyimides. In NTDA-based polyimides, the two imide groups were located in one naphthyl ring. The electron density in the carboxyl carbon atoms was decreased due to the strong electron withdrawing of the other imide group. On the other hand, in BNTDA-based polyimides, the imide groups were separated into two different and non-coplanar naphthyl rings. The conjugation was broken and the withdrawing effect of one imide group on the other was weak. Therefore, the electron density in the carboxyl carbon atoms in BNTDA-based polyimide was much higher than that of NTDA. The higher electron density made the nucleophilic attack of the water molecule on the carboxyl carbon atoms more difficult, resulting in the extreme hydrolytic stability of polyimides.

4. Conclusion

In summary, we have demonstrated two novel sulfonated polyimides with high water resistance by the introduction of BNTDA with a higher electron density in the carboxyl carbon atoms. The copolymers maintained their reasonably high mechanical properties and proton conductivities after aging at 100 °C for 800 h, while SPIs from NTDA and ODADS could not keep their mechanical properties at 80 °C for more than 200 h. In addition, these SPIs also possessed acceptable proton conductivities and very lower methanol permeability. The results mentioned above indicate that SPIs from BNTDA are promising candidate materials for high temperature PEMFCs.

References

[1] Costamagna P, Srinivasan S. J Power Sources 2001;102:253.
[2] Mehta V, Cooper JS. J Power Sources 2003;114:32.
[3] Kordesech K, Simander G. Fuel cells and their applications. Weinheim: Wiley-VCH; 1996.
[4] Eisenberg A, Yeager HL. Perfluorinated ionomer membranes. In: ACS symposium series, vol. 180. Washington, DC: American Chemical Society; 1982.
[5] Inzelt G, Pineri M, Schultze JW, Vorofyntsev MA. Electrochim Acta 2000;45:240.
[6] Mauritz K, Am Moore RB. Chem Rev 2004;104:4535.
[7] Hickner MA, Ghassem H, Kim YS, Einsla BR, McGrath JE. Chem Rev 2004;104:4587.
[8] Li QF, He RH, Jensen JO, Bejerrum NJ. Chem Mater 2003;15:4896.
[9] Kerres JA. J Membr Sci 2001;185:3;
Yin Y, Yamada O, Tanaka K, Okamoto K. Polym J 2006;38:197–219.
[10] Gemes C, Mercier R, Sillion B, Cornet N, Gebel G, Pineri M. Polymer 2001;42:359.
[11] Zhang Ym, Litt MH, Savinell RF, Wainright JS. Polym Prepr (Am Chem Soc Div Polym Chem) 2000;41:1561.
[12] Fang J, Guo X, Harada S, Watari T, Tanaka T, Kita H, et al. Macromolecules 2002;35:9022–8.
[13] Guo X, Fang J, Watari T, Tanaka T, Kita H, Okamoto K. Macromolecules 2002;35:6707–13.
[14] Einsla BR, Hong YT, Kim YS, Wang F, Gunduz N, McGrath JE. J Polym Sci Part A Polym Chem 2005;42:862–74.
[15] Asano N, Aoki M, Suzuki S, Miyatake K, Uchida H, Watanabe M. J Am Chem Soc 2006;128:1762–9.
[16] Asano N, Miyatake K, Watanabe M. Chem Mater 2004;16:2841–3.
[17] Watari T, Fang J, Tanaka K, Kita H, Okamoto K, Hirano T. J Membr Sci 2004;230:111–20.
[18] Yin Y, Suto Y, Sakabe T, Chen S, Hayashi S, Mishima T, et al. Macromolecules 2006;39:1189–98.
[19] Chen X, Yin Y, Tanaka K, Kita H, Okamoto K. High Perform Polym 2006;18:637–65.
[20] Sroog CE. Prog Polym Sci 1991;16:561–694.
[21] Rusanov AL. Adv Polym Sci 1994;111:115–75.
[22] Gao J, Wang Z. J Polym Sci Part A Polym Chem 1995;33:1627–35.
[23] Li Y, Jin R, Cui Z, Wang Z, Xing W, Qiu X, et al. Polymer 2007;48: 2280–7.