

Synthesis and characterization of polydioxolane polyurethane ionomer

WEIHUA ZHU, XINLING WANG, BING YANG, LEI WANG, XIAOZHEN TANG
School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China
E-mail: zwh2@263.net

CHANGZHENG YANG
School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210008, People's Republic of China

A series of novel sodium salts of sulfonated polyurethane ionomers with polydioxolane as soft segment was successfully synthesized and their properties were characterized by means of Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and complex impedance analysis. As the ionization level increased, the compatibility of the hard segments and soft segments was improved and the glass transition region of soft segment became broader. The effects of ionization level, temperature, chemical components of soft segment on ionic conductivity of ionomers were investigated in detail. Adjusting the ionization level and incorporating PEG soft segment into the PDXL-PU ionomers, a new type of solid polymer electrolyte material with good mechanical properties and high ionic conductivity could be obtained.

© 2001 Kluwer Academic Publishers

1. Introduction

In recent years, solid polymer electrolytes (SPE) have been extensively studied due to their potential applications, such as extrathin and rechargeable lithium batteries, chemical sensors, all-solid-state displays, electrochromic devices, and so on [1–4]. However, most of the ionic conductive polymers investigated were based on complexes of polymers with salts. A typical example is the complex of polyethylene oxide (PEO) and lithium salts that displays high ionic conductivity of 10^{-5} – 10^{-4} S/cm at room temperature. These ionic conductors are characterized by a bi-ionic transport mechanism, in which both cations and anions have been found mobile. When used as a rechargeable battery under an electric field, the migration of anions toward the cathode causes polarization and results in a serious decay of the DC conductivity and the time-dependent increase of the cell impedance [5], which are harmful to electrochemical devices. Therefore, for a number of applications, ionic conductors with single-ion transport character are required [3]. As far as the single-ionic conductors are concerned, anionic sites are fixed on polymer chains via a covalent bond, these anions are unable to migrate because of the entangled high molecular weight polymer chains. As a result, cations are the only carrier ions that can transmit electrons, which can provide the stable current in DC polarization. According to the literature [6–9], most single-ionic conductors are polyblends of ionomer and polyether or copolymers of ionomer and PEO-based macromer. In general, polyblend electrolytes show poor mechani-

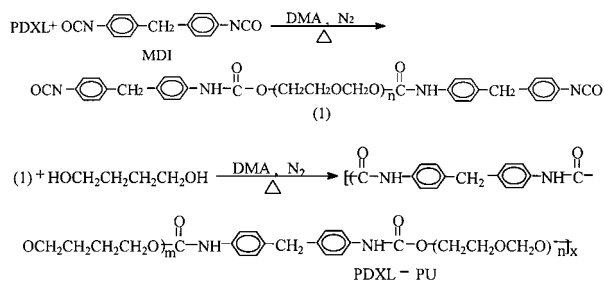
cal properties, and copolymer electrolytes exhibit low conductivity.

Various types of polyurethanes have been used as solid polymer electrolytes because of their good chemical stability, excellent mechanical properties, and low glass transition temperature (T_g) [2, 10]. Furthermore, polyurethane can be converted into ionomer that may have high ionic conductivity and good mechanical properties [3, 11–14]. Therefore, polyurethane ionomer is a good candidate for single-ionic conductor that can be used in practical devices.

2. Experimental

2.1. Materials

Diphenylmethane-4,4'-diisocyanate (MDI) (Aldrich Chemical Co.) was degassed and purified by vacuum distillation. Poly(ethylene glycol) (PEG) (M_n 1000, Aldrich Chemical Co.), polydioxolane (PDXL) (M_n 880, Aldrich Chemical Co.), poly(tetramethylene oxide) (PTMO) (M_n 1000, Aldrich Chemical Co.) were dried at 60°C in a vacuum oven for 72 h before use. 1,4-butanediol (BD) (Riedel-de Haën Co. Germany) was dried by refluxing over CaH_2 for 4 h to exclude trace water and then distilled under vacuum. The solvent *N,N'*-dimethylacetamide (DMA) (Shanghai Solvent Factory, Shanghai, China) was dried and distilled before use. Sodium hydride (NaH) (Aldrich Chemical Co., Milwaukee, WI) was a complex of 60% NaH and 40% paraffin oil. γ -Trimethylene sultone (TMST) was bought from Aldrich Chemical Co. Both NaH and TMST were used as received.



Scheme 1 Synthetic route to polydioxolane polyurethane (PDXL-PU).

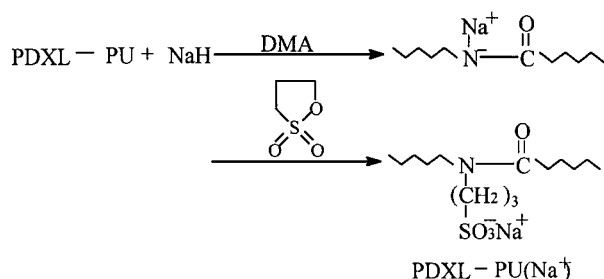
2.2. Preparation of polyurethane

Based on the molar ratio of polyether:MDI:BD 1:3:2, several segmented polyurethanes involving different polyether soft segment (PDXL, PEG, PTMO or PDXL/PEG) were prepared by a typical two-step condensation reaction. The reaction procedure is outlined in Scheme 1.

The segmented polyurethane was synthesized under nitrogen atmosphere, and 0.15 wt% dibutyltin dilaurate was used as catalyst. The solution of PDXL in DMA was added dropwise to the solution of MDI in DMA at 40°C. The mixture was stirred at 70°C for 4 h. Then the temperature was decreased to 40°C, and BD (solvated in DMA) was added into the reacting liquid within 0.5 h. To ensure complete reaction, the mixture was stirred at 75°C for an additional 2 h. Then the polymer solution was precipitated into a large amount of distilled water. After filtration, the deposition was put into alcohol for 24 h. The material obtained was dried in a vacuum-drying oven at 60°C for at least 48 h.

2.3. Synthesis of polyurethane ionomer

To prepare the ionomers, the polyurethane precursor was first dissolved in DMA (5 wt%). The mixture solution was cooled to -5°C in a salt-ice bath under nitrogen. And a stoichiometric amount of NaH was added into the solution under vigorous stirring. After 1 h, an equivalent amount of TMST was added and the mixture was stirred at room temperature for 1 h, and then at 50°C for another hour. Some solvent was removed through vacuum distillation. The ionomer was recovered by precipitation into toluene, further washed, and extracted with methanol to remove any residual TMST and NaH. Then ionomer was dried at 60°C for 24 h and then further dried in a vacuum drying oven at 60°C for 48 h. The reaction procedure is shown in Scheme 2.



Scheme 2 Synthetic route to polydioxolane polyurethane ionomer.

2.4. Preparation of solid polymer electrolyte film

Films of polydioxolane polyurethane ionomers were prepared by solution-casting. The ionomer was solvated in DMA, and the concentration was ~10 wt%. The solution was poured onto a Teflon plate. After the solvent evaporated at 60°C in an oven for 24 h, the films were transferred to a vacuum oven and further dried at 70°C for at least 48 h to remove the residual solvent.

2.5. Measurements

Infrared spectra were recorded on a Nicolet 170 SX FT-IR spectrophotometer, whose resolution was 2 cm⁻¹, in the range of 400–4000 cm⁻¹. The thermograms of polyurethane ionomers were recorded using a differential scanning calorimeter (Perkin Elmer DSC-2C) at a heating rate of 20 K/min from 150 K to 470 K. Dynamic mechanical analysis was carried out on a Rheovibron DDVII-C dynamic viscoelastometer over a temperature range beginning at 423 K and terminating at 473 K, the frequency used was 110 Hz, and the rate was 2 K/min. The frequency of sample collection was 1/2 K. The ionic mobility was measured with the voltage polarity reversing method described in a previous study [3]. Ionic conductivity measurements with alternating current were conducted on a 378 Electrochemical Impedance System produced by EG & G Princeton Applied Research in a frequency range of 10 Hz–10 MHz and a temperature range from room temperature to 120°C. The electrolyte films were cut to a required size, and were sandwiched between two silver electrodes. When measured, the cell was kept in a temperature-controlled dry box and the conductivity was tested at each temperature after equilibration for 30 min.

The ionic conductivity of the samples was calculated by

$$\sigma = (1/R_B)d/s \quad (1)$$

where σ was the ionic conductivity, d was the thickness of the sample, S was the area of the Ag electrode, and R_B was the bulk resistance of the sample.

3. Results and discussion

3.1. Composition of PDXL-PU ionomers

The ionization level was controlled by adjusting [NH]/[TMST] molar ratio. The predicted value of ionization level was determined by the designed molar ratio value of [EO]/[Na⁺], where EO represents the ether oxygen unit of the polyurethane ionomer investigated. As far as the sample PDXL-PU-20-Na⁺ is concerned, PDXL is the soft segment, PU means polyurethane, 20 is the designed molar ratio value of [EO]/[Na⁺], and Na⁺ is the cation ionomer.

3.2. Infrared studies

Infrared spectra of PDXL-PU are listed in Table I. In Table I, the strong infrared absorption at 1110 cm⁻¹ corresponds to the C–O–C stretching of the polyurethane soft phase. The C=O region is defined by two

TABLE I Infrared spectra of PDXL-PU

λ/cm^{-1}		Group	
3334	Strong	$\nu(\text{N—H})$	Amino group
1729	Very strong	$\nu(\text{C=O})$	Carbonyl (non-bonded)
1703	Very strong	$\nu(\text{C=O})$	Carbonyl (bonded)
1598	Strong	$\nu(\text{C=C})$	Aromatic ring
1413	Strong	$\nu(\text{C—C})$	Aromatic ring
1110	Very strong	$\nu(\text{C—O—C})$	Ether group

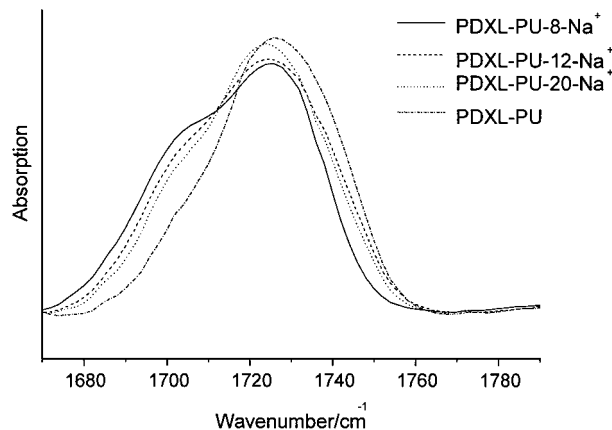


Figure 1 Infrared spectra of the carbonyl region of PDXL-PU ionomers.

modes in PDXL-PU. The first at 1729 cm^{-1} is assigned to the free C=O stretching vibration while the second is attributed to the hydrogen-bonded C=O stretching at 1703 cm^{-1} , which is due to amino groups located in the hard segment, hydrogen bonded with carbonyls.

Fig. 1 shows the C=O infrared region of PDXL-PU and PDXL-PU ionomers at different ionization levels. The infrared spectra was normalized to the CH_2 region (3000 to 2770 m^{-1}) in order to compensate for differences in signal intensity due to varying sample thickness and sample composition. It is obvious that the free carbonyl absorption peak at about 1730 cm^{-1} decreases, whereas the hydrogen-bonded carbonyl absorption peak at about 1703 cm^{-1} increases gradually as the ionization level increases. This indicates that the microphase separation of PDXL-PU ionomer systems increases with the increase of ionization level, which is consistent with the results in the literature [3].

3.3. Differential scanning calorimetry (DSC) analysis

DSC thermograms of 1:3:2 series polyether polyurethanes are shown in Fig. 2. DSC results are listed in Table II.

As shown in Fig. 2 and Table II, the glass transition temperature of the soft segment increases and the temperature range of the glass transition becomes broader with the increase of PEG content. All these demonstrate that PEG is compatible with PDXL and the introduction of PEG into this system may improve the phase compatibility of soft segments and hard segments. Results also show that T_g of PDXL-PU is 221.4 K , which is 24.6 K below T_g of PEG-PU, similar to that of PTMO-PU. This suggests that the soft segment of PDXL-PU

TABLE II DSC data of 1:3:2 series

Samples	T_g (K)			ΔC_p (J/g deg)
	Onset	Midpoint	ΔT	
PDXL-PU	213.7	221.4	71.1	0.3864
PDXL-PEG-PU 1:1	218.5	228.2	88.6	0.5166
PDXL-PEG-PU 1:2	233.8	244.3	83.6	0.5208
PEG-PU	239.2	246.0	65.1	0.5964
PTMO-PU	211.5	226.6	84.8	0.3696

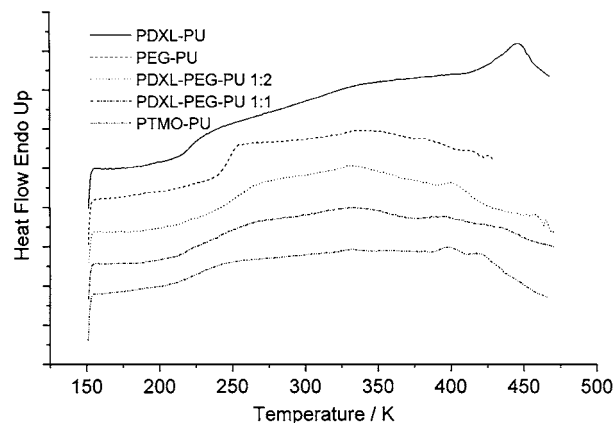


Figure 2 DSC curves of 1:3:2 series polyether polyurethanes.

has high ether group density and good flexibility, therefore, PDXL-PU can be used in the field of solid polymer electrolytes (SPE) as an excellent polymer host.

3.4. Dynamic mechanical thermal analysis (DMA)

DMA results of polyurethane ionomers, expressed as the absolute modulus ($|E|$) versus T on logarithmic scales are shown in Fig. 3 and the DMA data are listed in Table III.

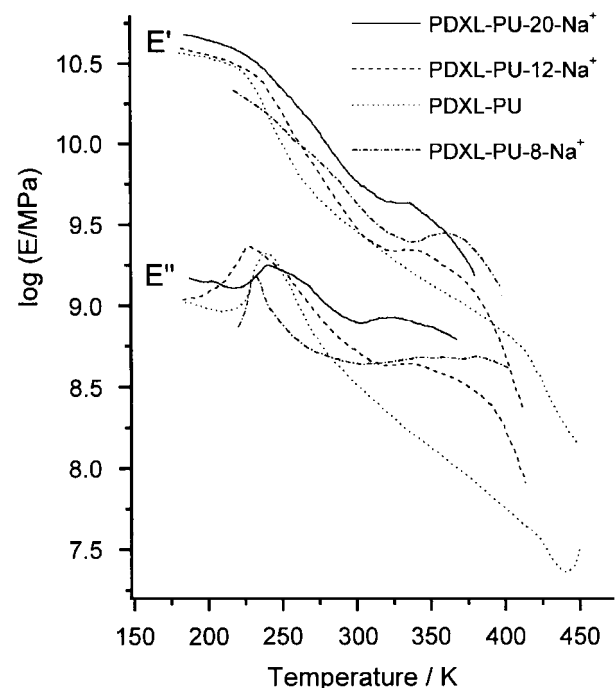


Figure 3 Dynamic mechanical analysis spectra of PDXL-PU and PDXL-PU ionomers.

TABLE III DMA data of PDXL-PU and PDXL-PU ionomers

Samples	PDXL-PU	PDXL-PU-8-Na ⁺	PDXL-PU-12-Na ⁺	PDXL-PU-20-Na ⁺
T _g (K)	229.8	221.8	216.2	226.8

As shown in Fig. 3, the DMA spectrum of PDXL-PU exhibits a typical two-phase character, which is due to the existence of microphases of both hard segments and soft segments in the bulk. According to previous assignment [10], thermoplastic polyurethanes are diblock, flexible elastomers consisting of a soft phase (polyether or polyester) reinforced by condensation with a hard phase. As it is known, thermoplastic segmented polyurethanes are linear $-(A-B)_n-$ block copolymers. They consist of relatively flexible soft segments (SS) and stiff hard segments (HS). Because of the existence of the strong hydrogen bonding between the hard segments, as well as the thermodynamically incompatibility between the hard and soft segments phase, the glassy or semi-crystalline HS domains act as thermoreversible physical crosslinks and reinforcing fillers, while the SS phase provides the flexibility of these elastomers. This phase-segregated morphology promotes hydrogen bonding within the hard domain between urethane C=O and N-H moieties on adjacent polymer chain segments.

Compared with the unionized sample, all the samples of PU ionomers have evident rubbery plateau zones in the $E'-T$ curves. As the ionization level increases (molar ratio $[EO]/[Na^+]$ decreases), the position of the plateau zone shifts to a higher temperature region, along with widening of the plateau zone. This suggests that the hard segments of ionomer samples aggregate to form microzones that are physical supporting points in the bulk.

As shown in Table III, glass transition temperatures of ionomers are all lower than the unionized one because of the increase of microphase separation. Thus is consistent with research results obtained by Schilov and coworkers [15]. In polyurethane ionomers, the formation of ionic aggregates leads to suppression of crystallization of the polyether soft segments. It can be noted that inhibition of polyether chain crystallization favours decreasing the glass transition temperature of the polyurethane ionomers investigated. The PDXL-PU-20-Na⁺ sample has a higher T_g than the ones of higher ionization level. It demonstrates that the separation of microphases in this bulk increases with the ionization level. The PDXL-PU-12-Na⁺ sample has the lowest T_g , therefore, the degree of microphase separation is the greatest.

3.5. Ionic conductivity

Fig. 4 shows the temperature dependence of ionic conductivity of PDXL-PU series ionomers at different ionization levels. Fig. 5 shows the temperature dependence of ionic conductivity of PDXL-PEG-PU series ionomers with different PEG contents.

The experimental data in Fig. 4 and Fig. 5 indicate that the ionic conductivities of all ionomer samples ap-

parently increase with increase of temperature. This can be easily understood on the basis of the ion transport mechanism in SPE. For a SPE material under the electric field, ion transport mainly occurs in the amorphous region of the polymer matrix and is associated with the local segmental motions of polymer chains [16]. As the temperature increases, the mobility of polymer chains increases, and the fraction of free volume in the SPE system increases accordingly, which leads to the increase of ionic conductivity of the solid polymer electrolyte.

As shown in Fig. 4, the ionization level has a great effect on ionic conductivity of PDXL-PU ionomers at room temperature, while, at temperatures above 90°C, ionic conductivities of samples with different ionization level are similar. Results also show that the ionic conductive property of PDXL-PU ionomer is lower than that of PEG-PU ionomer.

Fig. 5 reveals that when $[EO]/[Na^+]$ is kept constant, ionic conductivity of the sample increases with the incorporation of PEG soft segment. Ionic conductivity of $2 \times 10^{-5} \text{ Scm}^{-1}$ can be reached at 100°C and at room temperature ionic conductivity is above 10^{-7} Scm^{-1} ,

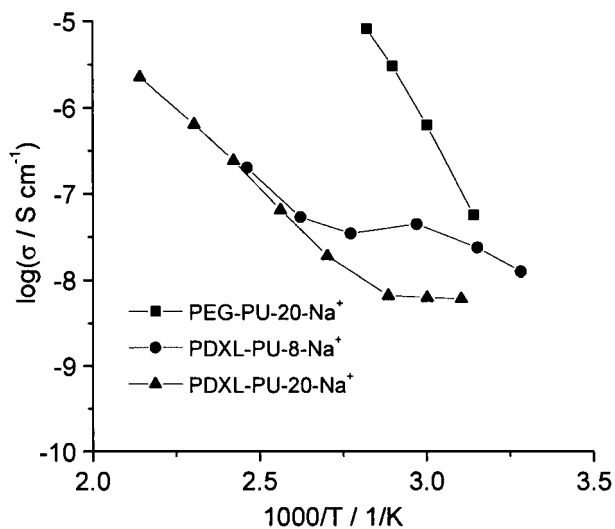


Figure 4 Effect of temperature on ionic conductivity of PDXL-PU ionomers.

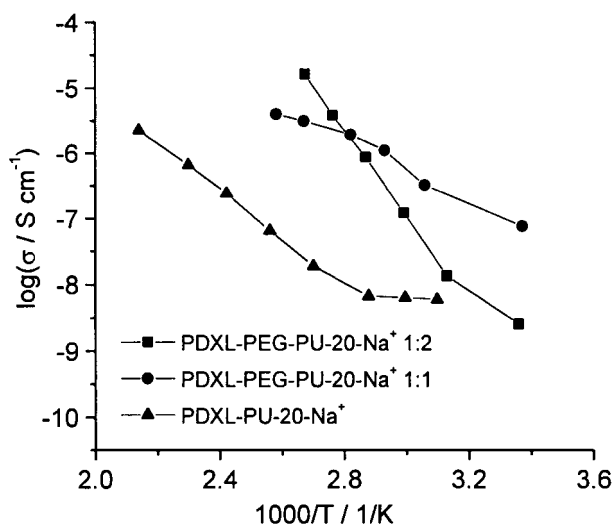


Figure 5 Effect of temperature on ionic conductivity of PDXL-PEG-PU ionomers.

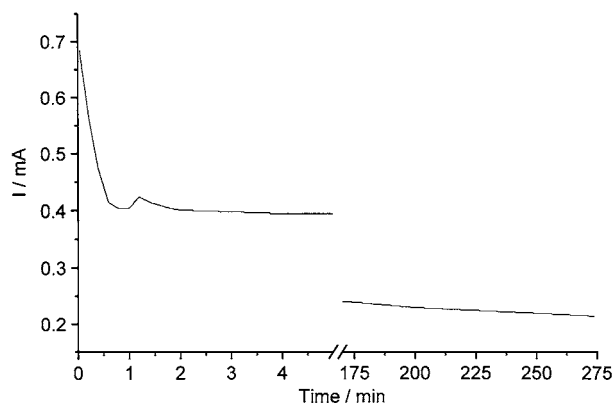


Figure 6 Current-time cure of PDXL-PU-20- Na^+ after the polarity is reversed at 25°C. The polarization time is 1 h and polarization voltage is 3.0 V.

which is still higher than that of a poly(ethylene oxide)/salt complex. It is due to the incorporation of PEG into the PDXL-PU ionomer system as soft segment; the ordered structure of PDXL segment is destroyed and amorphous domains of soft segments are obtained, which helps improve ionic conductivity.

In addition, there is no linear relationship found in Fig. 4 and Fig. 5, which indicates that, for two ionomer systems, the temperature dependence of conductivity could not be well expressed by the Arrhenius equation.

3.6. Ion transport number

In order to verify the assumption of the single ion transport mechanism of PDXL-PU ionomers, ion mobility of the PDXL-PU-20- Na^+ sample was measured with the voltage polarity reversing method. Fig. 6 shows the typical current-time curve of PDXL-PU ionomer after the reversal of the applied voltage polarity. There is only one shoulder peak on the curve within the 275 min experiment. This result demonstrates that the flight time of the cation is 1.35 min, and that of the anion is longer than 275 min. So it is deduced that the cation transport number is larger than 0.99. This result suggests that the PDXL-PU ionomer system is characterized by a single-ion transport mechanism.

4. Conclusions

A series of novel polydioxolane polyurethane ionomers with different ionization levels were prepared and characterized by various methods. The new PDXL-PU

ionomers exhibit good film-forming ability, typical elastomeric behavior, high conductivity, and are characterized by a single ion transport mechanism. The ionization level, temperature, chemical components of the soft segment significantly influence the ionic conductivity of the ionomers. Through controlling the ionization level and chemical components of the soft segment, we can obtain very promising ionic conductive polymer electrolytes with high ionic conductivity and good dimensional stability. For the PDXL-PU series ionomers investigated, the temperature dependence of conductivity does not follow the Arrhenius equation.

Acknowledgements

The authors are grateful to the National Natural Science Foundation of China for its financial support of this research.

References

1. L. WANG, B. YANG, X. L. WANG and X. Z. TANG, *J. Appl. Polym. Sci.* **71** (1999) 1711.
2. X. L. WANG, H. LI, X. Z. TANG and F. C. CHANG, *J. Polym. Sci., Polym. Phys.* **37** (1999) 837.
3. H. S. XU and C. Z. YANG, *ibid.* **33** (1995) 745.
4. M. SHILATA, T. KOKAYASHI, R. YOSOMIYA and M. SEKI, *Eurp. Polym. J.* **36** (2000) 85.
5. K. ONISHI, M. MATSUMOTO and Y. NAKACHO, *Chem. Mater.* **8** (1996) 469.
6. D. BENRABAH, S. SYLLA and F. ALLOIN, *Electrochim Acta* **40** (1995) 2259.
7. S. S. ZHANG, Z. H. DENG and G. X. WAN, *J. Macromol. Sci. Chem.* **A29**(1) (1992) 77.
8. T. FUJINAMI, A. TOKIMIMUNE and M. A. METTA, *Chem. Mater.* **9** (1997) 2236.
9. Z. DENG, Q. XU and Y. ZHENG, *Gong Neng Cai Liao* (Chinese) **5** (1991) 22.
10. A. FERRY, P. JACOBSSON, J. D. VANHEUMEN and J. R. STEVENS, *Polymer* **37** (1996) 937.
11. X. WEI and X. H. YU, *J. Polym. Sci., Polym. Phys.* **35** (1997) 225.
12. B. K. KIM and Y. M. LEE, *Colloid. Polym. Sci.* **270** (1992) 956.
13. J. P. SANTERRE and J. L. BRASH, *Ind. Eng. Chem. Res.* **36** (1997) 1352.
14. S. A. VISSER and S. L. COOPER, *Macromolecules* **24** (1991) 2576.
15. V. V. SHILOV, V. V. SHEVCHENKO, P. PISSIS and N. S. KLIMENKO, *Solid State Ionics* **120** (1999) 43.
16. Y. SUNGHOE, I. KIMIO, J. M. WILLIAM and L. H. SHAW, *Macromolecules* **28** (1995) 5063.

Received 24 October 2000
and accepted 16 July 2001