

Study of Polyurethane/Sulfonated Dimethyl Fumarate Complex

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ABSTRACT: In this study linear polyether polyurethanes (PU) and sulfonated dimethyl fumarate (SDMF) were successfully synthesized and a series of novel solid polymer electrolytes, based on the complexes of PU and SDMF, were prepared. Fourier transform-Raman spectroscopy (FT-Raman), ¹H-NMR, differential scanning calorimetry (DSC), atomic force microscopy (AFM), and complex impedance analysis were utilized to investigate the chemical structure, microscale morphology, and ionic conductive property of this system. Results show that the ionic conductivity of the PU/SDMF series increases with increasing temperature. In the salt concentration range investigated, there is a maximum ionic conductivity for the PU/SDMF system. When the molar ratio of the ether oxygen and sodium cation is about 24, the optimum compatibility between the hard and soft segments is realized and the highest soft-segment T_g is reached. A further increase in salt concentration causes the aggregation and precipitation of SDMF, and the decrease of the soft-segment T_g . © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 67–74, 2002; DOI 10.1002/app.10205

Key words: polyurethane; sulfonated dimethyl fumarate; ionic conductivity; morphology; solid polymer electrolytes

INTRODUCTION

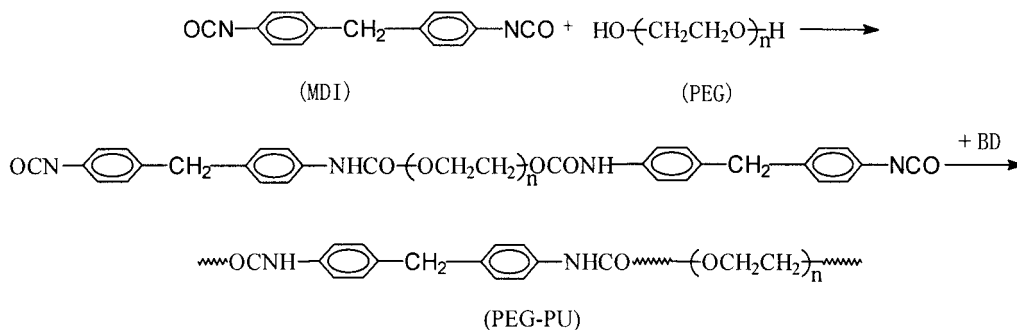
Since the pioneering work by Wright^{1–3} on ion conduction in a polyethylene oxide (PEO)/lithium salt complex was published, solid polymer electrolytes (SPE) have been studied with much interest for their potential applications in solid-state electrochemical devices.^{4–7} The main advantages of polymer electrolytes are favorable mechanical properties, ease of fabrication of thin films of de-

sirable sizes, and an ability to form effective electrode–electrolyte contacts.⁸ Most of the researchers have concentrated on designing novel polymer electrolytes possessing high ionic conductivity, good mechanical properties, and thermal stability for technological applications.⁹ Sodium-ion-conducting polymer electrolytes^{10–12} have been investigated based on PEO, polypropylene oxide (PPO), or polybismethoxy ethoxy phosphazene (MEEP) complexed with NaI, NaClO₄, NaSCN, or NaCF₃SO₃. However, little has been reported for polymer/organic salt complex systems. The conventional SPE based on organic polymer matrices, which dissolve inorganic salts, are referred to as *bi-ionic* conductors.⁴ In such bi-ionic conductors, the migration of anions toward the cathode

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Scheme 1

causes polarization and results in a serious decay of the DC conductivity and time-dependent increase of the cell impedance.¹³ These electrolytes are unsuitable for a rechargeable battery.

Recently, various types of polyurethanes (PU) have been used as host matrices of SPE because of their good chemical stability, excellent mechanical properties, and low glass-transition temperature.^{4,14–16} In the present study we report a novel polymer electrolyte system based on the complexes of PU and organic sodium salt, sulfonated dimethyl fumarate (SDMF). We expect that the large size of the SDMF anion ($\text{C}_6\text{H}_9\text{O}_4\text{SO}_3^-$) hinders the migration of anions toward the cathode under electric field, eventually minimizing the polarization. Therefore, sodium cations become the only carrier ions that can transmit electrons in the system. Several experimental techniques such as $^1\text{H-NMR}$, FT-Raman, atomic force microscopy (AFM), and complex impedance analysis are employed to characterize this polymer electrolyte system. The major objective was to investigate the effect of SDMF content on the morphology and ionic conductive property of PU/SDMF complexes.

EXPERIMENTAL

Materials

Polyethylene glycol (PEG, $M_n = 1000$; Aldrich Chemical Co., Milwaukee, WI) was dried at 70°C in a vacuum oven for 48 h before use. 4,4'-Methylenebis(phenyl isocyanate) (MDI; Aldrich) was purified by vacuum distillation. 1,4-Butanediol (BD; Riedel-de Haën, Seelze, Germany) was dried by refluxing over CaH_2 for 4 h to exclude trace water and then distilled under vacuum. The solvent *N,N'*-dimethyl acetamide (DMA; Shanghai

Solvent Factory, China) was dried and distilled before use. Dimethyl fumarate (DMFu), sodium hydrogen sulfite (NaHSO_3), dimethyl sulfoxide (DMSO), and calcium hydride (all from Aldrich) were used without further purification.

Synthesis of Polyurethane and Sulfonated Dimethyl Fumarate

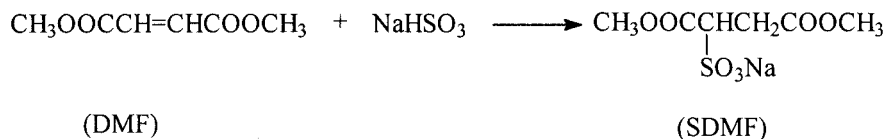
A polyethylene glycol polyurethane (PEG-PU) material (MDI : BD : PEG = 3 : 2 : 1) was prepared by a typical two-step condensation reaction. The reaction procedure is outlined in **Scheme 1**.

The segmented polyurethane was synthesized under nitrogen atmosphere, and 0.15 wt % dibutyltin dilaurate was used as catalyst. The solution of PEG in DMA was added dropwise to the solution of MDI in DMA at $50\text{--}60^\circ\text{C}$ and stirred for 1 h. Then BD was slowly added dropwise and stirred for an additional 1 h. To ensure a complete reaction, the mixture was stirred at 80°C for 2.5 h. Then the polymer solution was precipitated into a large amount of distilled water. After filtration, the precipitate was put into ethanol for 24 h. The material obtained was dried in a vacuum-drying oven at 60°C for at least 48 h.

The sulfonated dimethyl fumarate (SDMF) was prepared by dissolving DMFu and NaHSO_3 in methanol and water solution and refluxing at 80°C for 8 h. The solvent was removed under vacuum. The product was extracted by DMSO, precipitated by an abundant amount of acetone, and dried under vacuum at 60°C for 24 h. The reaction route is shown in **Scheme 2**.

Preparation of Polymer Films

Films of PEG-PU/SDMF complex were prepared using a solution-cast technique. The typical procedure was carried out by dissolving the appro-



Scheme 2

appropriate amount of the PEG-PU and SDMF in DMA solvent, and then pouring the solvent mixture 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 60°C for at least 24 h to remove the residual solvent.

Characterization

Differential scanning calorimetry (DSC) thermograms were recorded over the temperature range -100 to 100°C using a Perkin-Elmer DSC2-C instrument (Perkin Elmer Cetus Instruments, Norwalk, CT) at a heating rate of 10°C min⁻¹. Fourier transform (FT)-Raman spectra with a wavenumber resolution of 2 cm⁻¹ were recorded at 25°C using a Bruker IFS66 (Bruker Instruments, Billerica, MA) with a Raman module FRA 106 and a near infrared YAG laser with wavelength 1064 nm. ¹H-NMR spectra (300 MHz) were recorded on a Bruker ARX 300 spectrometer at 25°C using chloroform-*d* as a solvent and TMS as an internal standard. AFM analysis was carried out on a Nano-Scope IIIa SPM analyzer (Digital Instruments, Santa Barbara, CA) at 25°C utilizing the Tapping mode. Ionic conductivity measurements with alternating current were conducted on an HP 4192A (Hewlett-Packard, Palo

Alto, CA) impedance analyzer in the frequency range from 10 to 10⁶ Hz over the temperature range 25–100°C. The films were cut to a required size (10 mm in diameter and 0.2–0.3 mm in thickness) and were sandwiched between two silver electrodes.

The ionic conductivity of the samples was calculated by

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

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

RESULTS AND DISCUSSION

Structure of SDMF

The structure of SDMF was characterized by FT-Raman and ¹H-NMR techniques. Figure 1 shows the 1000–1800 cm⁻¹ region of the Raman spectrum of DMFu and SDMF. It can be seen that, after DMFu was sulfonated by NaHSO₃, the C=C stretching band at about 1658 cm⁻¹ disappears entirely and a new band at about 1060 cm⁻¹ ap-

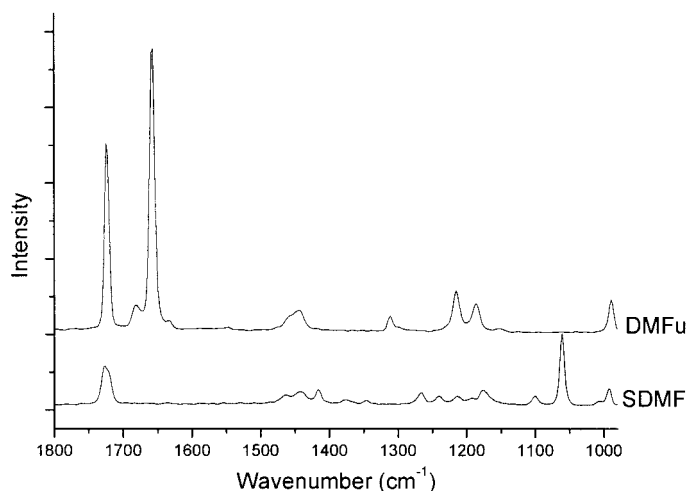


Figure 1 Raman spectra in the 1000–1800 cm⁻¹ region for DMFu and SDMF.

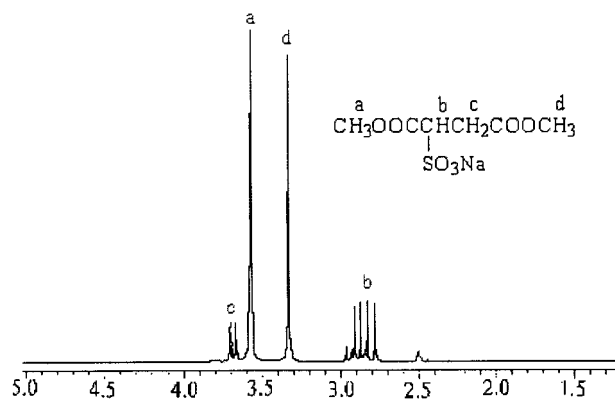


Figure 2 $^1\text{H-NMR}$ spectra of SDMF in CDCl_3 at 25°C .

pears in the Raman spectrum of SDMF. This result indicates that the expected addition reaction between DMFu and NaHSO_3 indeed took place. Figure 2 gives the $^1\text{H-NMR}$ spectrum of SDMF. It is obvious that there are different chemical shifts, corresponding to four kinds of protons at 2.86, 3.38, 3.56, and 3.68 ppm, respectively; the ratios are approximately 3 : 2 : 1 : 3. This is consistent with the expected structure of SDMF. In addition, there are some small peaks visible in Figure 2, which might be associated with the formation of by-product in the addition reaction between DMFu and NaHSO_3 .

Differential Scanning Calorimetry

The glass-transition temperature (T_g) of the PU/SDMF system was measured by DSC to evaluate

the compatibility between the hard and soft segments after introducing SDMF into the PU elastomer. The DSC thermograms of the PU/SDMF series are shown in Figure 3 and DSC data are listed in Table I. It is noted that $[\text{EO}]/[\text{Na}^+]$ here is the molar ratio of the ether oxygen atom and sodium cation, which is utilized to indicate the concentration of doped salt. The higher the $[\text{EO}]/[\text{Na}^+]$ ratio, the lower the salt concentration.

It can be found that the T_g of the PEG soft segment increases dramatically when a small amount of SDMF is introduced into the PU matrix. Results show that the T_g of the PU/SDMF-24 sample is about 15°C higher than that of PU without SDMF. However, a further addition of the salt causes the T_g to decrease. The former is attributed to the improved phase compatibility between the hard and soft segments brought about by the introduction of SDMF into the PU host matrix.¹⁴ The solvation of the sodium cation by the PEG soft segment partially arrests the local motion of the polymer segment by the formation of transient crosslinks, leading to an increase in the soft-segment T_g . On the other hand, the coordination between sodium cation and carbonyl group in the urethane linkage causes breaking of hydrogen bonding and rearrangement of the hard-segment microdomains.^{17,18} More hard-segment chains enter soft-segment regions, thus restricting the movement of soft-segment chains and resulting in a higher soft-segment T_g .

When the salt concentration is further increased ($[\text{EO}]/[\text{Na}^+] < 24$), the soft-segment T_g

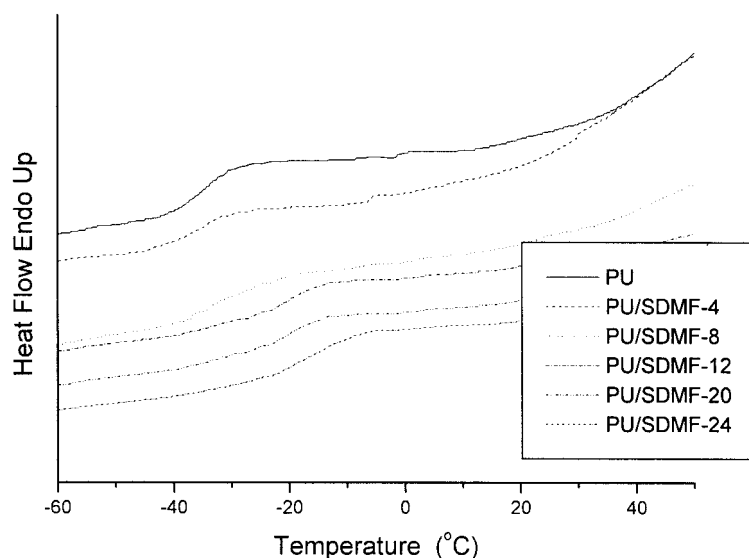


Figure 3 DSC thermograms of PU/SDMF series.

Table I DSC Data of PU/SDMF Series

Sample	[EO]/ [Na ⁺]	T_g (°C)		ΔC_p (J g ⁻¹ degree)
		Onset	Midpoint	
PU/SDMF-4	4	-37.9	-31.2	0.31
PU/SDMF-8	8	-35.5	-29.0	0.32
PU/SDMF-12	12	-28.6	-22.3	0.31
PU/SDMF-20	20	-28.2	-20.3	0.31
PU/SDMF-24	24	-29.5	-20.2	0.48
PU	—	-40.7	-34.9	0.46

apparently drops, as shown in Figure 3 and Table I. This result can be assigned to the plasticizing effect generated by the formation of a charge-neutral contact ion pair. With increasing salt concentration, the coulomb attractions in polymer/salt complexes become strong, giving rise to the formation of neutral ion pairs and neutral multiplets. The neutral ion pairs and multiplets lose the ability to provide ionic crosslinks in the system. Therefore, the solvated degree of the sodium cation with the oxygen of soft-segment ether linkage is decreased. Consequently, the soft-segment mobility is enhanced and the soft-segment T_g is reduced.

FT-Raman Spectroscopy

Figure 4 shows the 500–1200 cm⁻¹ region of the Raman spectrum as a function of salt concentration for the PU/SDMF series. According to previous literature,¹⁹ the Raman band at about 1030–1065 cm⁻¹ corresponds to the $\nu_s(\text{SO}_3)$ mode of the

[C₆H₉O₄SO₃⁻] anion. The low-frequency bands at about 1032 and 1042 cm⁻¹ were assigned to so-called free anions not interacting directly with sodium cations and contact ion pairs, respectively. The component at about 1052–1056 cm⁻¹ was attributed to triple ions and higher-order aggregates. However, it is not possible to distinguish between free anions and solvent-separated ion pairs because the frequency shift for the latter is expected to be small. From the multicomponent nature of the $\nu_s(\text{SO}_3)$ mode at about 1030–1065 cm⁻¹, we conclude that there are extensive cation–anion interactions present in the PU/SDMF system investigated.

As seen in Figure 4, the fraction of free anions and ion pairs increases with increasing salt concentration until [EO]/[Na⁺] reaches 12, and then falls off slightly at higher concentrations. Meanwhile, the feature at about 1052–1056 cm⁻¹, corresponding to triple ions and aggregates, increases monotonically over the entire concentra-

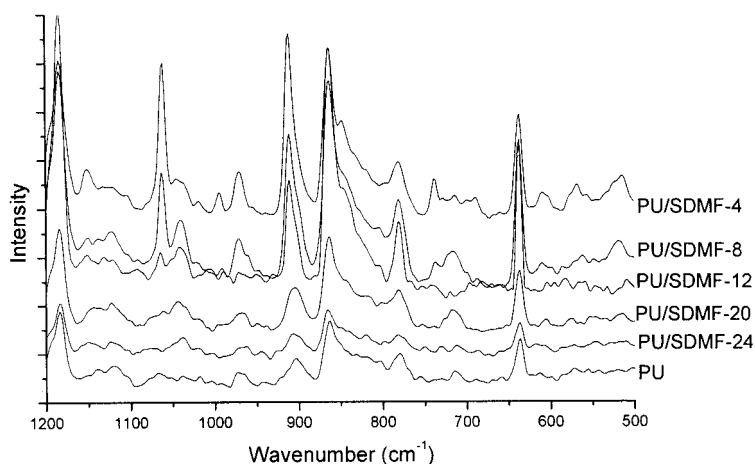


Figure 4 Raman spectra of PU/SDMF series in the 500–1200 cm⁻¹ region as a function of salt concentration.

tion range. This may be attributed to the fact that, with increasing salt concentration, interionic coulomb forces in the system increase correspondingly, thus leading to the formation of ion pairs at low salt concentrations and ion aggregates at high salt concentration. This result is in agreement with previous findings in other polymer/salt systems.^{18,20–22}

Moreover, it can be seen that the intensity of the 910 cm^{-1} band increases with increasing salt concentration. This band at about 910 cm^{-1} might be assigned to the *trans* conformation of the ethylene glycol unit, known to be adopted whenever completely disordered structures are attained.²² The intensity increase indicates an increase in the *trans* conformation population of PEG chain induced by the interaction between the sodium cation and the ether units.

Atomic Force Microscopy

AFM was utilized to investigate how the morphology of a PU-based electrolyte was affected by the incorporation of alkali metal salt into the polymer host matrix. Figure 5 shows AFM images of PU/SDMF complexes.

The AFM topographic image of a pure PU sample reveals a typical phase-separated morphology [Fig. 5(a)]. Bright, circle aggregates, which might be hard-segment-rich regions, disperse in a dark soft-segment-rich matrix. For diblock thermoplastic PU, phase separation is a result of both the segmental polarity difference and hydrogen bonding within the hard domain between urethane C=O and N—H moieties on adjacent polymer chain segments.^{20,23} With the introduction of SDMF into the system, significant changes take place in surface morphology. When $[\text{EO}]/[\text{Na}^+]$ is 24, a relatively flat surface morphology without any obvious aggregates is obtained, as shown in Figure 5(b). This is attributed to the competition between hydrogen bonding and alkali metal cation coordination after the incorporation of SDMF into PU elastomer, especially between the hard segments of the host polymer matrix.²⁰ The effect of salt ions is to increase the coordination with polymer chains and decrease the hydrogen bonding between the hard segments of PU, which improve the compatibility between the hard and soft segments. Consequently, the driving force for phase separation is lessened and the phase mixing is increased. With increasing salt concentration, completely different aggregates appear on the sample surface [Fig. 5(c)], which might be

attributed to the precipitation of SDMF. Because of interionic electrostatic forces, as well as the incompatibility between incorporated salt and nonpolar polymer matrix, salt always tends to aggregate.¹⁴ Moreover, a series of ionic aggregations, including ion pairs, multiplets, and clusters, also form when the salt content exceeds a critical salt concentration. All these may eventually lead to salt precipitation.²² When the salt concentration is further increased, the size and fraction of bright SDMF aggregations, as expected, apparently increase, as illustrated in Figure 5(d). Therefore, from morphology observations of the PU/SDMF system investigated, we find that the content of incorporated salt significantly influences the surface morphology of a polymer/salt complex.

Ionic Conductivity Analysis

Figure 6 shows the relationship between the ionic conductivity (σ) and $[\text{EO}]/[\text{Na}^+]$ at different temperatures for PU/SDMF series. It was found that all the PU/SDMF complexes exhibit a maximum of ionic conductivity at a particular critical concentration. When $[\text{EO}]/[\text{Na}^+]$ reaches 12, the highest ionic conductivity is obtained, approaching 10^{-8} S cm^{-1} at room temperature and exceeding 10^{-6} S cm^{-1} at 100°C . Further addition of SDMF brings about the decrease of ionic conductivity, which is caused by the combination of two opposite effects.²⁴ With increasing salt concentration, the number of charge carriers increases; meanwhile, neutral ion pairs and neutral multiplets, which do not contribute to conductivity, also form. The former effect predominates and enhances the ionic conductivity of sample at low salt concentrations ($[\text{EO}]/[\text{Na}^+] > 12$), whereas the latter effect is dominant and reduces the ionic conductivity at high salt concentrations. Therefore, there is a maximum of ionic conductivity for PU/SDMF series over the whole salt concentration range investigated.⁵

In addition, the experimental data indicate that the ionic conductivity of all samples apparently increases with increasing temperature. It can be ascribed to the fact that, when the temperature is increased, the mobility of polymer chains is enhanced, and the fraction of free volume in the system increases correspondingly, which is favorable to the enhancement of ionic conductivity. On the other hand, the number of charge carriers also increases with increasing temperature. All these lead to an increase in ionic conductivity for PU/SDMF complexes.

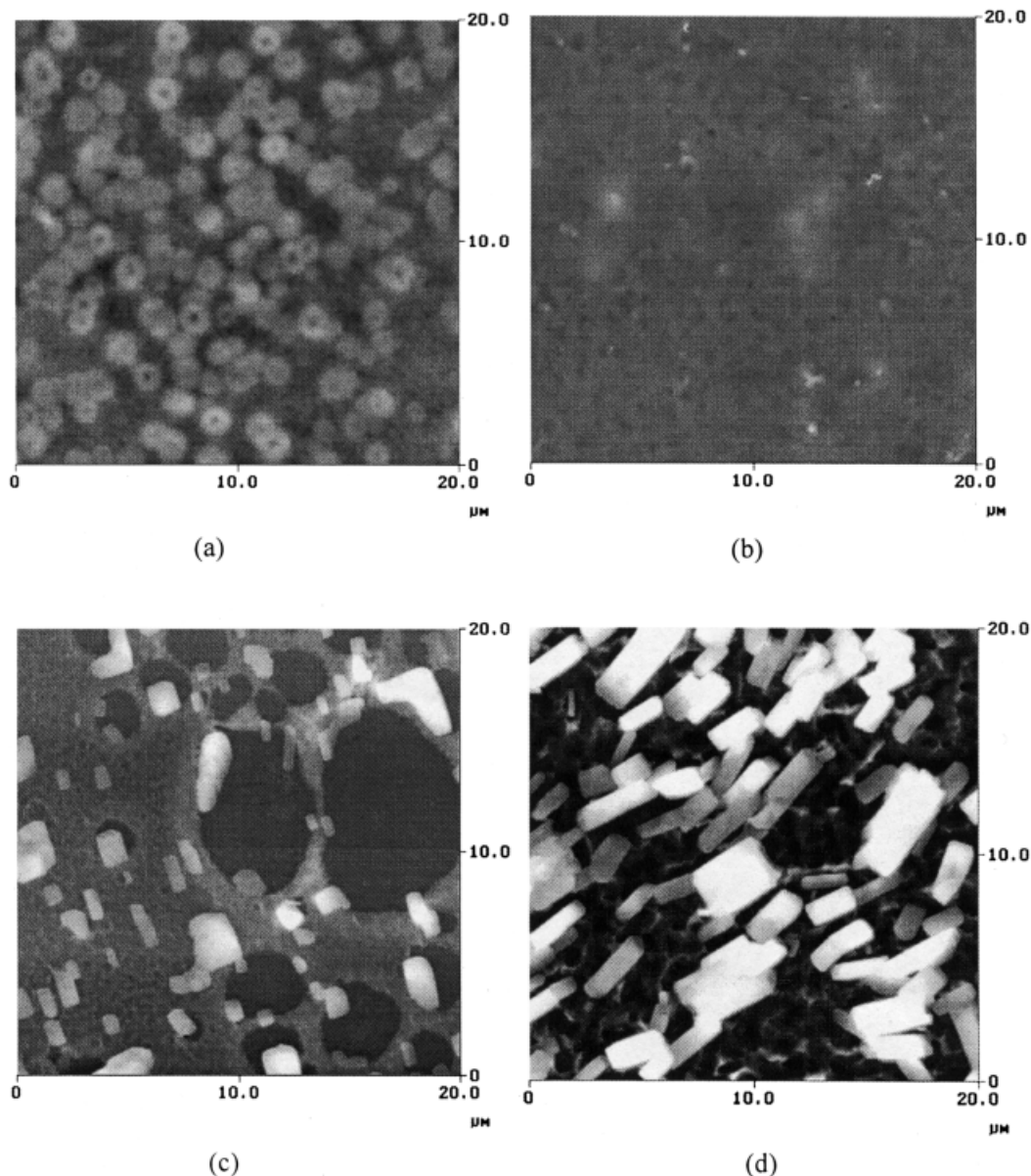


Figure 5 AFM topographic images of PU/SDMF series (scan width 20 μm ; vertical scale 400 nm): (a) Pure PU; (b) PU/SDMF-24; (c) PU/SDMF-12; (d) PU/SDMF-8.

CONCLUSIONS

Polymer electrolytes consisting of PU matrix dissolving SDMF were prepared and their ionic conductive properties and morphology were investigated as solid ion conductors. The results are summarized as follows.

The content of incorporated salt in the PU/SDMF system significantly influences the surface morphology and ionic conductivity of the samples. Within low salt concentration range, as the con-

tent of salt increases, the compatibility between the hard and soft segments improves, and the ionic conductivity of electrolytes is apparently enhanced. When $[\text{EO}]/[\text{Na}^+]$ is 24, the optimum compatibility between the hard and soft segments is realized and a flat surface morphology is revealed. When $[\text{EO}]/[\text{Na}^+]$ reaches 12, the highest ionic conductivity is attained. With a further increase in salt concentration, the fraction of neutral ion pairs and multiplets increases dramatically, and incorporated SDMF tends to segregate

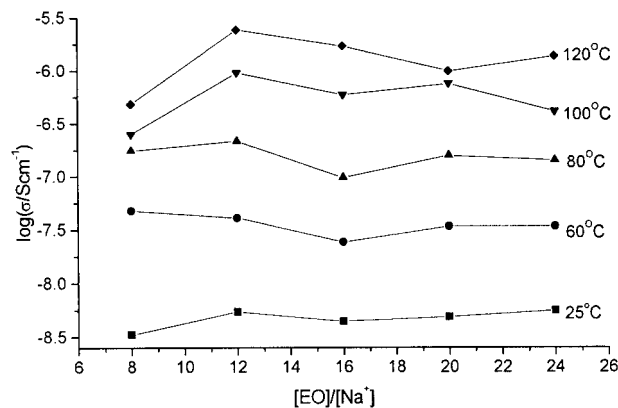


Figure 6 The effect of $[EO]/[Na^+]$ on the ionic conductivity at different temperatures for PU/SDMF series.

and precipitate. Consequently, ionic conductivity of the PU/SDMF complex decreases and the soft-segment T_g decreases correspondingly.

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