

Synthesis and Characterization of Novel Crosslinked Polyurethane–Acrylate Electrolyte

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ABSTRACT: Flexible, transparent, and crosslinked polymer films were synthesized by polymerization of PEG-modified urethane acrylate using a simple method. A series of novel solid polymer electrolytes and gel electrolytes were prepared based on this type of polymer film. To understand the interactions among salt, solvent, and polymer, the swelling behaviors of the crosslinked polymer in pure propylene carbonate (PC) and liquid electrolyte solutions (LiClO_4/PC) were investigated. The results showed that the swelling rate in the electrolyte solution containing moderate LiClO_4 was greater than that in pure PC. Thermogravimetric analysis (TGA) also supported the interaction between the solvent and polymer. The morphology and crystallinity of the

crosslinked polymer and polymer electrolytes were studied using atomic force microscopy (AFM) and wide-angle X-ray diffraction (WAXD) spectroscopy. The effects of the content of the electrolyte solution on the ionic conductivity of gel electrolytes were explored. The dependence of the conductivity on the amount of the electrolyte solution was nonlinear. With a different content of the plasticizer, the ionic conduction pathway of the polymer electrolytes would be changed. The best ionic conductivity of the gel electrolytes, which should have good mechanical properties, was $4 \times 10^{-3} \text{ S cm}^{-1}$ at 25°C . © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 340–348, 2003

INTRODUCTION

Solid polymer electrolytes can be used in many high technological areas and have attracted much research in the past 30 years. Most of the research has concentrated on designing novel polymer materials possessing high ionic conductivity, good mechanical properties, as well as thermal stability for industrial applications.^{1–3} Gel-type electrolytes, in which organic polymers are impregnated with electrolyte solutions, have good ionic conductivity, almost comparable to that of liquid electrolytes.⁴ At the same time, it has been suggested that gel electrolytes could suppress the formation of lithium dendrites in lithium batteries.⁵ So, gel-type electrolytes may be especially valuable in the future.

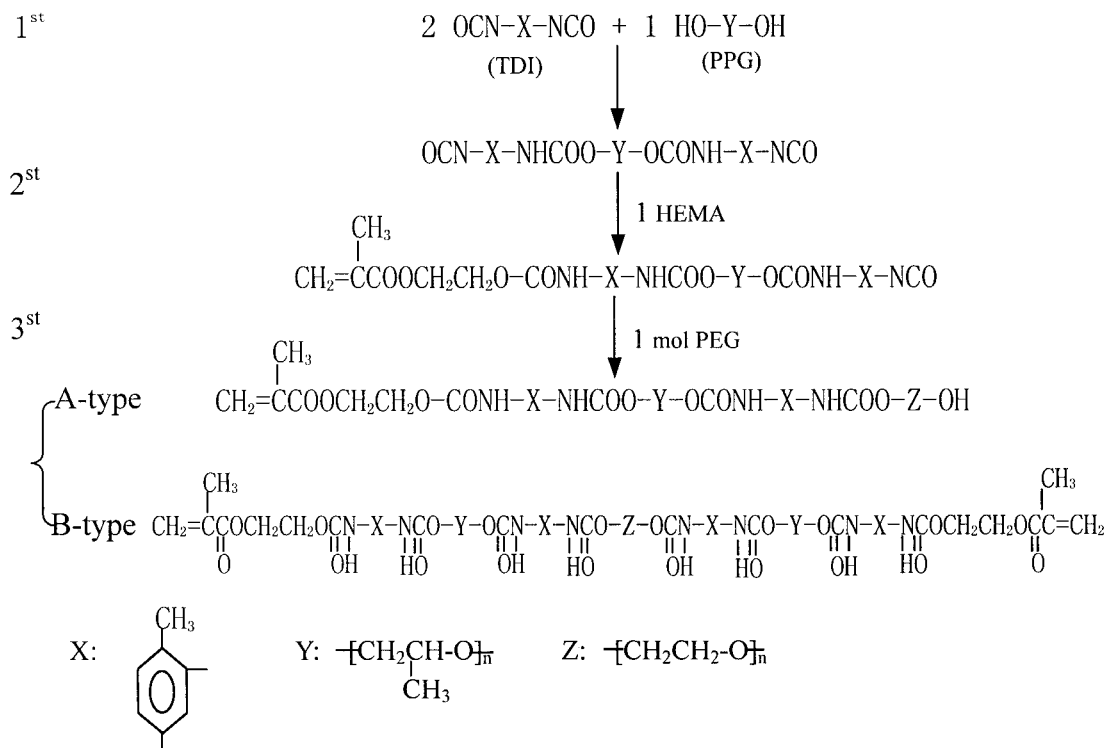
There are several polymers that have been successfully employed as the polymer matrix of gel electrolytes: poly(vinylidene fluoride) (PVDF), polyacrylonitrile (PAN), and poly(methyl methacrylate) (PMMA).⁶ Kim and Seung studied the relative order of the polymer affinity for organic carbonates among four polymers: PAN, PMMA, PVDF, and the poly(vinylidene fluoride)–hexafluoropropylene (PVDF–HFP) copolymer. The solvent retention ability, mechanical

strength, and subambient temperature conductivity of the gel polymer electrolytes were investigated on the basis of the polymer–solvent affinity.⁴

Gel-type electrolytes without covalent crosslinking are liquefied at high temperature. For instance, PAN-based gel-type electrolytes are liquefied around 100°C . Liqueficient gel-type electrolytes lose their inhibition effect on lithium dendrite formation and have poor mechanical properties.⁵ At the same time, crosslinking could depress the crystallinity and a chemically crosslinked polymer could hold much more electrolyte solution.⁷

It can be difficult to process crosslinked polymers into films with a controllable thickness under laboratory conditions. Hence, studies on crosslinked gel polymer electrolytes are limited. Polyurethanes and polyacrylates are well known for their many excellent properties. They have also been shown to be good materials for solid polymer electrolytes or gel polymer electrolytes. Wen et al. synthesized a series of polyurethane electrolytes, including a thermoplastic polyurethane gel electrolyte and waterborne polyurethane single-ion electrolytes.^{3,8} A simple method to make films with a controllable thickness has been developed; using this method, we obtained transparent, flexible, and crosslinked gel polymer films. These polymer films are a complex of polyacrylate and polyurethane. In this work, polymer electrolytes were prepared based on polyurethane–polyacrylate crosslinked polymer films. The understanding of the inter-

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Scheme 1 Synthetic route of UA macromonomer.

actions among the components in gel electrolytes is crucial.^{6,9} The interactions among the salt, the solvent, and the polymer of the electrolytes were studied by the swelling behaviors and thermogravimetric analysis (TGA). Wide-angle X-ray diffraction (WAXD) and atomic force microscopy (AFM) were used to explore the microphase structure of the polymer and the electrolytes. The ionic conductive mechanism of the gel electrolytes also is discussed.

EXPERIMENTAL

Materials

In the synthesis of a PEG-modified urethane acrylate macromonomer, 2,4-toluene diisocyanate (TDI; Aldrich Chemical Co.), poly(propylene glycol) (PPG, $M_n = 1000$; Shandong Dahua Chemical Plant), 2-hydroxyethyl methacrylate (2-HEMA; C.P. grade, Tianjing Chemical Reagent Experimental Factory), poly(ethylene glycol) (PEG, $M_n = 600$, Aldrich Chemical Co.), and dibutyltindilaurate were used. TDI was vacuum-distilled before use. The inhibitor in 2-HEMA was removed through a removing column. 2,2-Azobisisobutyronitrile (AIBN; A.R. grade, Aldrich Chemical Co.) was dried at 30°C in a decompressed condition after being recrystallized. Dioxane and propylene carbonate (PC; Shanghai Solvent Factory) were used as received. Lithium perchlorate (LiClO_4 ; A.R. grade,

Shanghai Chemical Reagent Factory) were dried at 120°C in a vacuum oven for 10 h before use.

Synthesis of PEG-modified urethane acrylate macromonomer (PEG-UA)¹⁰

The reaction procedure and molecular structure are shown in Scheme 1. The reaction was carried out in a four-necked glass reactor equipped with a stirrer, a thermometer, and an inlet and outlet system for nitrogen gas. In the first step, TDI and PPG were poured into the glass reactor under nitrogen gas. Dibutyltindilaurate, 0.5 wt %, was added under stirring. The reaction temperature was increased to 50°C so that 2 mol of TDI was reacted with 1 mol of PPG, resulting in a molecular structure having isocyanates on its end sides. In this stage, the reaction temperature must be controlled carefully so as not to increase the molecular weight. This temperature was maintained for 3 h, then increased to 75°C to attain an acceptable rate of reaction. The change of the NCO value during the reaction was measured using a dibutylamine back-titration method to determine the end point of the reaction.

In the second step, the temperature was decreased to room temperature. HEMA, 1 mol, was slowly added into the reactor and reacted at 45°C. Then, the temperature was increased to 65°C for 2.5 h, which introduced a reactive vinyl group to the molecular ends as a polymerizable group.

In the third step, after dissolving 0.5 wt % of dibutyltindilaurate, 1 mol PEG was poured into the reactor at room temperature. The reaction temperature was maintained at 50°C for 4 h and at 65°C for 1 h. The reaction end point was determined by the disappearance of the NCO stretching absorption (2270 cm^{-1}) in IR spectroscopy.

Preparation of crosslinked UA polymer¹¹

PEG-UA was completely dissolved in dioxane (including 0.25 wt % AIBN; PEG-UA: dioxane 1:3 by weight). A series of glass pieces, separated with the required interspaces, acted as a template. The template was inserted into a thin aluminum tube (diameter was 2.5 cm). The mixture of PEG-UA with dioxane was transferred into the tube. The mixture was saturated with dry nitrogen for 5 min and the tube sealed under nitrogen. The tube with the reactant was heated to 55°C for 8 h to carry out gelation. After gelation, the crosslinked gel polymer films were taken out from the middle of two pieces of glasses. After being fully washed with a large amount of acetone, these gel polymer films were dried in a convection oven at 40°C for 48 h, then dried in a vacuum oven at 80°C for 24 h and stored in a dry box filled with dried nitrogen.

Preparation of the polymer electrolytes

To prepare the gel-type electrolytes, the polymer films were immersed in quantitative liquid electrolyte solutions: 1, 2, and 3M LiClO₄ in PC. The swelling processes were carried out in a box filled with dried nitrogen. The ratios of the polymer to the electrolyte solution were measured by weighing the films before and after soaking. The gel electrolyte film thickness was 0.7–1.0 mm. The films were stored in an airtight box. The gel-type polymer electrolytes were dried in a convection oven at 80°C for 48 h, then dried in a vacuum oven at 100°C for 48 h to get solid polymer electrolytes. The solid polymer electrolyte was stored in a dry box filled with dried nitrogen.

Molecular weight

The molecular weight and the molecular weight distribution of the PEG-UA were measured using a Perkin-Elmer Series 200 GPC analyzer and a 1 wt % solution of the PEG-UA in THF was injected into the GPC column at a flow rate of 2 mL min^{-1} at 40°C using polystyrene standards.

Swelling behavior measurement

To examine the swelling behavior of the crosslinked polymer, the dry films (approximate dimensions: 15

$\times 15 \times 0.5\text{ mm}$) were immersed in solvent and liquid electrolyte solutions: 1, 2, and 3M LiClO₄ in PC. The swelling processes were carried out in a glove box at room temperature. The films were withdrawn at different times; the solvent on the surface of the films was removed with a filter paper. The swelling ratios of the polymer were determined by weighing the films before and after soaking. The swelling ratio is expressed as

$$\text{Swelling ratio} = (W - W_0)/W_0$$

where W_0 is the initial weight of the film and W is the weight after swelling.

To measure the LiClO₄ content of the liquid electrolyte solutions that was sucked into the crosslinked polymer at different swelling ratios, several pieces of dry films were synchronously immersed in 1M LiClO₄ in PC. The films were taken out from the electrolyte solution at different times and dried in a convection oven at 80°C for 48 h, then dried in a vacuum oven at 100°C for 48 h to get dry electrolyte films. The LiClO₄ content of electrolyte solutions sucked into the polymer (C_s) is defined as

$$C_s = (W_d - W)/(W - W_0)$$

where W_d is the weight of the sample after drying and W_0 and W are the same as above.

TGA

TGA was carried out using a Perkin-Elmer thermogravimetric analyzer, Model TGA 7. The measurements were performed at a heating rate of $10^\circ\text{C min}^{-1}$ from 15 to 450°C in a nitrogen atmosphere.

WAXD

The diffractograms of the samples were taken on a D/MAX-1200X diffractometer. CuK α radiation was used. The results were recorded using a scintillation counter. The 2θ scanning rate was 4° min^{-1} . The diffractograms were recorded in the range of the diffraction angle $2\theta = 5\text{--}50^\circ$.

Morphology observation

The morphologies of the polymer film and the gel electrolyte film were examined using AFM. AFM analysis was carried out on a Digital Instruments Nanoscope IIIa SPM analyzer with a scanning rate of 2.001 Hz.

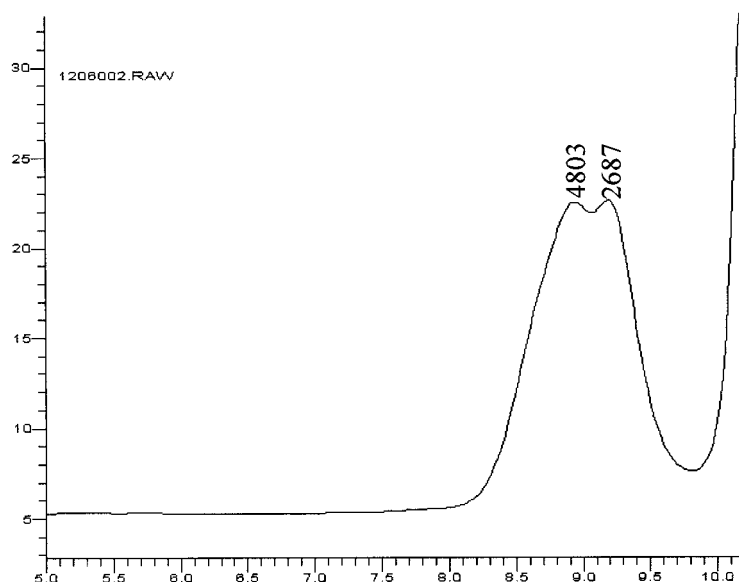


Figure 1 GPC curves of PEG-modified UA macromonomer.

Conductivity measurements

Ionic conductivities of the gel electrolytes were measured from the a.c. impedance spectra taken from 20 to 85°C using a Hewlett-Packard 4192A LF impedance analyzer over a frequency range of 1 Hz to 1 MHz. The films were cut to a required size (10 mm in diameter and 0.7–1.0 mm thick) and were sandwiched between two copper 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 sample was calculated by

$$\sigma = (1/R)d/S$$

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

RESULTS AND DISCUSSION

Synthesis of crosslinked UA polymer

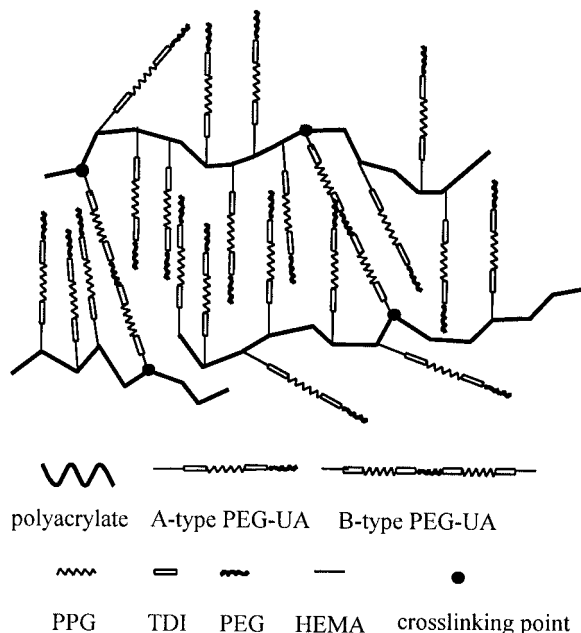
PEG-UA was synthesized in three steps (Scheme 1) and was reported in our former work.¹² PEG-UA is composed mainly of A- and B-type molecules. A-type molecules are in the majority, and B-type, in the minority. As a B-type molecule has two carbon-carbon double bonds, it could be considered as a crosslinker. The theoretical molecular weight value of the A-type is 2078 g mol⁻¹, and the B-type, 3556 g mol⁻¹. The molecular weight distribution (MWD) of PEG-UA was measured by GPC. The MWD curves are shown in Figure 1 and are bimodal. The average experimental

peak molecular weights are 2687 and 4803 g/mol, approaching the theoretical values.

PEG-UA was dissolved in dioxane and polymerized as a macromonomer initiated by AIBN to produce a crosslinked polymer network. Compared with linear or normal crosslinked polyurethane, the crosslinked UA polymer exhibited some different characteristics. A traditional crosslinked polyurethane was prepared through crosslinking of the hard segment or soft segment. The crosslinked UA polymer consisted of a multiplex component. The main chain was polyacrylate and the side chain was polyurethane. As a whole, the system was a crosslinked network. There were large quantities of comblike structures with end-capped PEO chains. The network structure of the polymer is shown in Scheme 2; this structure led to improved mechanical properties, suppressed the crystallization of PEG, and increased the mobility of the PEG chains. At the same time, the density of the network structure could be controlled by the concentration of the macromonomer PEG-UA in the solvent. The mobility of the PEG chains, which affected many properties of the electrolytes based on this type of polymer, was mutative with different densities of the network.

Swelling properties

To investigate the interaction between the polymer and lithium ions in liquid electrolyte solutions, the swelling behaviors of the polymer in pure PC and electrolyte solutions were studied (Fig. 2). The salt concentration in the solution varied from 1 to 3M. The polymer could absorb large quantities of solvent or



Scheme 2 Structure model of crosslinked UA polymer network.

electrolyte solutions⁸ and could be used as gel electrolytes. The swelling rate and saturated weight were obtained from Figure 2; the swelling behaviors in different liquids were very different, with three different behaviors observed.

A moderate rate of swelling was observed in the pure solvent. The rate of swelling gradually decreased until reaching an equilibrium value when the saturated swelling ratio was about 3.2. In the presence of 1 mol/L LiClO₄, the swelling rate of the polymer greatly increased. To determine why the swelling rate in an electrolyte solution was enhanced by the presence of

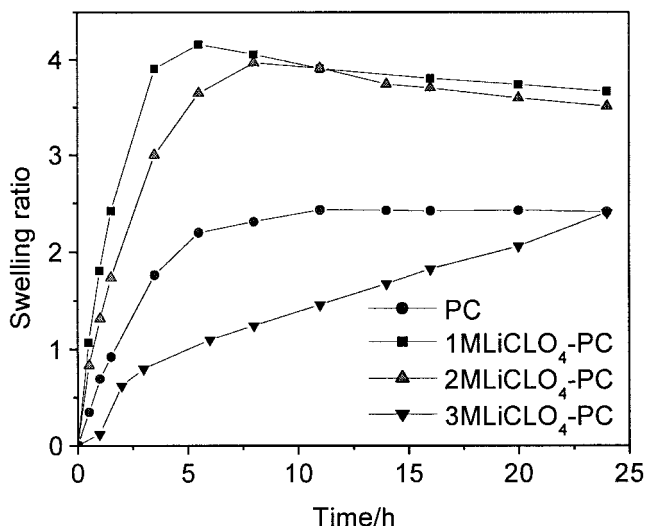
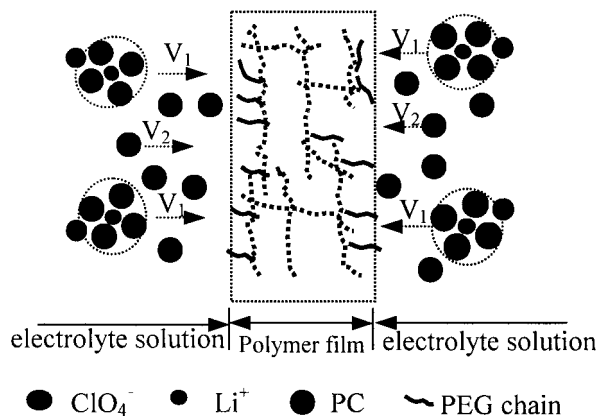


Figure 2 Swelling ratios of crosslinked UA polymer in solvent PC and different electrolyte solutions.



Scheme 3 Sketch of the swelling process of crosslinked polymer in 1M electrolyte solution.

LiClO₄, the LiClO₄ content of the electrolyte solutions incorporated into the polymer (C_s) at different swelling ratios (Scheme 3) was measured. In the electrolyte solutions (1 or 2M LiClO₄ in PC), both free and lithium ion-bound PC molecules were observed. When the polymer films were immersed in solutions, both kinds of molecules would diffuse toward the film. Their relative rates of diffusion are given by V_1 and V_2 , respectively. If $V_1 = V_2$, then the C_s would be equal to that of the electrolyte solution (1 mol/L or 8.19 wt %). If $V_2 > V_1$, the C_s should be low at the beginning and then increase gradually to 8.19%. As can be seen in Figure 3, the C_s was high when the swelling was not saturated and then descended gradually, which shows that $V_1 > V_2$. As there are large quantities of PEG side chains at the surface and inside the polymer films, the interaction between the lithium ions and the PEG side chains could explain the larger rate V_1 .¹³ As the salt concentration in the electrolyte solution was increased (surpassing 1M), the swelling rate of the polymer would decrease. As can be seen in Figure 2, the swell-

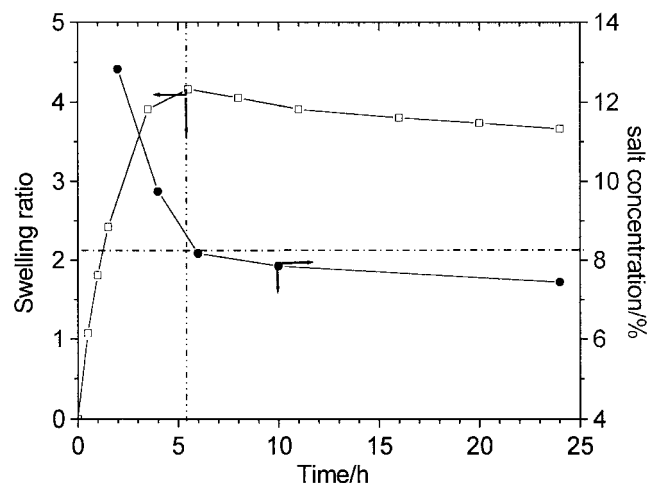


Figure 3 LiClO₄ concentration of liquid electrolyte incorporated into the polymer (C_s) at different swelling ratios.

ing rate in 2M LiClO₄/PC was slightly less than that with 1 mol/L. When the salt concentration in the solution increased to 3M, a dramatic change in the swelling cure was observed. At a high salt concentration, the swelling rate was very low and remained stable. In the presence of large quantities of salt, there are no free solvent molecules in the electrolyte solution. Virtually, all solvent molecules were associated with salt or ions, limiting molecular motions.

TGA

The thermal degradation processes are shown in Figure 4. The degradation of the crosslinked UA polymer, starting at about 316°C, showed the maximum weight loss rate at 390°C. The presence of only one peak indicates that the polymer is stable. The gel electrolytes had three peaks. The first peak is ascribed to the loss of the solvent PC. From Figure 4(a), there was still a small quantity of the solvent held by the polymer film. Table I compares the solvent loss under 220°C

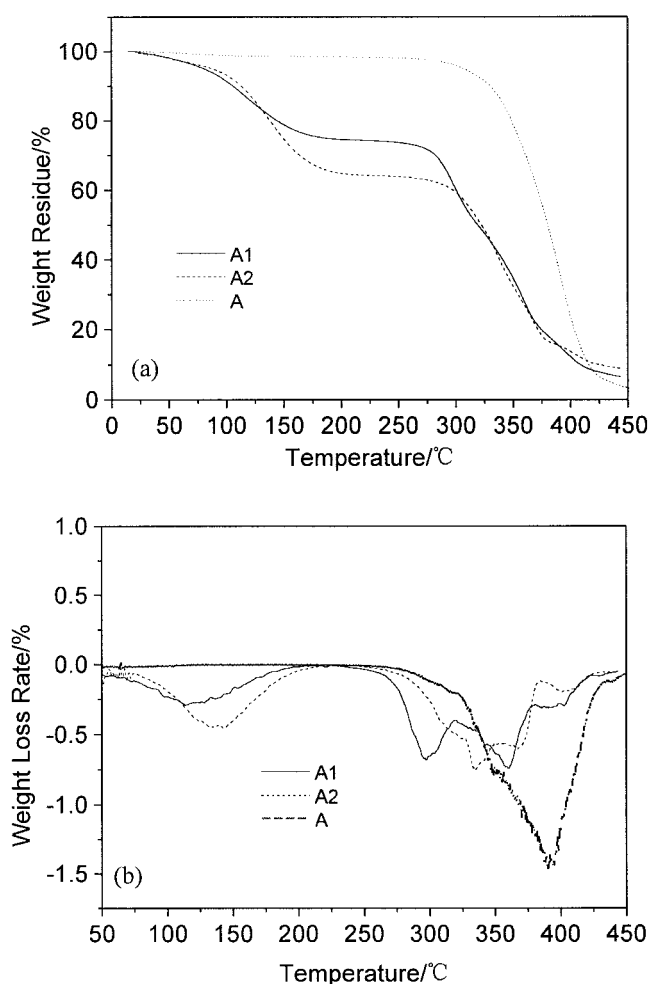


Figure 4 TG curves and DTG curves of (A) crosslinked polymer and gel electrolytes: (A1) 33 wt % LiClO₄/PC (1M); (A2) 50 wt % LiClO₄/PC (1M).

TABLE I
Solvent Loss Weight Under 220°C and Residual Weight of Different Gel Electrolytes

Sample	Solvent (PC) content	Weight loss at the first peak	Solvent residual weight
A311	29%	25.4%	3.6%
A312	43%	36.2%	6.8%

and the residual solvent weight of two kinds of gel electrolytes with different solvent contents. At the same time, the endothermic peak of the polymer became bimodal and shifted to the low-temperature side, which shows that there is obvious interaction between the solvent and the polymer.¹⁴

Crystalline behavior

WAXD measurements revealed a short-range periodicity in the crystalline parts of the samples. Here, therefore, information about the structure of the crystalline phase can be derived and the influence of solvent (PC) and salt on the crystalline phase of the crosslinked UA polymer and its structure can be investigated. It is also possible to calculate the ratio of the crystalline to amorphous regions by profile analysis. The separation of the crystalline reflections from the broad peak, a halo, from the amorphous phase, was performed by profile analysis using the program by Petkov and Bakalatchev.¹⁵ The results from this analysis were used for the calculation of the mass fraction of the crystalline phase relative to the total mass of the sample (w_{cr}).⁹

Figure 5 gives wide-angle diffractograms of the crosslinked polymer, gel polymer electrolyte, and solid polymer electrolyte over the range 5° to 50°. They showed obvious differences. PEG and linear polyurethane with PEG was crystalline. The crystals induced a decrease of the ionic conductivity. When the polymer was crosslinked, the degree of crystallinity was greatly reduced. The wide-angle diffractogram for the crosslinked polymer [Fig. 5(a)] reveals that the degree of crystallinity is very low.

According to Tegenfeldt et al.,⁹ the total crystallinity (w_{cr}) of the samples diminishes with an increasing amount of plasticizer and salt added to the polymer matrix; the relative crystallinity decreases from 0.31 to 0.05 with 70% of the liquid electrolyte. The WAXD intensity profile of the gel electrolyte is shown in Figure 5(b); the gel electrolyte displayed only one diffuse reflection from 5° to 50°, which was very broad and of strong intensity in the range 10°–30° of 2θ . The scattering reflection maxima were centered at 20.6°, and the corresponding spacing (d) was at 4.308 Å. Such a result suggested an amorphous structure of both hard and soft segments.¹⁴ There was little crystallinity remaining in the system.

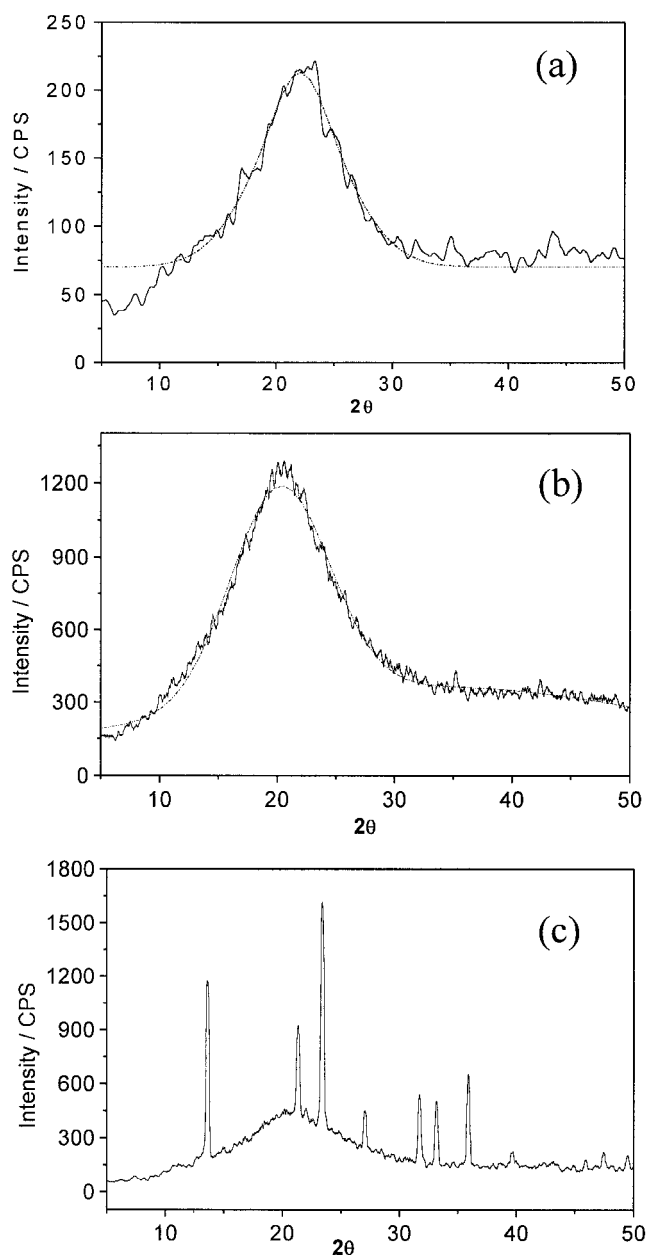


Figure 5 WAXD diffractograms of crosslinked polymer and electrolytes: (a) crosslinked polymer; (b) gel polymer electrolyte containing 50 wt % LiClO_4/PC (1M); (c) solid polymer electrolyte with 26 wt % LiClO_4 .

Figure 5(c) shows wide-angle diffractograms of solid polymer electrolytes containing a large amount of salt (26 wt % LiClO_4). It was obvious that the sample was a semicrystalline compound. In the table, the reflection maxima with the corresponding spacings (d) and their intensities are listed (Table II). There were seven very sharp diffraction peaks of the crystalline phase, some of which came from the crystallization of salt and some belonged to the orderly arrangement of hard segments and soft segments. The high concentration of salt resulted in an increase of the

TABLE II
X-ray Diffraction Maxima with Corresponding Angle (2θ), Spacing (d), Relative Intensity, and Half-widths of the Solid Polymer Electrolyte

Reflection	2θ ($^\circ$)	d (\AA)	Intensity	Half-widths ($^\circ$)
1	13.62	6.496	80	0.160
2	21.34	4.160	48	0.280
3	23.42	3.759	100	0.200
4	27.06	3.292	24	0.280
5	31.72	2.819	29	0.240
6	33.18	2.698	26	0.280
7	35.92	2.498	36	0.280

glass transition temperature and crystals of the polymer.

Morphology

Figures 6 and 7 show AFM images of the crosslinked UA film and the gel electrolyte film. Under different magnifications, phase separation and aggregates of macromolecule chains of the samples could be observed. The surface image of crosslinked UA was very flat and uniform [Fig. 6(a)], which indicated that the polymer film had no large polymeric aggregates or phase separation. With higher magnification, Figure 6(b) reveals that, on a different scale, roughness was present. The image showed a polymer with pronounced heterogeneity, because the polymer contained two kinds of microregions enriched by soft segments or hard segments.¹⁶ The orderly arrangement of molecule chains or segments resulted in partial crystallization, which could be verified by diffractogram analysis.

Figure 7 shows AFM images traced on the surface of a gel electrolyte film containing 50 wt % LiClO_4/PC . The polymer network cannot be dissolved; it swells by addition of a solvent. The gel polymer exhibits a rough and regular surface; some of small polymeric particles, which are microgels for higher network densities, disperse on the surface region.⁴ The crosslinked UA polymer could absorb and hold a large quantity of liquid electrolytes as a crosslinking network structure, but the microgels still could not dissolve in the solvent,

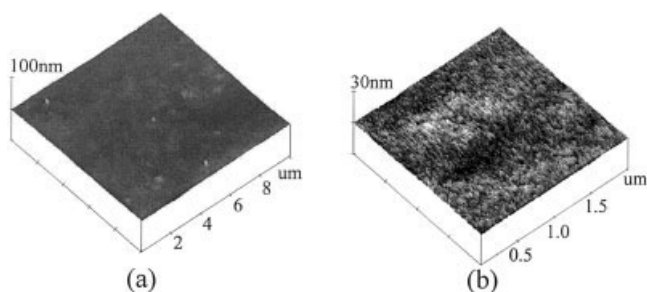


Figure 6 Surface AFM images of the crosslinked UA polymer film with different magnifications.

which evolved a phase separation. Of course, more polymer chains were miscible with liquid electrolytes, so an orderly arrangement of polymer segments and polymer crystals was not evident, consistent with the analysis above.

Kim and Seung divided polymers into two groups: high-affinity (PMMA and PAN) and low-affinity [P(VDF-HFP) and PVDF] polymers.⁴ From the AFM images of the samples in this work and the four kinds of gel electrolytes studied by Kim and Seung, the solvent/polymer affinity of the crosslinked UA polymer was determined to be intermediate between high-affinity and low-affinity polymers.

Ionic conductivity

In Figure 8, the temperature dependence of the ionic conductivity of the gel polymer electrolytes is shown. Different samples were prepared by changing the content of the electrolyte solution in the range 33–66 wt %. The ionic conductivity of the samples increased with increasing the amount of the electrolyte solution. The highest ionic conductivity is 4×10^{-3} at 25°C. The conductivity increased rapidly from sample A1 to sample A2. By increasing the liquid electrolyte concentration from 50 wt % (A2) to 66 wt % (A3), the rate of increase of the conductivity declined.

For sample A1, the apparent role of PC was to act as a plasticizer to the polymer electrolyte, which could increase the mobility and the concentration of the ionic charge carriers. In polymer electrolytes, a high ionic mobility is required. It has been demonstrated that this factor is intimately connected with the segmental motion of polymer chains. The addition of a plasticizer into the system could lead to a decrease of the glass transition temperature and increase of the mobility of the polymer segments.^{8,17}

When the content of the liquid electrolyte increased beyond 50 wt %, the ions transport mainly in the plasticizer domain and the polymer merely serves as a host matrix. Between a 33 and 50 wt % liquid electrolyte concentration, the conduction pathways of the

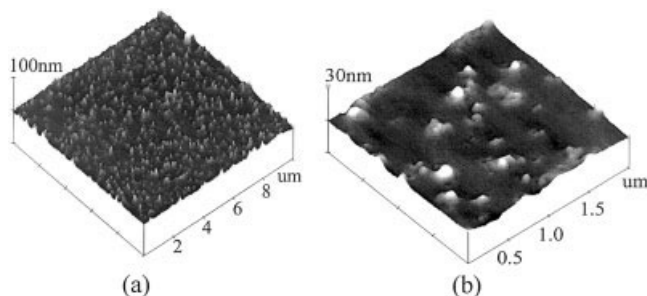


Figure 7 Surface AFM images of the gel polymer film containing 50 wt % crosslinked UA and 50 wt % LiClO₄/PC (1M) with different magnifications.

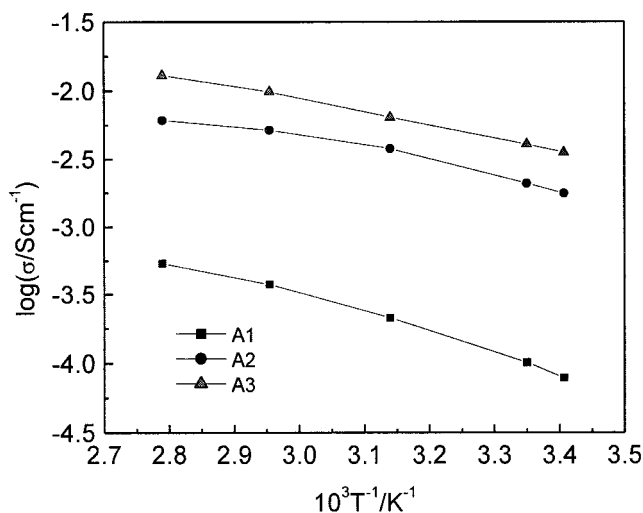


Figure 8 Arrhenius plots of ionic conductivity of gel polymer electrolytes containing different contents of liquid electrolyte (1M LiClO₄/PC): (A1) 33, (A2) 50, and (A3) 66 wt %.

polymer electrolytes gradually transform; the effect of the liquid electrolyte content on the ionic conductivity is crucial. When the conduction pathways in the plasticizer domain have been formed, the effect of the liquid electrolyte content on the ionic conductivity decreases.¹⁸

CONCLUSIONS

The crosslinked poly(UA) polymer films could absorb/hold large quantities of electrolyte solutions and be used as gel electrolytes. The gel electrolytes can have high ionic conductivity. There are interactions among the polymer matrix, salt, and solvent. The polymer can attract and dissolve salt. Most of polymer chains are miscible with the liquid electrolyte, and the interaction between the polymer and the solvent can decrease the thermal degradation temperature of the polymer. As to the crosslinking network structure, some polymeric particles could not dissolve in the solvent, which results in phase separation and which offers favorable mechanical properties for the electrolytes. With different contents of the plasticizer, the polymer and plasticizer have different roles in the polymer electrolyte. A small quantity of the plasticizer can increase the mobility of the polymer segments; the transport of ions depend mainly on the movement of polymer segments. A large quantity of the plasticizer can form a conduction pathway in the plasticizer domain, and the polymer merely serves as the host matrix. When the plasticizer was up to 50 wt %, the ions transported mainly in the plasticizer domain and the gel electrolyte exhibited a high ionic conductivity.

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