

Polymer Gel Electrolytes Based on Thermoplastic Polyurethane

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ABSTRACT: Series of gel electrolytes based on thermoplastic polyurethane (PU) with different organic additives were prepared and studied. Structural characterization was carried out by differential scanning calorimetry (DSC), dynamic mechanical analyzer (DMA), scanning electron microscopy (SEM), and atomic force microscopy (AFM). The results showed that propylene carbonate (PC), *N,N*-dimethylformamide (DMF), polyethyleneglycol 400 (PEG400), and glycerol played roles of plasticizers and were miscible with soft-segment in PU matrix, which led to increase of the polymer segmental mobility, which in turn led to decrease of glass transition temperature (T_g), while, diethyl carbonate

(DEC) and diethylene glycol dimethyl ether (DGDE) showed no effectiveness of plasticizers. Ionic conductive properties of the electrolytes, examined by complex impedance analyzer, showed that ionic conductivities of the samples increased with the increase of organic additive content, and the sample with PEG400 as organic additive showed an ionic conductivity of $1.8 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2310–2315, 2003

Key words: conducting polymers; polyurethanes; structure–property relations; atomic force microscopy

INTRODUCTION

With excellent ionic conductivity properties, gel electrolytes have attracted ever-increasing interest in recent years, due to its potential application in all solid-state rechargeable lithium batteries^{1–3} and other electrochemical devices.^{4–5} In general, gel electrolytes are obtained by incorporating a larger quantity of liquid plasticizer and/or solvents to a polymer matrix that is capable of forming a stable gel with the polymer host structure. Some polymeric materials, such as poly(ethylene oxide),⁶ poly(acrylonitrile),⁷ poly(methyl methacrylate),⁸ poly(vinyl chloride),⁹ and poly(vinylidene fluoride),¹⁰ have been used as host polymer for gel electrolytes.

With low glass transition temperature (T_g) and good mechanical properties, polyurethane (PU) has been shown to be a good host polymer for solid polymer electrolytes (SPE),^{11–12} thermoplastic PU with oligo-poly(ethylene oxide) as soft segment is chosen to act as host polymer for gel electrolytes, and series of gel electrolyte samples composed of PU, lithium perchlorate (LiClO_4), and organic additives are prepared in this study. Effects of organic additives on T_g , microphase structure and ionic conductivities of samples are discussed in detail.

EXPERIMENTAL DETAILS

Chemicals and samples

Thermoplastic PU is prepared according to reference.¹³ Polyethyleneglycol 400 (PEG400), propylene carbonate (PC), diethyl carbonate (DEC), diethylene glycol dimethyl ether (DGDE), glycerol, *N,N*-dimethylformamide (DMF), and Tetrahydrofuran (THF) are of C.P. grade, which are bought from Shanghai Chemical Factory (PR China). LiClO_4 is of A.R. grade and is obtained from Shanghai No. 2 Chemical Factory (PR China).

All the samples are prepared by the solvent casting technique. PU, organic additives, and LiClO_4 are dissolved in THF, and then the solutions are cast into a Teflon plate. Film forms in an oven at 60°C and is then dried in a vacuum drying oven for 48 h at 60°C. The composition of solid polymer electrolyte samples are listed in Table I. Here, mole ratio of ether groups in PU to Li^+ , O/Li^+ , is kept constant with a value of 8.

Apparatus

Differential scanning calorimetry (DSC) scans are carried out on a Perkin–Elmer Pyris-1 DSC in a temperature range of -100 – 100°C with a temperature increase rate of $20^\circ\text{C min}^{-1}$, and nitrogen of 20 ml min^{-1} is used. Dynamic mechanical analysis (DMA) is carried out on a Rheometric Scientific DMTA-IV DMA in a temperature range of -100 – 100°C , with frequency of 1, 10, 50, and 100 Hz, and temperature increase rate is 3°C min^{-1} , samples size is $3.0 \times 0.5 \times (0.04–0.06)$

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TABLE I
Composition of Gel Electrolyte Samples

Samples	Organic additives (wt%)
PU/20% PC/LiClO ₄ -8	PC (20)
PU/20% DEC/LiClO ₄ -8	DEC (20)
PU/20% DGDE/LiClO ₄ -8	DGDE (20)
PU/20% PEG400/LiClO ₄ -8	PEG400 (20)
PU/20% DMF/LiClO ₄ -8	DMF (20)
PU/20% glycerol/LiClO ₄ -8	Glycerol (20)
PU/5% PEG/LiClO ₄ -8	PEG400 (5)
PU/10% PEG/LiClO ₄ -8	PEG400 (10)
PU/30% PEG/LiClO ₄ -8	PEG400 (30)
PU/40% PEG/LiClO ₄ -8	PEG400 (40)
PU/50% PEG/LiClO ₄ -8	PEG400 (50)
PU/60% PEG/LiClO ₄ -8	PEG400 (60)

cm³. Scanning electron microscopy (SEM) analysis is carried out on a HITACHI S2150 scanning electron microscope. Atomic force microscopy (AFM) analysis is carried out on a NanoScape IIIa SPM Digital Instrument.

Complex impedance measurements are carried out on a Hewlett Packard 4192A LF impedance analyzer in a frequency range of 5 Hz–13 MHz and a temperature range from room temperature to 120°C, and the testing system was a cell of Cu|gel electrolyte|Cu. The bulk resistivity, R_B can be obtained according to Cole–Cole plot, then ionic conductivity can be calculated from the equation $\rho = (1/R_B) d/s$, here, d and s are the thickness and the area of sample, respectively.

RESULTS

Morphology structure of gel electrolyte samples

PU is a kind of polymer with hard- and soft-segment and there is microphase separation between soft- and hard-segment in the PU matrix.^{13–14} DMA spectra of PU, PU/LiClO₄-8 and PU/20% PEG400/LiClO₄-8 (Fig. 1) show that storage modulus (E') transition region of PU/20% PEG400/LiClO₄-8 is narrower than that of PU or PU/LiClO₄-8. According to litera-

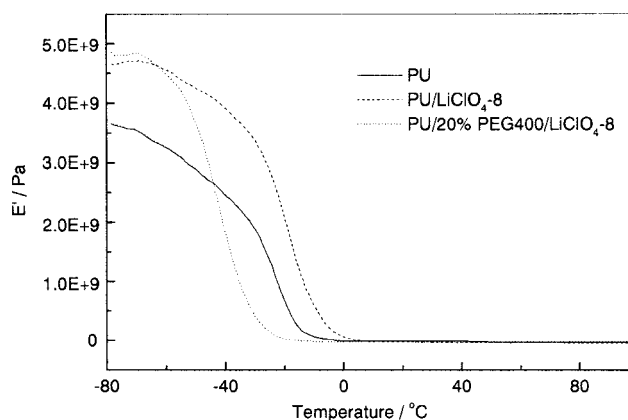
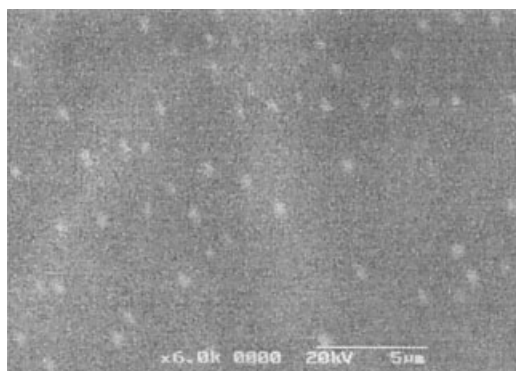


Figure 1 DMA spectra of PU, PU/LiClO₄-8, and PU/20% PEG400/LiClO₄-8.

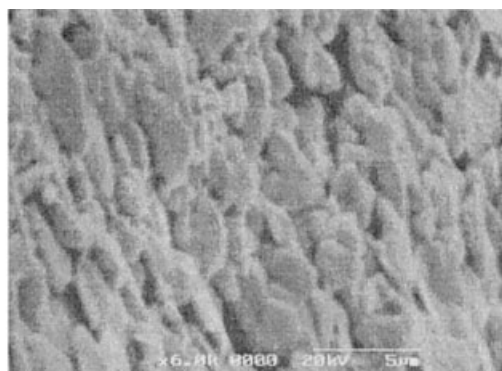
ture,^{12,14} this result means that microphase separation in the sample is enhanced when PEG400 is used as organic additive.

SEM images in Figure 2 also show that, with PEG400 as organic additive, microphase separation in PU matrix increased and there are evident polymeric aggregates in the sample. Previous studies^{13,15–16} point out that hard-segment in PU matrix was responsible for polymeric aggregates. In fact, the structure of PEG400 is similar to that of soft-segment in PU, so that PEG400 is miscible with soft-segment of PU but not miscible with hard-segment, which results in enhancement of microphase separation.

Effect of organic additives on microphase separation in PU matrix is further examined by taking AFM photographs. Figure 3 shows the AFM images traced on the surface of gel electrolyte samples with different organic additives. The surface AFM image of PU/20% DGDE/LiClO₄-8 is flat, while other samples exhibit rough surfaces, and there are polymeric aggregates dispersed on the surface region. In accordance with the SEM image, for the sample with PEG400 as organic additive, the polymeric aggregates are larger and



(a) PU/LiClO₄-8



(b) PU/20%PEG400/LiClO₄-8

Figure 2 Cross-sectional SEM images of gel electrolyte with PEG400 as organic additive.

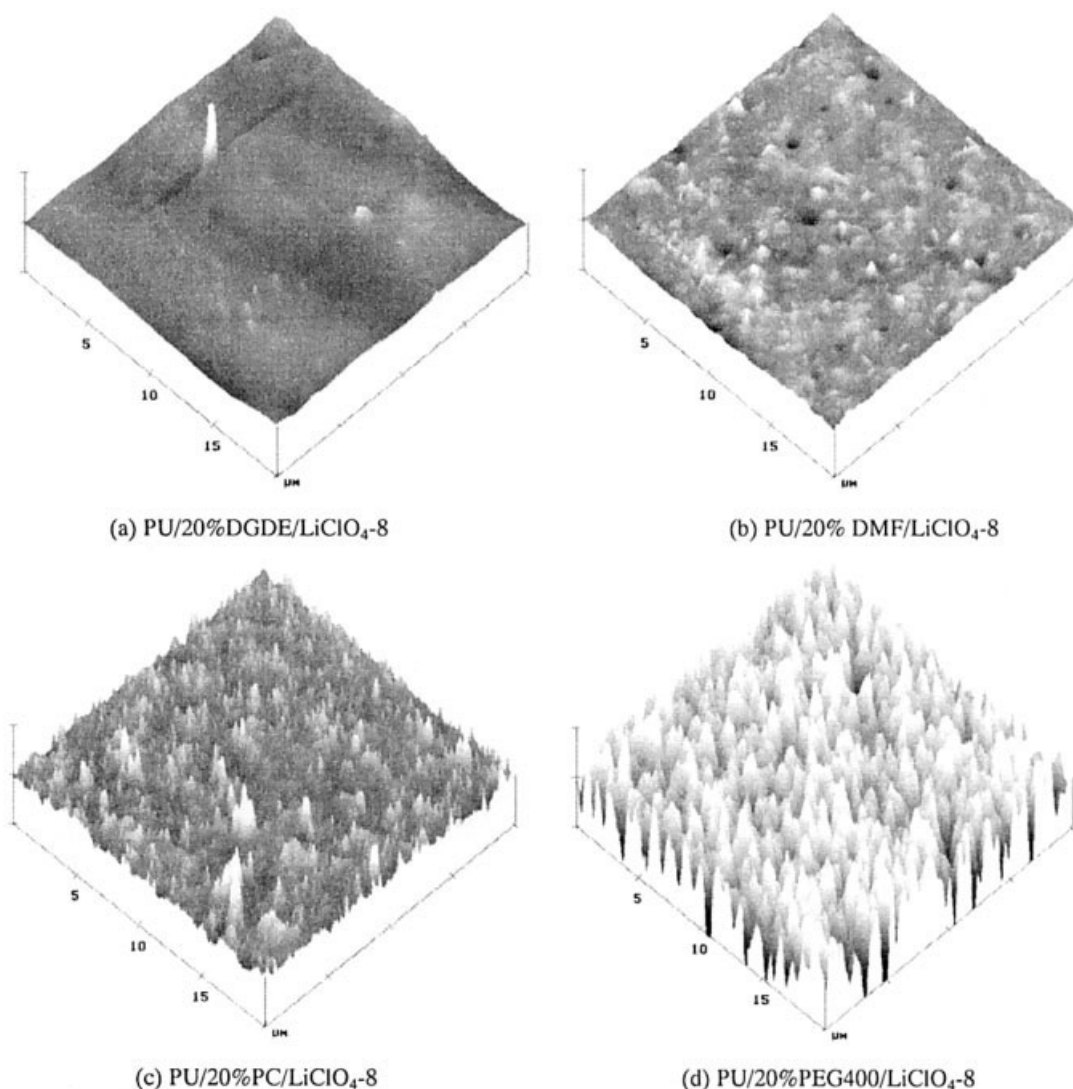


Figure 3 AFM images of gel electrolytes with different organic additives (vertical scale 100 nm).

more evident. Relationship between PEG400 content and microphase separation of PU matrix is shown in Figure 4. It is clear that, with increase of PEG400 content, the number of polymeric aggregates and the microphase separation in the PU matrix increase.

Micrograph images thus show that, when PC, DMF, or PEG400 are used as organic additives in gel electrolyte samples, microphase separation, and polymeric aggregation are enhanced, which suggested that PC, DMF, and PEG400 are more miscible with soft-segment than with hard-segment of PU matrix, and the miscibility of PC, PEG400, or DMF with soft-segment of PU matrix means that these organic additives act as plasticizer in the soft-segment enriched domains.

Polymer segmental mobility of gel electrolyte samples

Figure 5 shows DSC curves of gel electrolyte samples with different organic additives and DSC data of the

samples are listed in Table II. It is found that PU/LiClO₄-8 has a T_g higher than that of PU. As expected, organic additives have great effect on the T_g of the electrolytes. T_g s of samples with PC, DMF, PEG400, or glycerol as organic additive are lower than that of PU/LiClO₄-8, while, the T_g of the sample with DEC as organic additive is higher than that of PU/LiClO₄-8. DSC data also show that DGEC has small effect on T_g of the electrolyte. Effects of PEG400 content on T_g s of gel electrolyte samples are listed in Figure 6 and Table III. The results show that T_g s of the samples decrease with increase of PEG400 content.

It has been reported that metallic ions associate with polar groups in polymer chains, which result in a change of polymer chain mobility.¹⁷ Here, the host polymer of gel electrolyte samples is thermoplastic PU with oligo-poly(ethylene oxide) as soft segment. DSC curves show that this polymer host is highly amorphous. Association of lithium ions with ether group

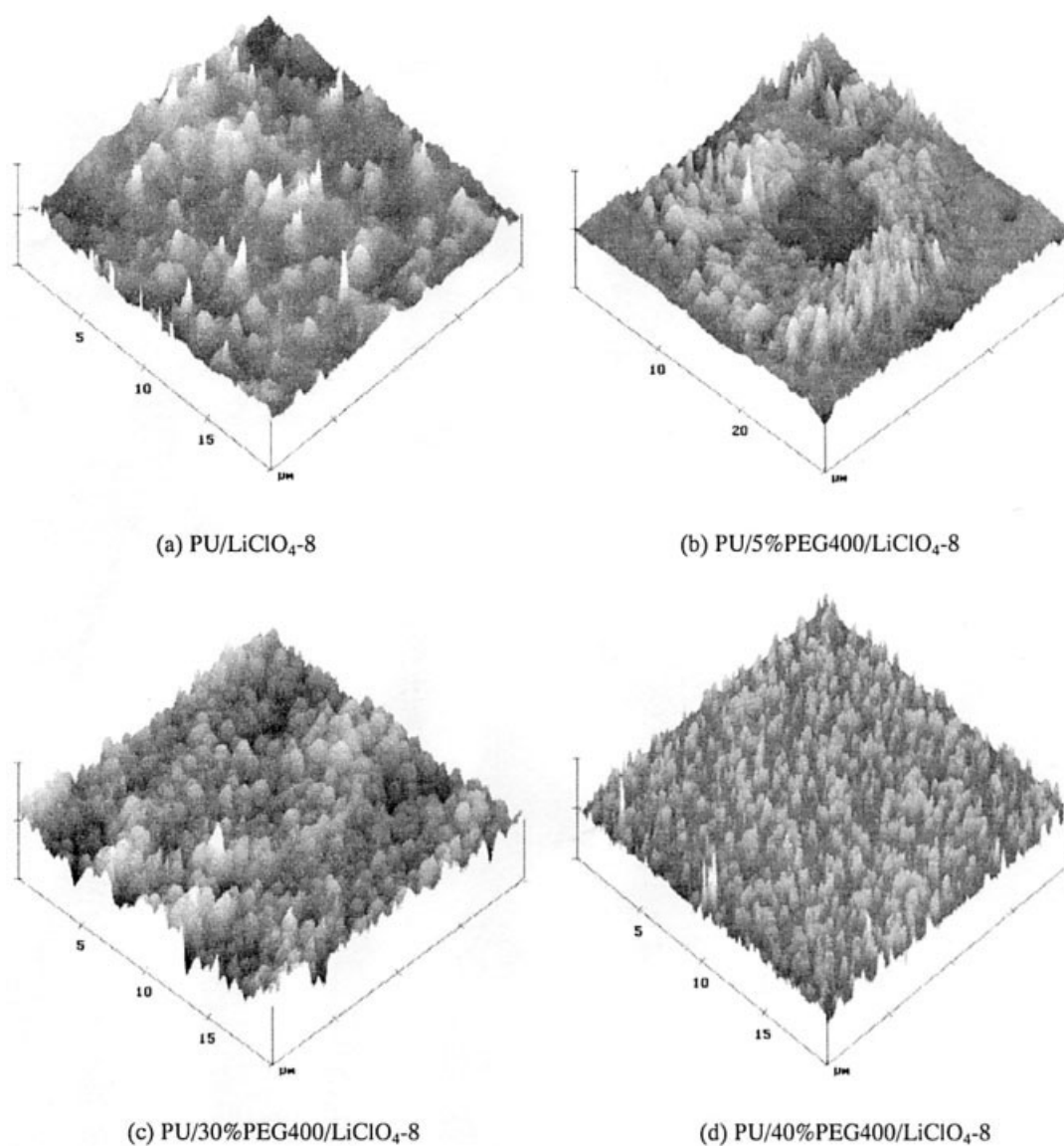


Figure 4 AFM images of gel electrolytes with different PEG400 content (vertical scale 200 nm).

reduces the polymer segmental mobility, which gives a T_g of PU/LiClO₄-8 higher than that of PU.

In general, ion conduction of polymer-based electrolyte can be strikingly improved through incorporation of plasticizers.¹⁸⁻¹⁹ In addition to resulting in great ion dissociation, plasticizers increase the polymer segmental mobility, which leads to a decrease of T_g . For the gel electrolytes discussed here, organic additives of PC, DMF, PEG400, and glycerol play roles of plasticizers and are miscible with soft-segment in PU matrix, which leads to increase of the polymer segmental mobility and thus a decrease of T_g , while DEC and DGEC show no effectiveness of plasticizers. When the content of PEG400 in gel electrolytes increases, an increase of polymer segmental mobility and a decrease of T_g result.

Ionic conductive property of gel electrolyte samples

In PU-based electrolyte, soft-segment domains are responsible for ion conduction.^{12,14} The previous literatures¹¹⁻¹⁶ report that morphologic structure and soft-segmental mobility of PU-based electrolyte have great effects on ion conduction.

Ionic conductivities of the gel electrolytes with different organic additives are shown in Figure 7. It is found that, for all the gel electrolyte samples, ionic conductivity increases with increase of temperature. The sample with PC as organic additive has higher ionic conductive property than samples with other organic additives. At room temperature, ionic conductivities of the samples follow the sequence: PC > PEG400 > glycerol > DMF ≈ DGDE > DEC. Ac-

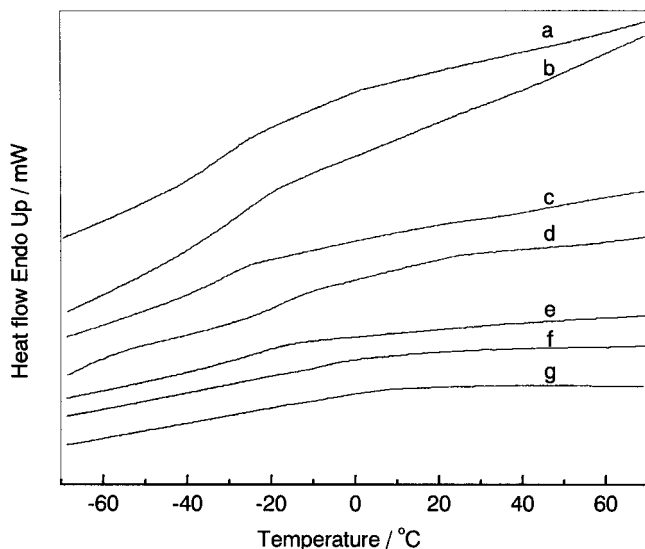


Figure 5 DSC curves of gel electrolyte samples with different organic additives. (a) PEG400, (b) glycerol, (c) PC, (d) DMF, (e) pure PU, (f) DEC, (g) DGDE.

TABLE II
DSC Data of Gel Electrolyte Samples With Different Organic Additives

Samples	Organic additives	Glass transition temperature (T_g)/°C
PU/20% PC/LiClO ₄ -8	20% PC	-39.0
PU/20% DEC/LiClO ₄ -8	20% DEC	-17.5
PU/20% DGDE/LiClO ₄ -8	20% DGDE	-21.1
PU/20% DMF/LiClO ₄ -8	20% DMF	-26.4
PU/20% glycerol/LiClO ₄ -8	20% glycerol	-37.1
PU/20% PEG400/LiClO ₄ -8	20% PEG400	-38.7
PU/LiClO ₄ -8	—	-20.3
PU	—	-30.2

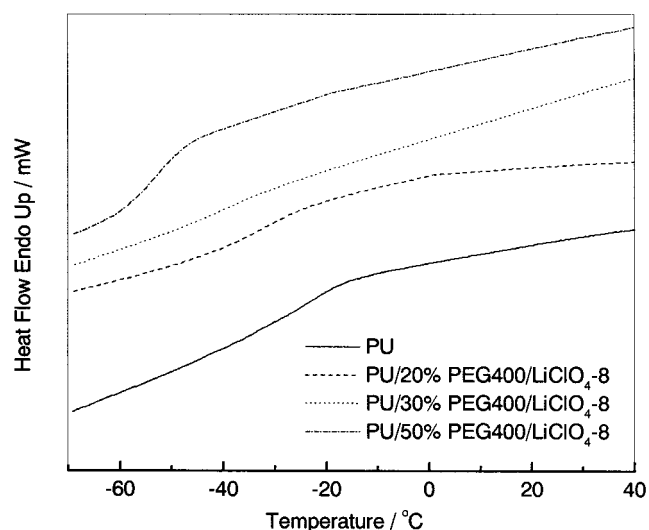


Figure 6 DSC curves of gel electrolytes with different PEG400 content.

TABLE III
DSC Data of Gel Electrolyte Samples

Samples	Organic additives PEG400 (%)	T_g /°C
PU/5% PEG400/LiClO ₄ -8	5	-28.2
PU/20% PEG400/LiClO ₄ -8	20	-38.7
PU/30% PEG400/LiClO ₄ -8	30	-48.3
PU/50% PEG400/LiClO ₄ -8	50	-59.9

According to DSC data of the samples, a sequence of T_g is obtained: PC < PEG400 < glycerol < DMF < DGDE < DEC, then mobility of polymer chain should follow the sequence of PC > PEG400 > glycerol > DMF > DGDE > DEC, as found for the sequence of ionic conductivity. This coincides with the fact that higher mobility of the polymer chain usually leads to higher ionic conductivity.²⁰⁻²¹

Effects of PEG400 content on ionic conductive property of the samples (Fig. 8) show that, with increase of PEG400 content, ionic conductivity of the gel electrolyte samples increases. For the sample of PU/50% PEG400/LiClO₄-8, an ionic conductivity above $1.8 \times 10^{-5} \text{ S cm}^{-1}$ is reached at room temperature.

CONCLUSIONS

In this work, PC, DMF, PEG400, glycerol, DEC, and DGEC are used as organic additives in gel electrolytes with PU as polymer host. Study on the gel electrolytes shows that PC, DMF, PEG400, and glycerol play the role of plasticizers, which leads to an increase of microphase separation between soft- and hard-segment in PU matrix. This in turn leads to an increase of polymer segmental mobility, and results in an improvement on ionic conductivity of the gel electrolytes.

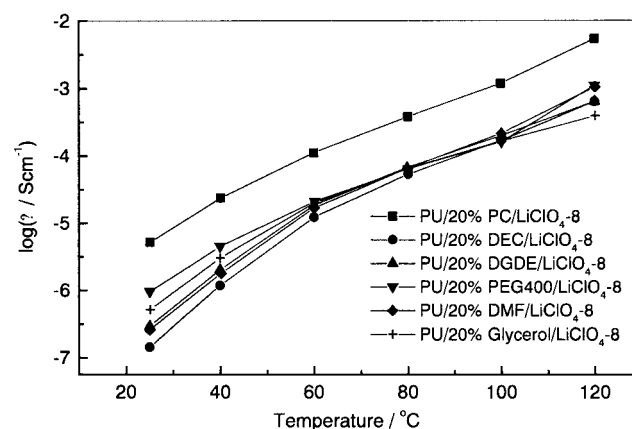


Figure 7 Ionic conductivities of gel electrolytes with different organic additives.

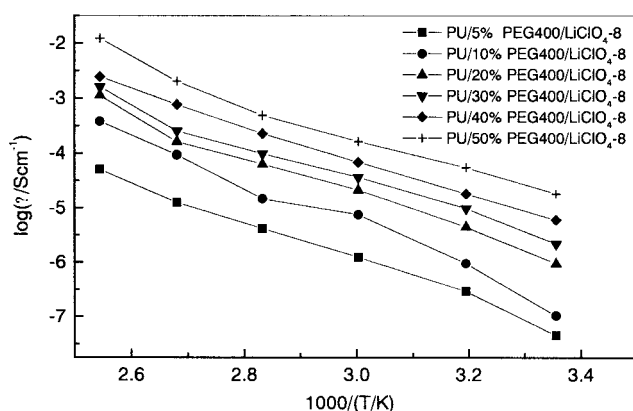


Figure 8 Ionic conductivities of gel electrolytes with different PEG400 content.

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