

Preparation and Characterization of Novel Crosslinked Poly[glycidyl methacrylate–poly(ethylene glycol) methyl ether methacrylate] as Gel Polymer Electrolytes

Dan Luo, Yang Li, Mujie Yang

Key Laboratory of Macromolecular Synthesis and Functionalization, Ministry of Education, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

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ABSTRACT: In this study, glycidyl methacrylate was copolymerized with poly(ethylene glycol) methyl ether methacrylate to obtain a copolymer {poly[glycidyl methacrylate–poly(ethylene glycol) methyl ether methacrylate] [P(GMA–PEGMA)]}, which was crosslinked with α,ω -diamino poly(propylene oxide) (Jeffamine) at various weight ratios and molecular weights to form novel gel polymer electrolytes (GPEs). The crosslinked copolymers were characterized by Fourier transform infrared spectroscopy and thermal analysis. The crosslinked polymers were amorphous in the pristine state and became crystallized after they were doped with lithium electrolyte. Furthermore, the crosslinking degree of the crosslinked polymers increased with increasing weight ratio of Jeffamine, and both the swelling properties and mechanical behaviors of the crosslinked polymers were

heavily affected by the weight ratio and molecular weight of Jeffamine. The ionic conductivity (σ) of the GPEs from the crosslinked copolymers was determined by alternating-current impedance spectroscopy. A higher molecular weight and increased weight ratio of Jeffamine resulted in a higher σ . The GPE based on P(GMA–PEGMA) crosslinked with an equal weight of Jeffamine D2000 exhibited the highest σ of 8.29×10^{-4} S/cm at 25°C and had a moderate mechanical strength. These crosslinked copolymers could be potential candidates for the construction of rechargeable lithium batteries. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 120: 2979–2984, 2011

Key words: copolymerization; crosslinking; differential scanning calorimetry (DSC); polyelectrolytes

INTRODUCTION

With the increasing demand for electric vehicles, portable electronics, and implantable medical devices, the research and development of new series of polymer electrolytes for rechargeable lithium batteries has remained popular for decades because of their better performance in safety, fabrication, and energy density compared to liquid electrolytes.^{1,2}

Poly(ethylene oxide) (PEO), which is capable of coordinating with lithium salts and facilitating ion transport, has been studied extensively as a solid polymer electrolyte (SPE).^{3,4} However, the ionic conductivity (σ) of PEO-based SPE at room temperature was not sufficient for its practical use in batteries because of its linear structure, which tends to crystallize to hinder the mobility of polymer chains.⁵ Recently, comblike polymers with oligomeric PEO in the side chains have attracted interest for use

in polymer electrolytes because the pendant PEO side chains may alter the matrix flexibility and the fast side-chain motion can increase the mobility of the dissolved ions, thus improving their conductivity.^{6,7}

In comparison, gel polymer electrolytes (GPEs) are prepared by the addition of liquid electrolytes to an electrochemically inert polymer, such as polyacrylonitrile,^{8,9} poly(methyl methacrylate),^{10,11} or poly(vinylidene fluoride).^{12,13} σ of GPEs at room temperature is higher than that of SPE because of the plasticizers swollen in the polymer. Introducing a comblike PEO into GPEs has been proven to be an effective way to increase the conductivity.¹⁴ However, these GPEs exhibit a relatively low mechanical strength. Crosslinkable components are considered to form polymers with the network structure, with the aim of improving the mechanical properties of the resulting GPEs.^{15,16}

Poly(propylene oxide) (PPO) has a structure similar to which can dissolve lithium salts in the polymer and form ion–polymer complexes, and the complete amorphous structure enables the ions to transfer faster than PEO.^{17,18} Some network-structured GPEs based on copolymers with an epoxy function crosslinked by α,ω -diamino poly(propylene oxide) (Jeffamine) with a high σ at ambient room

Correspondence to: Y. Li (liyong@zju.edu.cn) or M. Yang (yangmj@zju.edu.cn).

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temperature and improved mechanical properties have been reported.^{19,20}

To better understand the role of the amino-terminated PPO in GPE and to obtain a high σ with the mechanical integrity of the polymer membrane preserved, we synthesized the copolymer poly[glycidyl methacrylate–poly(ethylene glycol) methyl ether methacrylate] [P(GMA–PEGMA)] with epoxy groups and soft PEO side chains. The structure of the cross-linked polymers with different compositions were characterized by Fourier transformed infrared (FTIR) spectroscopy and differential scanning calorimetry (DSC). The effects of the molecular weight and the content of curing agent in the crosslinked copolymers on the swelling properties, mechanical strength, and σ of the corresponding GPEs were investigated.

EXPERIMENTAL

Materials

Glycidyl methacrylate (GMA; Aldrich, USA) and poly(ethylene glycol) methyl ether methacrylate (PEGMA; number-average molecular weight = 475, Aldrich) were stored under refrigeration at -20°C . PPO polyamines (Huntsman Corp., USA), with equivalent weights of active hydrogen of 115 g/equiv (Jeffamine D400) and 514 g/equiv (Jeffamine D2000), respectively, were dehydrated at 80°C *in vacuo* for 24 h before use. The lithium electrolyte [dimethyl carbonate (DMC): diethyl carbonate (DEC): ethylene carbonate (EC) = 1 : 1 : 1 w/w/w LiPF₆ 1.0M, Zhangjiagang Guotai-Huarong New Chemical Materials Co., Ltd., Jiangsu, China] was stored in a desiccator before use. Other reagents were of analytical grade and were used as received.

Polymer synthesis

The copolymerization of GMA and PEGMA (weight ratio = 3/1) was conducted at 70°C for 6 h in a single-necked flask in an N₂ atmosphere with azobisisobutyronitrile as the initiator and toluene as the solvent. Upon cooling, the mixture was precipitated in methanol, filtered, washed with methanol, and then dried *in vacuo* at 40°C for 24 h to obtain P(GMA–PEGMA) (yield = 52.3%).

Preparation of the gelled crosslinking polymer electrolytes

The copolymer P(GMA–PEGMA) and Jeffamine D400 or Jeffamine D2000 were dissolved in *N,N*-dimethylformamide at different weight ratios and then heated at 80°C for 8 h with vigorous stirring for precrosslinking. The resulting mixture was poured onto a polytetrafluoroethylene plate; then,

the solvent was evaporated at room temperature, and curing followed at 100°C for 24 h. The obtained specimens, which are denoted as GPD400(21) [P(GMA–PEGMA)/Jeffamine D400 = 2/1 w/w], GPD400(11) (weight ratio = 1/1), GPD2000(21) [P(GMA–PEGMA)/Jeffamine D2000 = 2/1 w/w], and GPD2000(11) (weight ratio = 1/1), were dried *in vacuo* at 40°C before use. Finally, the GPEs were obtained by immersion of the resulting polymer membranes into liquid electrolyte for 2 h.

Measurements

FTIR spectra were recorded on a Bruker VECTOR-22 Spectrometer, Germany.

¹H-NMR measurements were performed on a Bruker Advance DMX 500 spectrometer with deuteriochloroform (CDCl₃) as a solvent. Thermal analysis was done in a TA DSC Q100 (USA) differential scanning calorimeter under an N₂ atmosphere at a heating rate $10^{\circ}\text{C}/\text{min}$ from -80 to 150°C .

The epoxide equivalent weight (EEW) of the P(GMA–PEGMA) copolymer was determined by the reaction of a known quantity of resin with a known quantity of hydrochloric acid and back-titration of the remaining acid to determine its consumption.²¹ EEW was calculated to be 175 g/equiv, so the molar fraction of the GMA unit in the copolymer P(GMA–PEGMA) could be calculated from the following equation:

$$\text{Molar fraction of GMA units} = \frac{1}{1 + (\text{EEW} - 142)/475}$$

where 142 and 475 are the unit weights of the GMA and PEGMA units, respectively. Thus, the molar fraction of GMA units in the copolymer P(GMA–PEGMA) was calculated to be 93%.

The percentage swelling (S_w) was obtained with the following equation after the resulting membranes were dipped into the lithium electrolyte [DMC : DEC : EC = 1 : 1 : 1 (w/w/w) LiPF₆ 1.0M]:

$$S_w = (W - W_0)/W_0 \times 100\%$$

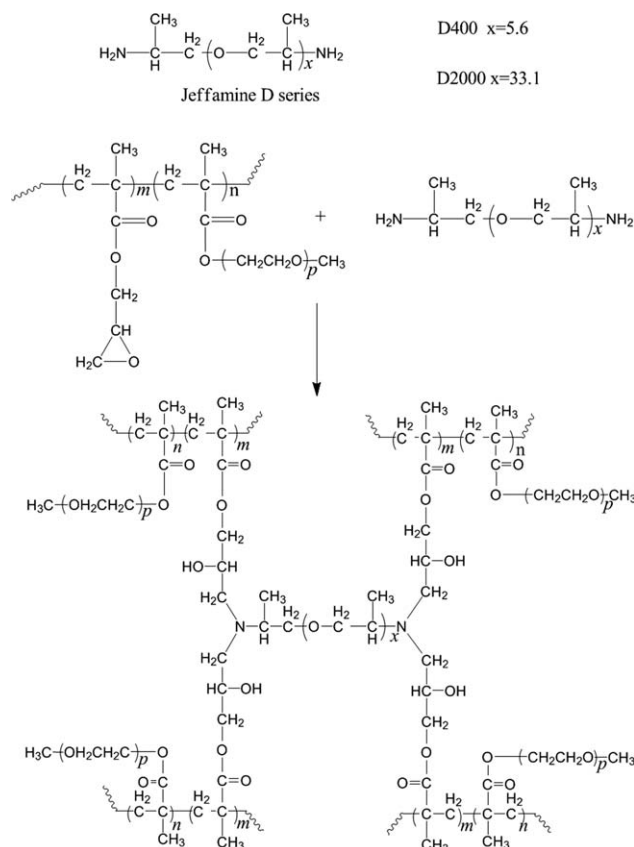
where W_0 and W are the weights of the dried and swollen films, respectively.

The crosslinking degree (CD) was measured in terms of the percentage gel content with the following equation:

$$\text{CD} = W_2/W_1 \times 100\%$$

where W_1 is the initial weight of the sample and W_2 is the weight of the sample after extraction with tetrahydrofuran (THF) for 24 h.^{21,22}

The mechanical properties of the crosslinked copolymer films were evaluated from stress–strain tests with an Instron model 5500 (USA) testing



Scheme 1 Illustration of the synthesis of P(GMA-PEGMA) and the crosslinked copolymer (x refers to number of repeating unit).

device. Tensile tests were carried out under a 1000-N load cell at a strain rate of 5 mm/min.

σ of the GPEs was determined by alternating-current impedance spectroscopy (EG&G model 273A potentiostat, USA). The membrane was sandwiched between two parallel stainless steel discs (distance = 1 cm). During the measurement, it was mounted in a sealed coin cell to prevent contamination of the sample. The frequency ranged from 100 kHz to 10 Hz at a perturbation voltage of 10 mV. σ was calculated from the electrolyte resistance (R_b) obtained from the intercept of the Nyquist plot with the real axis, the membrane thickness (l), and electrode area (A) according to the following equation:

$$\sigma = l/AR_b$$

RESULTS AND DISCUSSION

Characterization

The copolymer P(GMA-PEGMA) was prepared by simple radical polymerization. The synthesis of P(GMA-PEGMA) and the crosslinked polymer is illustrated in Scheme 1. The $^1\text{H-NMR}$ spectrum of the copolymer is shown in Figure 1. The chemical

shifts at 3.23 ppm (d), 2.84 ppm, and 2.64 ppm (e) were assigned to the proton resonance of the epoxide group.²³ The signals at 3.38 ppm (i) and 3.6 ppm (h) corresponded to the protons of methoxy ($-\text{OCH}_3$) and methylene, respectively. Additionally, the chemical shift at 4.11 ppm was assigned to $-\text{CH}_2$ protons of the poly(ethylene glycol) segment next to $-\text{OCO}=\text{}$.²⁴

Figure 2 shows the FTIR spectra of P(GMA-PEGMA) and the crosslinked copolymers with Jeffamine D400 or Jeffamine D2000 at different weight ratios as curing agents. In the spectrum of P(GMA-PEGMA), the absorption peak at 1730 cm^{-1} was ascribed to the $\text{C}=\text{O}$ stretching vibration, whereas the epoxy group was identified by the oxirane-ring unsymmetrical expansion and contraction vibrations at 908 , 850 , and 758 cm^{-1} . In contrast, broad shoulder peaks were observed at 930 and 908 cm^{-1} in the spectra of GPD400(21), GPD2000(21), and GPD2000(11), which indicated that the epoxy group in P(GMA-PEGMA) did not completely react with the amine group in Jeffamine D2000 and D400 because of the insufficient molar content of active hydrogen in Jeffamine relative to P(GMA-PEGMA). In the spectrum of the crosslinked copolymer GPD400(11), which showed a higher ratio of active hydrogen in Jeffamine to P(GMA-PEGMA), the absorption peak of epoxide at 908 cm^{-1} disappeared, and new bands at 930 cm^{-1} were observed, indicating that the epoxy group on P(GMA-PEGMA) reacted with Jeffamine D400 completely. The FTIR spectra analysis showed clearly the occurrence of the crosslinking reaction of P(GMA-PEGMA) with Jeffamine.

The CDs of the copolymers crosslinked with Jeffamine D400 and D2000, as obtained by extraction with THF, are listed in Table I. CD increased with increasing content of Jeffamine D400 and Jeffamine D2000. According to the previous results obtained

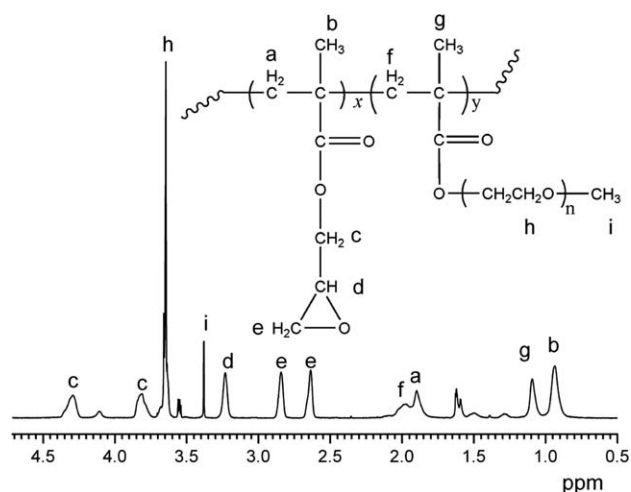


Figure 1 $^1\text{H-NMR}$ spectrum of P(GMA-PEGMA).

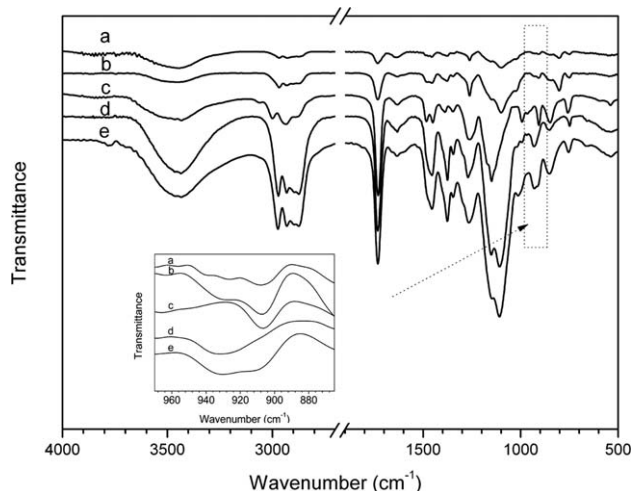


Figure 2 FTIR spectra of (a) GPD2000(21), (b) GPD400(21), (c) P(GMA-PEGMA), (d) GPD400(11), and (e) GPD2000(11).

from FTIR spectroscopy, the loss of the crosslinked copolymers GPD400(21), GPD2000(21), and GPD2000(11) were due to the incompletely reacted P(GMA-PEGMA) component by THF extraction. In contrast, the loss of GPD400(11) by extraction was probably due to the excessive unreacted Jeffamine D400 component. In addition, the copolymer crosslinked with Jeffamine D2000 showed a lower CD than the copolymer crosslinked with Jeffamine D400 because of less active molar content of hydrogen at the same weight ratio.

DSC traces (second heating runs) of P(GMA-PEGMA) and the crosslinked copolymer before and after it was doped with 1M LiPF₆/DMC/DEC/EC/liquid electrolyte are displayed in Figures 3 and 4, respectively. The results of the thermal analysis are summarized in Table II.

As shown in Figure 3, two glass-transition temperatures (T_g 's; $T_{g1} = 26.54^\circ\text{C}$ and $T_{g2} = 59.75^\circ\text{C}$) were observed for P(GMA-PEGMA); this indicated phase separation in the copolymer. It was reported that T_g of pure PGMA was 65°C ,²⁵ and T_{g2} might be related to the small domain of PGMA in the copolymer. After crosslinking with Jeffamine D400 and Jeffamine D2000 of various weight ratios, the T_g zone of the crosslinked copolymer membrane became wide. The wide glass transition of GPD400(21), which started at 21.1°C , covered the glass-transition zone of the small domain of PGMA in the copolymer,

TABLE I
Gel Fraction of the Copolymer [P(GMA-PEGMA)]
Crosslinked with Jeffamine

	GPD400 (21)	GPD400 (11)	GPD2000 (21)	GPD2000 (11)
CD (%)	98.11	99.17	95.26	98.75

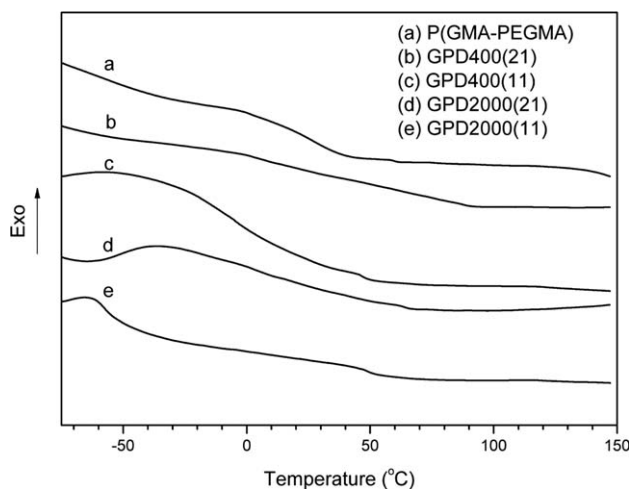


Figure 3 DSC traces of (a) P(GMA-PEGMA) and (b-e) P(GMA-PEGMA) crosslinked with Jeffamine: (b) GPD400(21), (c) GPD400(11), (d) GPD2000(21), and (e) GPD2000(11).

whereas GPD400(11) exhibited two T_g values ($T_{g1} = -4^\circ\text{C}$ and $T_{g2} = 47.35^\circ\text{C}$). The crosslinked copolymers exhibited two T_g values when Jeffamine 2000 was used as the curing agent. The slight inflection in the DSC curve of the Jeffamine D2000 crosslinked copolymer at high temperature was assigned to T_g of the PGMA segment. A wide zone of glass transition was also observed for the copolymer crosslinked with Jeffamine D2000, and T_{g1} decreased with increasing weight ratio of Jeffamine D2000. The broadening of the glass-transition zone was probably due to random crosslinking with the epoxy groups on the copolymer side chains, which resulted in a relaxation process with different relaxation times.²⁶ We concluded that the higher molecular weight of Jeffamine with longer PPO chains may have

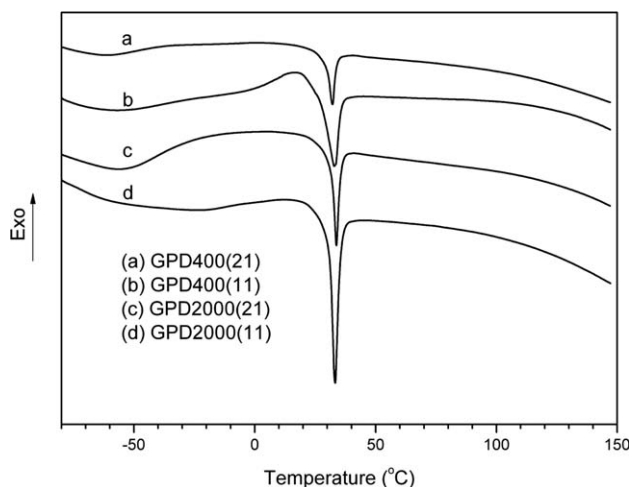


Figure 4 DSC traces of P(GMA-PEGMA) crosslinked with Jeffamine after doping with 1M LiPF₆ liquid electrolyte: (a) GPD400(21), (b) GPD400(11), (c) GPD2000(21), and (d) GPD2000(11).

TABLE II
Thermal Characteristics of P(GMA-PEGMA),
P(GMA-PEGMA) Crosslinked with Jeffamine,
and the Corresponding GPEs

	T_{g1} (°C)	T_{g2} (°C)	GPEs	
			T_{m1} (°C)	ΔH_{m1} (J/g)
P(GMA-PEGMA)	26.54	59.75	—	—
GPD400(21)	21.14	—	32.16	3.711
GPD400(11)	-4.00	47.35	32.84	11.60
GPD2000(21)	3.82	64.29	33.79	4.968
GPD2000(11)	-57.26	48.52	33.25	9.563

T_{m1} = melting point.

provided additional amorphous domains to facilitate the transportation of the lithium ion and increase the conductivity.

The absence of melting transition in all of the dry crosslinked copolymers in the range of analyzed temperatures in the thermograms indicated that they were in the amorphous state. However, after the uptake of the liquid electrolyte, part of the amorphous phase of the crosslinked copolymers became ordered because of the interactions of Li^+ with ether oxygen. One melting temperature (T_{m1}) was observed in the thermograms of all of the GPEs, and the apparent enthalpies of melting (ΔH_m 's) of the GPEs were low. With increasing weight ratios of Jeffamine D400 or D2000, the value of ΔH_m increased because of a greater number of interactions between Li^+ and the PPO chains.

Swelling properties

We investigated the swelling properties of the crosslinked copolymers by measuring the time dependence of the electrolyte uptake properties of the copolymers

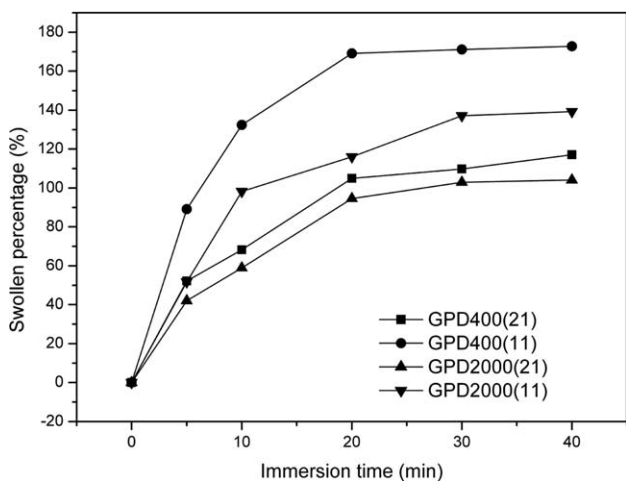


Figure 5 S_w as a function of immersion time in 1.0M LiPF_6 liquid electrolyte of P(GMA-PEGMA) crosslinked with Jeffamine of various weight ratios.

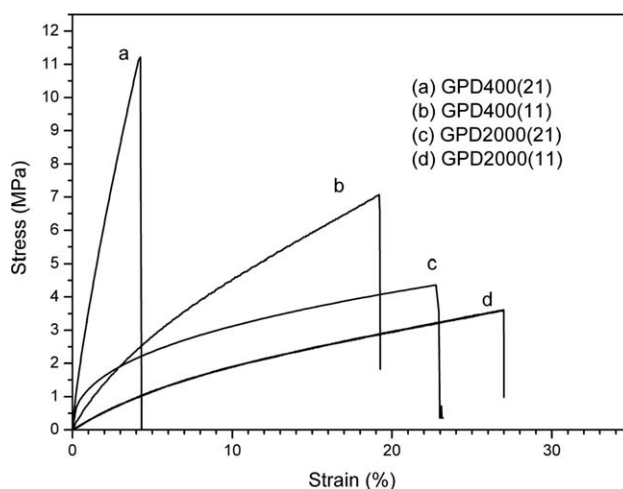


Figure 6 Stress-strain curves of P(GMA-PEGMA) crosslinked with Jeffamine D400 and D2000 membranes.

crosslinked with Jeffamine at different weight ratios, and the results are plotted in Figure 5. Both the swollen rate and the swelling degree after immersion in the electrolyte solution for 40 min increased greatly for the crosslinked copolymer with increasing weight ratio of Jeffamine D400 or D2000. The great effect of the content of Jeffamine on the swelling properties of the crosslinked copolymers may have similarly been due to the interactions of the liquid electrolyte solution with the PPO phase and also to the variation in CD. Accordingly, it may have had an effect on the σ values of the corresponding GPEs.

Mechanical properties

The mechanical properties of GPEs are as important as σ at room temperature for their practical applications. The copolymer poly(acrylonitrile-glycidyl methacrylate) was crosslinked with Jeffamine D400 or Jeffamine D2000 to improve its mechanical stability. The stress-strain relationships of the copolymers crosslinked with Jeffamine at various weight ratios are presented in Figure 6 and were used to evaluate the mechanical properties of corresponding GPEs. The crosslinked copolymer GPD400(21) membrane exhibited good mechanical behavior with a critical stress of 11.07 MPa and an elongation at break value of 4.28%. In contrast, the membranes of poly(acrylonitrile-glycidyl methacrylate) crosslinked with Jeffamine D2000 exhibited a lower critical stress but a higher elongation at break value than that crosslinked with Jeffamine D400. This may have been due to the longer chain of PPO in Jeffamine D2000, which in turn, promoted chain relaxation. Furthermore, with increasing content of Jeffamine D400, the critical strength of the crosslinked copolymer membrane decreased to 7.07 MPa, and the values of elongation at break increased. The same trend was

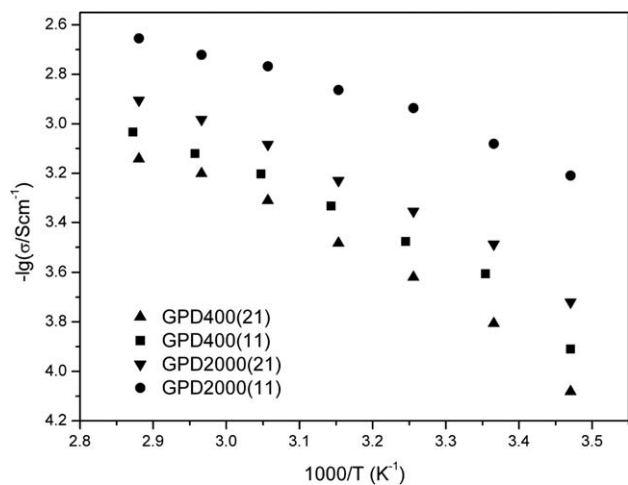


Figure 7 $-\lg \sigma$ versus $1000/T$ plot for GPEs based on crosslinked copolymers.

observed for the crosslinked copolymers with Jeffamine D2000 as a curing agent; this indicated that Jeffamine played the role of not only a curing agent but also a plasticizer.

Electrochemical properties

The effect of the temperature (T) on the conductivity of the GPEs based on P(GMA-PEGMA) crosslinked with Jeffamine at various weight ratios was investigated, and $-\lg \sigma$ versus $1000/T$ is depicted in Figure 7. The value of $\lg \sigma$ changed linearly with $1/T$; this indicated an Arrhenius-like behavior of conductivity according to eq. (1):

$$\sigma = \sigma_0 \exp(-E_a/KT) \quad (1)$$

where σ_0 is a constant, E_a is the activation energy, and K is Boltzmann's constant.

σ of the GPE based on GPD400(21) was the lowest because of the rigidity of the membrane. Also, σ of the crosslinked polymer-based GPEs increased with increasing weight ratio of Jeffamine, which was apparently due to the greater number of Li^+ ions coordinated to ether oxygen. Among all of the specimens investigated, the GPE based on GPD2000(11) exhibited the highest ionic conductivities in the range 15–75°C (8.29×10^{-4} S/cm at 25°C), although the GPE based on GPD400(11) showed the highest S_w in the liquid electrolyte among all of the samples. According to the DSC analysis, ΔH_m of the GPE based on GPD2000(11) were lower than that of GPD400(11); this suggested its lower crystallinity degree and higher chain mobility in GPD2000(11). Therefore, we propose that the higher molecular weight of Jeffamine D2000 relative to Jeffamine D400 led to the enhanced mobility of the PPO segments and facilitated ion conduction and the higher overall σ of the corresponding GPE.

CONCLUSIONS

P(GMA-PEGMA) was crosslinked with Jeffamine to prepare new GPEs. The molecular weights and weight ratios of Jeffamine had a great effect on the CD, swelling properties, and mechanical properties of the resulting crosslinked copolymers. σ of the GPEs based on the crosslinked copolymers obeyed Arrhenius behavior over the range 15–75°C and increased with increases in both the weight ratio and molecular weight of Jeffamine. The GPE obtained from P(GMA-PEGMA) crosslinked with an equal weight of Jeffamine D2000 exhibited the highest σ of 8.29×10^{-4} S/cm at 25°C.

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