

Novel Amphiphilic Polymer Gel Electrolytes Based on (PEG-*b*-GMA)-*co*-MMA

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ABSTRACT: Amphiphilic conetwork-structured copolymers containing different lengths of ethylene oxide (EO) chains as ionophilic units and methyl methacrylate (MMA) chains as ionophobic units were prepared by free radical copolymerization and characterized by FTIR and thermal analysis. Polymer gel electrolytes based on the copolymers complexed with liquid lithium electrolytes (dimethyl carbonate (DMC) : diethyl carbonate (DEC) : ethylene carbonate (EC) = 1 : 1 : 1 (W/W/W), LiPF₆ 1.0M) were characterized by differential scanning calorimetry and impedance spectroscopy. A maximum ion conductivity of 4.27×10^{-4} S/cm at 25°C was found for the polymer

electrolyte based on (PEG2000-*b*-GMA)-*co*-MMA with long EO groups. Moreover, the effect of temperature on conductivity of the amphiphilic polymer electrolytes obeys the Arrhenius equation. The good room temperature conductivity of the polymer electrolytes is proposed to relate to the enhancement in the amorphous domain of the copolymers due to their amphiphilic conetwork structure. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 1527–1533, 2010

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

INTRODUCTION

In recent years, polymer electrolytes for lithium ion batteries attracted great attention due to their distinct advantages over liquid electrolytes.^{1–3} However, there are still some challenges in the development of polymer electrolytes for practical applications: how to combine several properties, such as ionic conductivity, mechanical strength, and interfacial compatibility, efficiently in a single material.⁴

Polymer gel electrolytes are one of the most investigated polymer electrolytes because of their high ion conductivities comparable with that of liquid electrolytes at room temperature.^{5–7} However, their wide applications were hindered by the fact that the polymers usually only act as a passive component and a rigid matrix, and the coordination with liquid electrolytes improved the conductivity, but led to the deterioration in their dimension stability at the same time.⁸

Amphiphilic conetworks are two-component networks of covalently interconnected ionophilic/iono-

phobic phases of cocontinuous morphology. As such they can respond to changes in the medium by morphological isomerization, and have found applications in smart materials.⁹ For the amphiphilic conetwork polymers, the ionophilic component provides good compatibility with lithium ion and thus enhances ion conduction, while the conetwork structure is beneficial for their dimensional stability.¹⁰ As a result they are regarded as good candidate materials for polymer gel electrolytes featured with good mechanical stability while retaining high ion conductivity at the same time. But the reports in this field are quite scarce.

In this study, we prepared amphiphilic conetwork copolymers containing different lengths of ethylene oxide (EO) chains as ionophilic units and methyl methacrylate (MMA) chains as ionophobic units by employing the simple strategy of random free radical copolymerization. The choice of EO chains is based on the fact that poly(ethylene oxide) (PEO)-based materials are commonly used in polymer electrolytes for their ionophilic properties of lithium ions.^{11–14} The amphiphilic conetwork structure is expected to improve the mechanical and dimensional stability while retaining a high ionic conductivity.¹⁰ Moreover, the propensity to crystallization of EO chains would be suppressed to facilitate ion migration. The structure of the resulting copolymer network was examined and the conductivity behavior of corresponding polymer gel electrolyte investigated.

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EXPERIMENTAL

Materials

Glycidyl methacrylate (GMA) and methyl methacrylate (MMA) were purchased from Aldrich. They were dried over CaH₂ and purified by distillation before use. Poly(ethylene glycol)s with molecular weights of 200 (PEG-200) and 2000 (PEG-2000) were purchased from Sinopharm Chemical Co., and used without further purification. Dichloromethane was refluxed by CaH₂ and distilled before use. BF₃·OEt₂ (Lingfeng Chemical Reagent Co., Chemically Pure) was dried with activated molecular sieve (4Å). 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.) was stored in a desiccator before use. Other reagents were purchased from the domestic market and used as received.

Preparation of the copolymers

PEG-*b*-GMA was synthesized according to a method in previous study.¹⁵ In a typical procedure, PEG (10 g, 0.005 mol; *M_n* = 2000) and 14.30 g (0.1 mol) of GMA were dissolved in 150 mL of dried CH₂Cl₂. When the mixture was cooled to -10°C in an ice-salt bath, 1.6 mL (0.015 mol) of BF₃·OEt₂ was dropped into it by syringe quickly. After 40 min, a little methanol was added to the mixture to end the cationic polymerization. The resulting polymer was concentrated with a rotator evaporator and isolated by the pouring of the polymerization mixture into a large excess of ether. The resulting polymer was dissolved into methanol and reprecipitated in ether at least three times. A transparent, jellylike, viscous liquid was obtained. Then, the resulting block copolymers were kept in a refrigerator. The samples were freeze-dried before the measurements.

All the amphiphilic copolymers (P200GM21, P200GM11, P200GM12, P2000GM11, P2000GM12) were synthesized according to Scheme 1 with different (PEG200-*b*-GMA) /MMA weight ratios (2/1, 1/1, and 1/2) and (PEG2000-*b*-GMA)/MMA weight ratios (1/1 and 1/2), respectively.

Copolymerization of MMA and PEG-*b*-GMA with different feed ratio was carried out by first heating at 70°C (oil bath) for 6 h using Azo-bis-isobutyronitrile (AIBN) (1 wt %) as initiator and THF as medium in a three-necked flask with magnetic stirring and a condenser under N₂ atmosphere. The obtained prepolymer was then cast onto Teflon plate, dried in air, and cured in an oven at 80°C for 2 h and 100°C for another 1 h. Upon cooling, the obtained polymer film was washed with methanol several times, and dried under vacuum for 24 h to obtain the copolymer (PEG-*b*-GMA)-*co*-MMA.

Electrolyte preparation

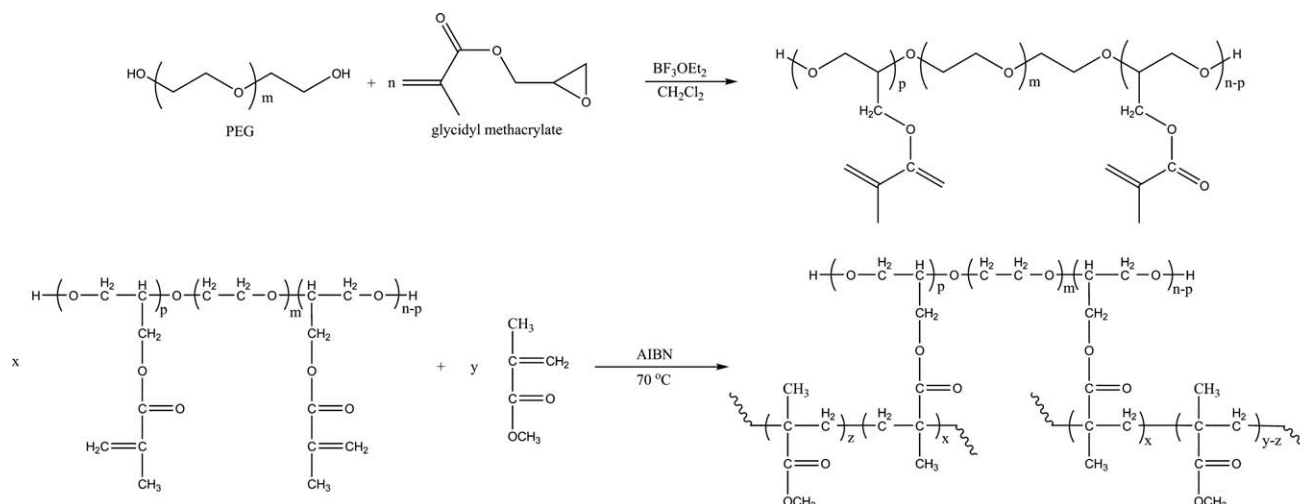
Gel electrolytes were prepared by swelling polymers obtained above with lithium electrolyte solutions. Samples of the gel electrolytes were then transferred to the desiccator before use.

Measurements

FTIR measurements were carried out on a Bruker Vector-22 spectrometer.

¹H-NMR was measured on a Varian Mercury Plus-300 NMR Spectrometer by using hexadeuteroacetone as solvent.

The number-averaged molecular weight and the polydispersity index (PDI) of the copolymer were obtained using gel permeation chromatography measurements (Waters1515, Waters Co.) with two columns (PLgel Mixed-C) at an eluent flow rate of 1 ml/min and calibrated with polystyrene standards.



Scheme 1 Synthesis of PEG-*b*-GMA and copolymer of (PEG-*b*-GMA)-*co*-MMA.

The percentage of swelling (S_w) was obtained with $S_w = (W - W_0)/W_0 \times 100\%$ (where W_0 is the weight of dried films and W is the weight of swelled films).

The degree of crosslinking was measured in terms of the percent gel content, using the equation $CD = W_2/W_1 \times 100\%$ (where W_1 is the initial weight of sample and W_2 is the weight of sample after extraction.) by the Soxhlet extraction for 24 h with THF as solvent.

The hydrophilicity of the membrane was characterized by using water contact angle measurement. The water droplet (volume = 1.0 μL) permeation process was recorded using speed optimum video measuring technology equipped with Dataphysics OCA20, Germany. The measurements were performed at 25°C and 60% relative humidity.

Thermal analysis was carried out in a TA DSC Q100 differential scanning calorimeter with refrigerated cooling system (RCS) under N_2 atmosphere, and the following temperature program was used to remove prior thermal history: (1) Equilibrate at 40°C; (2) Ramp 20°C/min to 150°C; (3) Isothermal for 3 min; 4. Equilibrate at -60°C; (5) Isothermal for 3 min, then ramp 10°C/min from -60 to 150°C.

The ionic conductivity (σ) of the amphiphilic co-network gel polymer electrolytes was determined by AC impedance spectroscopy (EG&G Model 273A potentiostat). The membrane was sandwiched between two parallel stainless steel discs ($d = 1$ 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. The ionic conductivity 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 the electrode area (A) according to the equation $\sigma = l/AR_b$.

RESULTS AND DISCUSSION

$^1\text{H-NMR}$ spectra and GPC data of PEG-*b*-GMA

The $^1\text{H-NMR}$ spectra of the resulting block copolymer PEG-*b*-GMA and prepolymer (PEG-*b*-GMA)-*co*-MMA are shown in Figure 1. The absence of chemical shift at 4.68 ppm, which is attributed to the hydroxyl group of PEG and the chemical shifts between 3.0 and 4.0 ppm of PEG-*b*-GMA indicate that GMA was grafted to both ends of PEG successfully by the ring-opening polymerization of epoxy groups. The molecular weights of the resulting copolymers are shown in Table I. The narrow molecular weight distribution of block copolymer PEG200-*b*-GMA ($M_w/M_n = 1.20$) and PEG2000-*b*-GMA ($M_w/M_n = 1.15$) was related to controlled/living cationic

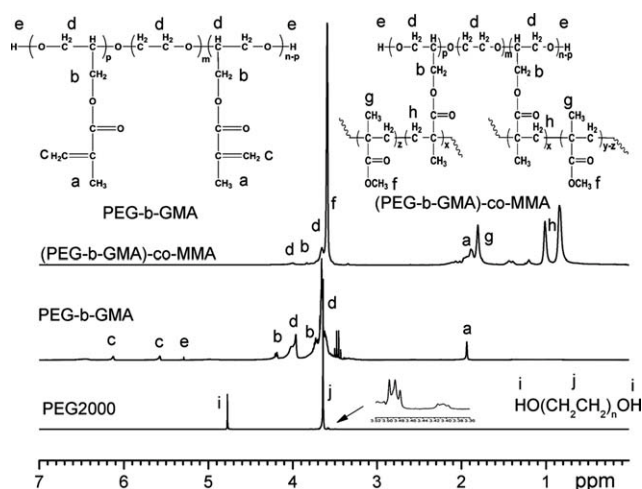


Figure 1 $^1\text{H-NMR}$ of PEG, PEG-*b*-GMA, and (PEG-*b*-GMA)-*co*-MMA.

polymerization, which was terminated by addition of methanol. Low molecular weights of the PEG-*b*-GMA are probably attributed to the relatively high reaction temperature (-10°C) (-70 to -30°C for typical cationic polymerizations) and the short reaction time. Evidently, the length of PGMA block was almost the same despite the difference of the length of PEG blocks. It showed that the molecular weight of the PEG precursors had little influence on the grafting of GMA.

From the figure, it is seen that the chemical shifts at 6.13 and 5.58 ppm ascribed to the vinyl group of PEG-*b*-GMA disappeared and the chemical shift at 3.65 ppm remained in the spectrum of prepolymer (PEG-*b*-GMA)-*co*-MMA, suggesting that PEG-*b*-GMA and MMA copolymerized by radical polymerization.

FTIR spectra of the (PEG-*b*-GMA)-*co*-MMA

The formation of the copolymer (PEG-*b*-GMA)-*co*-MMA was investigated by FTIR spectra. Figure 2(a) shows the IR spectrum of the copolymer PEG-*b*-GMA. The disappearance of characteristic absorption peaks of epoxy group at 907 cm^{-1} suggested the ring-opening reaction of epoxy group of GMA during the block copolymerization of PEG with GMA, and that at 1638 cm^{-1} is attributed to the vinyl group of GMA unit in the copolymer. Moreover, the absorption at 1728 cm^{-1} is due to the $-\text{C}=\text{O}$

TABLE I
Molecular Weights and its Distributions of PEG-*b*-GMA

Sample	M_n ($\times 10^3$)	M_w ($\times 10^3$)	PDI ^a	(EO) <i>m</i> - <i>b</i> -(GMA) <i>n</i>
PEG200- <i>b</i> -GMA	1.02	1.22	1.20	(EO) ₄ - <i>b</i> -(GMA) ₆
PEG2000- <i>b</i> -GMA	3.18	3.66	1.15	(EO) ₄₅ - <i>b</i> -(GMA) ₈

^a Polydispersity index.

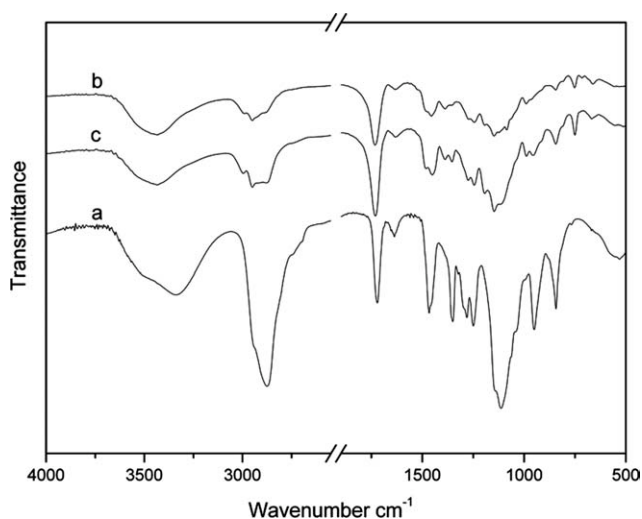


Figure 2 FTIR spectrum of the copolymer (a) PEG-*b*-GMA, (b) P200GM11, and (c) P2000GM11.

stretching vibration in GMA segments. The results of FTIR spectrum are consistent with the observations of $^1\text{H-NMR}$. Figure 2(b,c) present the IR spectrum of P200GM11 and P2000GM11, respectively. It can be seen that the ratio of the height of the peak at 1638 cm^{-1} corresponding to vinyl group to that at 1147 cm^{-1} corresponding to the ether group decreased greatly, which obviously results from the polymerization reaction of PEG-*b*-GMA with MMA.

Figure 3(b,d) illustrate the IR spectra of the copolymer P200GM11 and P2000GM11 in complexation with lithium salts, respectively. New peaks were observed in the spectroscopy. The weak shoulder peaks at around 1078 cm^{-1} and 1176 cm^{-1} in Figure 3(b) and 1083 cm^{-1} and 1108 cm^{-1} in Figure 3(d) can be attributed to the interaction between ($-\text{C}-\text{O}-\text{C}-$) group in the polymer and lithium ions. The FTIR spectra indicate there are some complexation reactions between lithium ions and the amphiphilic copolymer matrix.

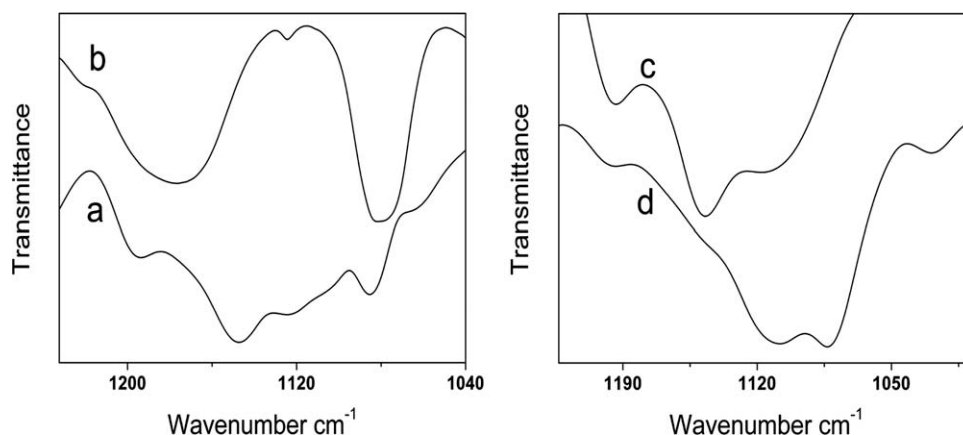


Figure 3 FTIR spectra of the copolymer (a) P200GM11, (b) doped P200GM11, (c) P2000GM11, and (d) doped P2000GM11.

Crosslinking degree and swelling properties

To evaluate the content of the PMMA in the amphiphilic copolymer, Soxhlet extraction of all materials by THF was carried out, and the insoluble fractions of all materials, which can be interpreted as an indication of crosslinking degree, are shown in Table II. It is clear that the crosslinking degree of these copolymers are in the order of P200GM21 > P200GM11 > P2000GM11 > P200GM12 > P2000GM12, increasing with the decreasing weight ratio of MMA to (PEG-*b*-GMA). It is found that all materials contain soluble component.

Figure 4 shows the swelling behavior of various amphiphilic conetworks. It can be seen clearly that the equilibrium swollen percentage of amphiphilic copolymer films in liquid electrolyte solution of 1 M LiPF_6 in DMC/DEC/EC increases with decreasing PMMA content. This can be attributed to the interaction of the liquid electrolyte solution with PEG phase. Moreover, it is found that materials with higher crosslinking have higher equilibrium degree of swelling.

The time required to swell the amphiphilic conetwork with a reasonable amount of liquid electrolyte is in the order of 1 h or more. Such a long time is certainly due to the absence of porosity in the amphiphilic conetwork film prepared through the solvent-free procedure¹⁶ that requires the liquid electrolyte to diffuse into the copolymer.

Amphiphilic properties

The hydrophilicity of the copolymers can be evaluated by static water contact angles. The correlation of the static contact angle and time of (PEG-*b*-GMA)-*co*-MMA conetworks are shown in Figure 5. The water contact angle of copolymer P200GM21 film and P200GM12 film was 111.6° and 75.0° at initial, and decreased slowly with the contact time. In contrast, the water contact angle of P200GM11 film

TABLE II
Degree of Crosslinking (CD%) and Glass Transition Temperature (T_{g1} and T_{g2}) of Different Copolymers

Copolymer	P200GM21	P200GM11	P200GM12	P2000GM11	P2000GM12
CD (%)	64.1	63.0	9.26	36.5	5.58
T_{g1} (°C)	-4.21	9.70	3.29	-34.8	-34.9
T_{g2} (°C)	47.0	87.3	58.9	28.8	44.0

(76.6°), P2000GM12 film (51.2°), and P2000GM11 film (45.5°) dropped considerably in the first several seconds and then decreased slowly. It indicates that the surface of the copolymer P200GM21 film and P200GM12 film are rich in PMMA phase while the other copolymer films have more PEO chains at the surface. The decrease of water contact angle with the contact time is due to the immigration of the hydrophilic block from the inner part to the outer surface.¹⁷ And the fact that the water contact angle of copolymer (PEG2000-*b*-GMA)-*co*-MMA is lower than that of copolymer (PEG200-*b*-GMA)-*co*-MMA indicates that longer EO chains in conetwork improved the hydrophilicity of the copolymer.

Thermal characteristics

The glass transition temperature (T_g) obtained from differential scanning calorimetry is characteristic of amorphous phase of the polymers. The thermograms of the original and lithium electrolyte-doped amphiphilic conetwork polymers are shown in Figures 6 and 7, respectively. The inflection point of the endothermic slope observed in the thermograms is taken as T_g and the endothermic peak denotes the melting temperature (T_m).

The apparent enthalpies of melting (ΔH_m) are derived from the area under the endothermic peaks.

The degree of crystallinity (χ) of the PEO fraction in the matrix is calculated from eq. (1):

$$\chi = \Delta H_m(\text{PEO}) / \Delta H_m^0(\text{PEO}) \quad (1)$$

where $\Delta H_m^0(\text{PEO}) = 205 \text{ J g}^{-1}$ is the heat of melting per gram of 100% crystalline PEO and $\Delta H_m(\text{PEO})$ is the apparent enthalpy of melting per gram of the PEO.

It can be seen that all of the conetwork polymers based on (PEG200-*b*-GMA)-*co*-MMA and (PEG2000-*b*-GMA)-*co*-MMA, which were prepared by the simple strategy of random free radical copolymerization, have two glass transition temperatures characteristic of amphiphilic conetwork polymer.⁹ The glass transition temperatures of each conetwork polymers obtained by thermal analysis are listed in Table II. The fact that T_{g1} and T_{g2} of conetworks based on (PEG2000-*b*-GMA)-*co*-MMA are lower than those of conetworks based on (PEG200-*b*-GMA)-*co*-MMA suggests that copolymers with longer EO groups may be more flexible.¹⁸ Compared to the homopolymers ($T_g(\text{PEO}) = -55^\circ\text{C}$ and $T_g(\text{PMMA}) = 106^\circ\text{C}$), the variation of T_{g1} and T_{g2} of the conetwork polymer may be attributed to the simultaneous chemical crosslinking and copolymerization of the monomers. The decrease in T_{g2} values of the PMMA component incorporated into conetwork compared with

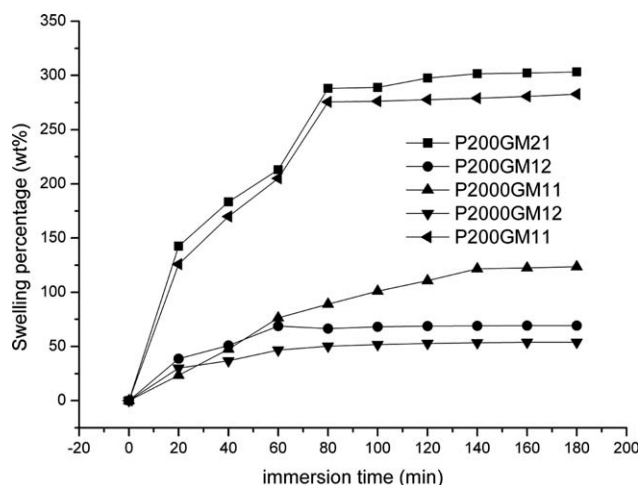


Figure 4 Swelling percentage as a function of the immersion time for different copolymer films in 1M LiPF₆/DMC/DEC/EC.

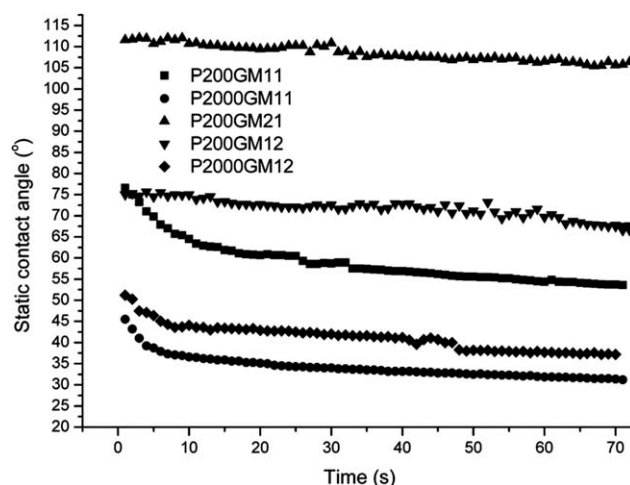


Figure 5 Static water contact angles of (a) (■) P200GM11, (b) (●) P2000GM11, (c) (▼) P200GM12, (d) (▲) P200GM21, and (e) (◆) P2000GM12 at various contact time.

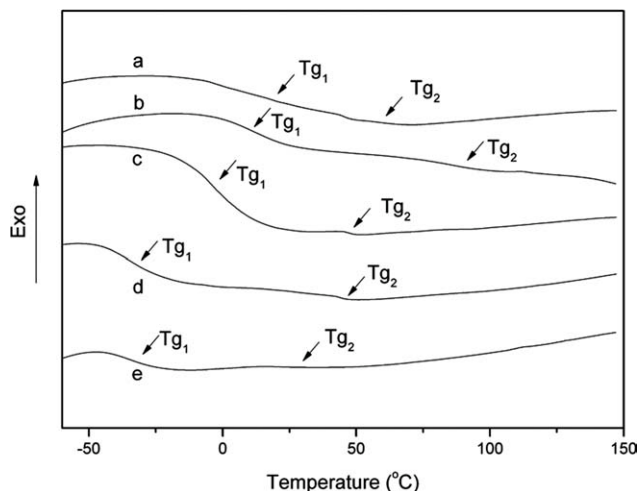


Figure 6 The thermograms of the copolymer (a) P200GM12, (b) P200GM11, (c) P200GM21, (d) P2000GM12, and (e) P2000GM11.

the T_g value of neat PMMA can be interpreted as a result of enhanced compatibility of PEG-*b*-GMA segments with PMMA.¹⁹

The trace of the polymer electrolyte showed that a crystallization process occurred after coordination of polymers with lithium salt. The value of χ of the amphiphilic polymer electrolyte (Typically $\chi_{P2000GM11} = 14.95\%$, $\chi_{P200GM11} = 15.68\%$, $\chi_{P200GM21} = 18.15\%$) revealed the low degree of crystallinity, which suggests that only a small portion of the EO groups rearrange more regularly after coordinating with lithium salt in amorphous domains. The appearance of T_c of P200GM21 indicated that conetworks with higher quantity of PEG segments results in higher degree of crystallinity after doping with liquid electrolyte. While the decrease of T_m of (PEG200-*b*-GMA)-*co*-MMA based electrolytes with the increase

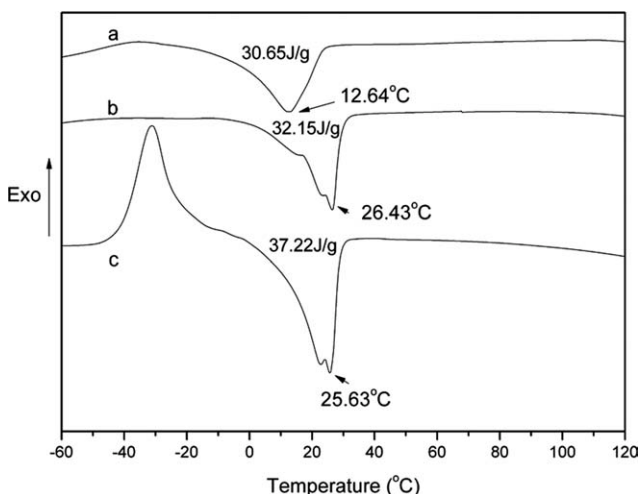


Figure 7 The thermograms of the copolymer (a) P2000GM11, (b) P200GM11, and (c) P200GM21 doped with lithium electrolytes.

of (PEG200-*b*-GMA) component can also be attributed to more PEG segments in the conetworks with more flexible chain movement.

Electrical properties

Impedance spectroscopy was used to evaluate the temperature dependence of the ion conductivity in the range between 10 and 50°C. The ionic conductivity of the gel-type polymer electrolytes was measured using two stainless steel (SS) electrodes plates at different temperatures to study the conduction behavior of the charge carriers in the plasticized amphiphilic polymer electrolyte system. Figure 8 shows the AC impedance spectra of SS/polymer electrolyte/SS cell measured at room temperatures. The absence of a semicircle at high frequency in the impedance spectrum suggests that only the resistive component of polymer electrolyte could be considered in the presence of a plasticizer.²⁰ And the constant phase element (CPE) behavior is mainly attributed to the diffusion process between the polymer electrolyte and the electrode.²¹ The intercept of the spectrum on the real axis gives the electrolyte resistance, and the ionic conductivity was calculated to be 10^{-4} S/cm. It is believed that the amphiphilic structure of the copolymers promotes the formation of amorphous domains (as can be seen from the low crystallinity of the polymer electrolytes), and thus is responsible for the high ionic conductivity of the polymer electrolyte.

The effect of temperature on conductivity of the amphiphilic polymer electrolytes was investigated and $-\lg\sigma$ vs. $1000/T$ is depicted in Figure 9. It is found that $\lg\sigma$ changed linearly with $1/T$, indicating an Arrhenius-like behavior of conductivity according to eq. (2).

$$\sigma = \sigma_0 \exp(-Ea/KT) \quad (2)$$

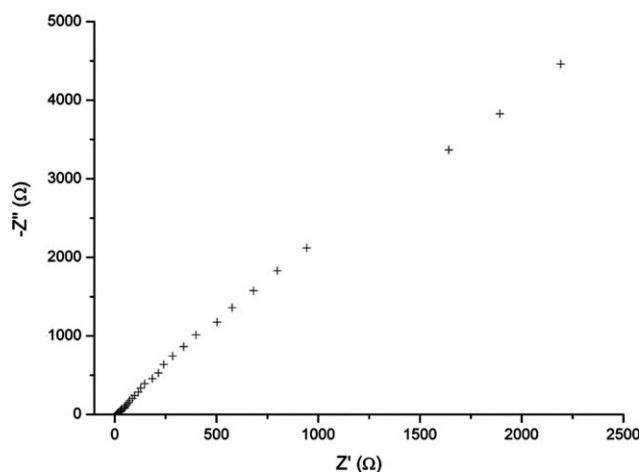


Figure 8 The AC impedance spectrum of SS/polymer electrolyte/SS cell measured at room temperature.

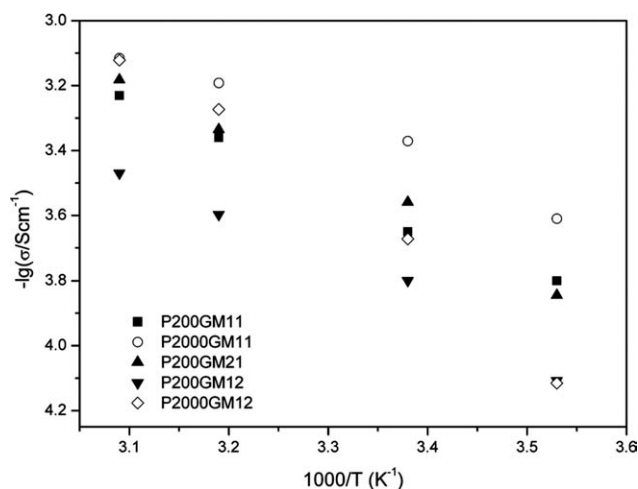


Figure 9 $-\lg\sigma$ vs $1000/T$ plot for gel polymer electrolytes based on copolymer (a) (\blacktriangle) P200GM21, (b) (\blacksquare) P200GM11, (c) (\blacktriangledown) P200GM12, (d) (\circ) P2000GM11 and (e) (\diamond) P2000GM12.

where σ_0 is a constant; E_a the activation energy; K the Boltzmann constant.

The maximum ionic conductivity was observed for the electrolyte based on P2000GM11, while the electrolyte based on P200GM12 exhibited the lowest ionic conductivity over the temperature range. It is also observed that with the decrease of PMMA content, the ionic conductivity of both (PEG200-*b*-GMA)-MMA and (PEG2000-*b*-GMA)-MMA based electrolyte increased, due to higher quantity of PEG segments and liquid electrolyte uptake percentage. Furthermore, the electrolytes based on the copolymers carrying longer EO groups showed higher ion conductivities as compared to those with shorter EO groups. This is consistent with results obtained from DSC measurements, though the electrolyte based on P200GM11 and P200GM12 have higher electrolyte uptake percentage than that based on P2000GM11. It can be inferred that the transportation of lithium ions in gel polymer electrolyte with higher crosslinking degree is inhibited. The steady increase in conductivity with temperature is interpreted as a hopping mechanism between coordinating sites, accompanied by local structural relaxation and segmental motion of the polymer.²⁰

CONCLUSIONS

Amphiphilic polymer gel electrolytes based on (PEG-*b*-GMA)-*co*-MMA were synthesized by means of radical copolymerization of monomers and multi-

functional macromonomers. Electrochemical measurements suggested that the new polymer electrolytes exhibited a high ionic conductivity of 10^{-4} S/cm at room temperature, and an Arrhenius-like behavior of the conductivity was observed. Copolymers with higher feed weight ratio of (PEG-*b*-GMA) have higher crosslinking degree which results in higher swollen percentage of liquid electrolyte solution, while the ion conductivity of (PEG2000-*b*-GMA)-*co*-MMA based gel electrolyte was higher than that of (PEG200-*b*-GMA)-*co*-MMA based gel electrolyte.

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