Relaxation Time and Conductivity of Comb-like Gel Polymer Electrolytes

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ABSTRACT: Using the copolymer of acrylonitrile (AN), methyl methacrylate (MMA), and poly(ethylene glycol) methyl ether methacrylate as a backbone and poly(ethylene glycol) methyl ether (PEGME) with 1100 molecular weight as side chains, comb-like gel polymers and their Li salt complexes were synthesized. The dynamic mechanical properties and conductivities were investigated. Results showed that the gel copolymer electrolytes possess two glass transitions: α-transition and β-transition. Based on the time–temperature equivalence principle, a master curve was constructed by selecting T_α as reference temperature. By reference to $T_0 = 50°C$, the relation between $\log \tau_c$ and c was found to be linear. The master curves are displaced progressively to higher frequencies as the content of plasticizer is increased. The relation between $\log \tau_p$ and the content of plasticizer is also linear. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 576–584, 2007

Key words: gel polymer electrolyte; glass transition; WLF equation; segmental motion; mechanical relaxation time

INTRODUCTION

Since the discovery of ionic conductivity in alkali metal salt complexes of polyethylene oxide by Wright in 1973,[1] a great deal of effort has been focused on the study of ion transport mechanisms and on the development of materials for technological applications. The solid polymer electrolyte (SPE) has become an important field of science and technology. We have been engaged in the synthesis of comb-like host polymers and the study of the properties of their Li salt complexes for many years.[2] A new amorphous comb-like gel copolymer (CGP) based on acrylonitrile (AN), methyl methacrylate (MMA), and poly(ethylene glycol) methyl ether methacrylate backbone and on an oligo oxyethylene side chain was synthesized in 2003 and published in 2005.[3] It was found that CGP and its Li salt complexes possess two glass transitions α- and β-transition in the temperature range from −100 to 100°C and show an unusual dependence of the ionic conductivity on the Li salt content, which has been ascribed to the movability of the CGP main chain at ambient temperature.[3] For this kind of special copolymer–Li salt gel complex having multiple glass transitions, there are some problems that should be solved: (1) whether or not the gel complexes system can be expressed by the famous Williams–Landel–Ferry (WLF) equation; (2) how does the motion of the macromolecular chains influence the conductivity? It has been well established that the temperature dependence of the ion conductivity in SPEs scales with the temperature dependence of the segmental motions and thus with the glass transition phenomena.[4] Therefore, the temperature dependence of the ion conductivity is usually discussed in the framework of the "free volume model" and can be described by the WLF (Williams–Landel–Ferry) equation.[5–7] With regard to segmental motion, it is known that the reciprocal of the relaxation time is informative for characterizing the backbone motion of a polymer.[8] The relaxation time can usually be determined by dielectric spectroscopy[9,10] and it can also be determined by the dynamic mechanical method.[5,11] In the present work, using the copolymer of AN, MMA, and poly(ethylene glycol) methyl ether methacrylate as backbone and poly(ethylene glycol) methyl ether as side chains, comb-like gel copolymers and their Li salt complexes were synthesized.[3] The lower T_g values and the excellent mechanical properties of these gel polymer electrolytes (GPEs) make the issues simplified and easily studied. The paper aims to do research on dynamic mechanical properties of comb-like polymer electrolytes, and to explore the conductive mechanism of comb-like gel polymer electrolytes by dynamic mechanical analysis (DMA). The average relaxation times of the specimens were determined
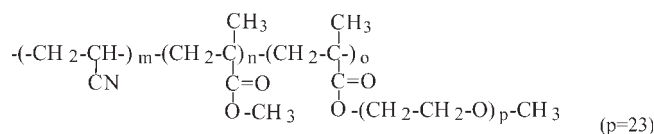
$$-(-CH_2-CH-)_m-(CH_2-\underset{\underset{\underset{O-CH_3}{C=O}}{CH_3}}{C})_n-(CH_2-\underset{\underset{\underset{O-(CH_2-CH_2-O)_p-CH_3}{C=O}}{CH_3}}{C})_o-$$

(p=23)

Scheme 1

through master curve construction. The effects of salt concentration, side chain length, and salt type on the segmental motion and conductivities of the gel copolymer–Li salt complexes were studied.

EXPERIMENTAL

Materials

Poly(ethylene glycol) methyl ether methacrylate (PEG-MEMA) with molecular weights of 1100 was a commercial product from Aldrich and used as received. Acrylonitrile, A.R. grade (Beijing Fuxing Chemical and Industrial Factory), methyl methacrylate, A.R. grade (Beitong Chemical and Industrial Factory), and ethylene carbonate (EC), A.R. grade (Aldrich) were used as received. Three different anion lithium salts, $LiClO_4$, $LiBF_4$, and $LiCF_3SO_3$, and a different cation salt, NH_4ClO_4, were selected for examining dynamic mechanical properties of comb-like gel polymer electrolytes. $LiClO_4$, $LiBF_4$, $LiCF_3SO_3$, and NH_4ClO_4 were A.R. grade (Aldrich). $LiClO_4$, $LiCF_3SO_3$, and $LiBF_4$ were dried under vacuum at 160°C for 24 h, and NH_4ClO_4 was dried under vacuum at room temperature for 24 h before use. Azobisisobutyronilrile (AIBN), C.P. grade (Beijing Chemical and Industrial Factory), was recrystallized in ethanol before use. N,N-dimethylformamide, A.R. grade (Beijing Chemical and Industrial Factory), was refluxed in the presence of calcium hydride for 24 h and distilled before use.

Synthesis of comb-like gel copolymer

The copolymerization of AN, MMA with poly(ethylene glycol) methyl ether methacrylate was achieved by dissolving PEGMEMA, molecular weight of 1100, in AN and MMA at a calculated molar ratio and then adding a definite amount of EC and AIBN to the mixture under a flow of nitrogen. The mixture was stirred continuously at 25°C. When the mixture was in a homogeneous phase, the reactant was protected with N_2 and the reaction proceeded for 24 h at 50°C. The temperature of reactant was then risen to 60°C. After the reaction was complete, the product was transferred to a vacuum glove box. The product of reaction involved is outlined in Scheme 1. The resulting CGPs having a PEGME side chain were designated Copolymer (40%EC), Copolymer (50%EC), and Copolymer (60%EC), respectively, according to the content of plasticizer (content of plasticizer/copolymer = 40%, 50 and 60%). Characterization of the comb-like copolymer is reported in the ref. 3.

Preparation of polymer electrolytes

The polymer electrolytes were prepared using a similar method earlier. And according to the desired polymer/Li ratio, a calculated amount of Li salt was added to a definite volume of the monomer solution. After mixing thoroughly, the samples obtained were reacted thoroughly in vacuum at 60°C for about 72 h.

Conductivity measurement

The polymer electrolyte film sandwiched between two stainless steel electrodes of 1 cm^2 area was placed in a glass vessel equipped with a temperature-controlled heater. The precision of the temperature reading was within ±0.5°C. Impedance measurements were taken on a Solartron 1470 battery test unit and Sdartron 1255B frequency response analyzer from Solartron Corp. The frequency range tested was from 10^{-1} to 10^6 Hz.

Dynamic mechanical analysis

The dynamic mechanical properties were examined on a Viscoelastometer from METRAVZB Corp. (France, Model MAK-04) at a heating rate of 3°C/min. The effective dimensions of the specimens were $20 \times 8 \times 2$ mm^3. Storage modulus E', loss modulus E'', and loss tangent values were measured at 7.8, 15.6, 20.0, 31.2, and 100 Hz at temperatures ranging from −70 to 120°C. The peak temperature of the loss tangent was assumed to be the glass-transition temperature. Frequency of 7.8 Hz was used to determine the peak of tan δ.

RESULTS AND DISCUSSION

Dynamic mechanical properties

Syntheses and properties of the new amorphous comb-like gel copolymer (CGP) based on AN, MMA, and poly(ethylene glycol) methyl ether methacrylate backbone and on an oligo oxyethylene side chain were referred to the ref. 3. Using the methods of esterification and polymerization, the copolymer acrylonitrile-methyl methacrylate-methyl/poly(ethylene glycol)methyl ether methacrylate and its comb-like gel polymer electrolyte were synthesized. Results indicated that the synthesized monomers and polymers are accurately according to the structures we designed. Its mechanical properties were very good, and the conductivity of comb-like gel polymer electrolytes was at magnitude range of 10^{-3} S/cm at ambient temperature.
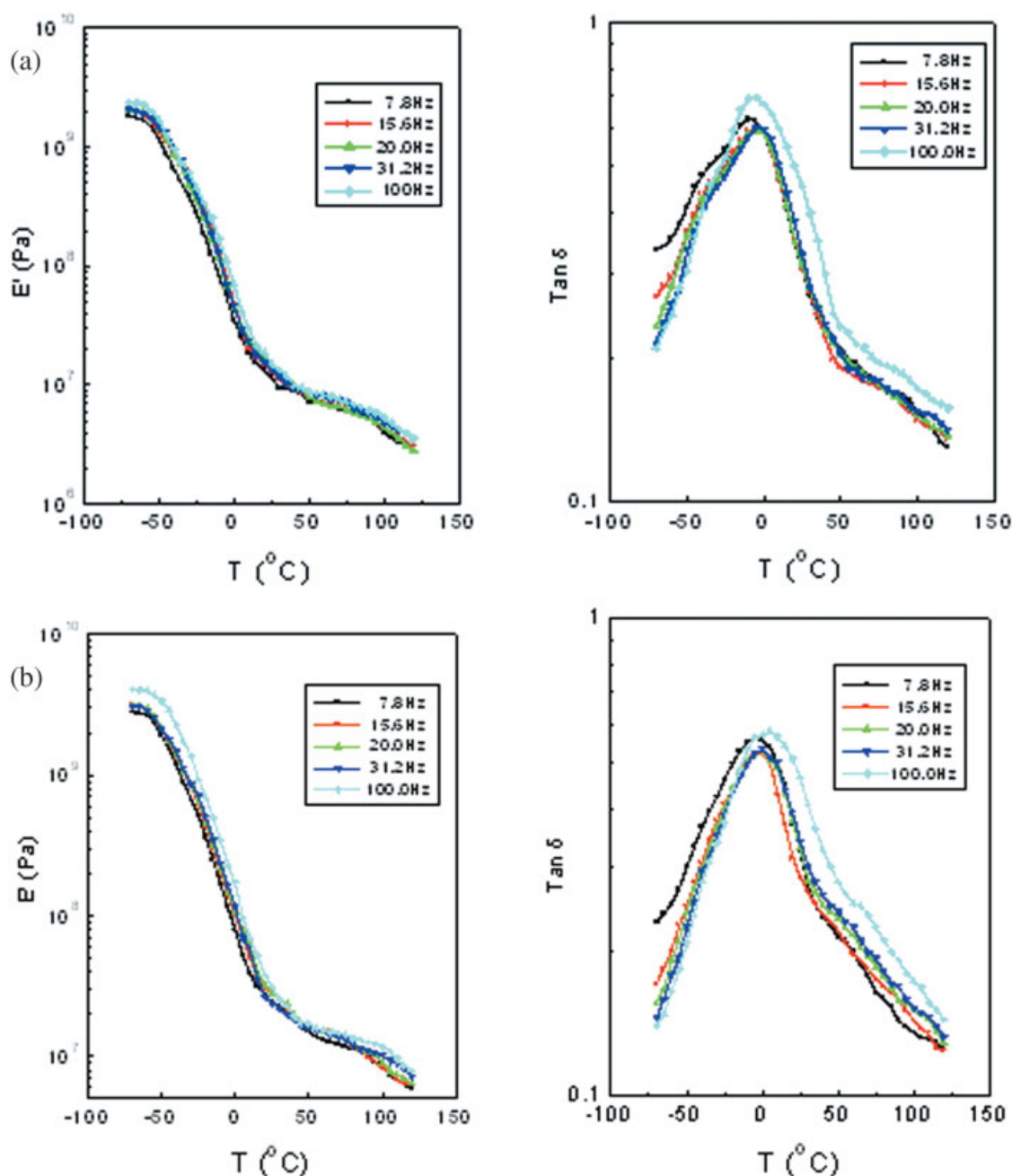
Figure 1 Dynamic mechanical spectra of Copolymer(60%EC)-LiClO$_4$. [LiClO$_4$] = 2.005 mol/kg polymer (a); 1.604 mol/kg polymer (b); 1.069 mol/kg polymer (c); 0.535 mol/kg polymer (d); 0.401 mol/kg polymer (e). Dynamic mechanical spectra of Copolymer(60%EC)-LiBF$_4$. [LiBF$_4$] = 1.069 mol/kg polymer (f). Dynamic mechanical spectra of Copolymer(60%EC)-LiCF$_3$SO$_3$. [LiCF$_3$SO$_3$] = 1.069 mol/kg polymer (g). Dynamic mechanical spectra of Copolymer(60%EC)-NH$_4$ClO$_4$. [NH$_4$ClO$_4$] = 1.069 mol/kg polymer (h). Dynamic mechanical spectra of Copolymer(40%EC, 50%EC, 60%EC) (i). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The dynamic mechanical curves of Copolymer (60%EC)-LiClO$_4$ are shown in Figure 1. It can be seen that there are two transitions in the temperature range studied. One is the main glass-transition α-transition (T_α) of the comb-like polymer and its Li salt complexes. The other is the β-transition (T_β), which is lower than the α-transition (T_α). The β-transition appears as a very weak feature on the low temperature, because the ratio of EO side chains to polymer was very little, about EO

side chains/polymer = 1/20(weight ratio). The values of T_α and T_β for the comb-like polymer and its Li salt complexes are listed in Table I. It is obvious that T_β is dependent on the content of lithium salt. Only the value of T_α in Table I for the Li concentration of 0.535 is different. All others are equal to $-5°C$. These present only one value below 0.535. Thus, T_α is initially constant with increasing concentration and then shows a minimum value. It seems that the value is constant,
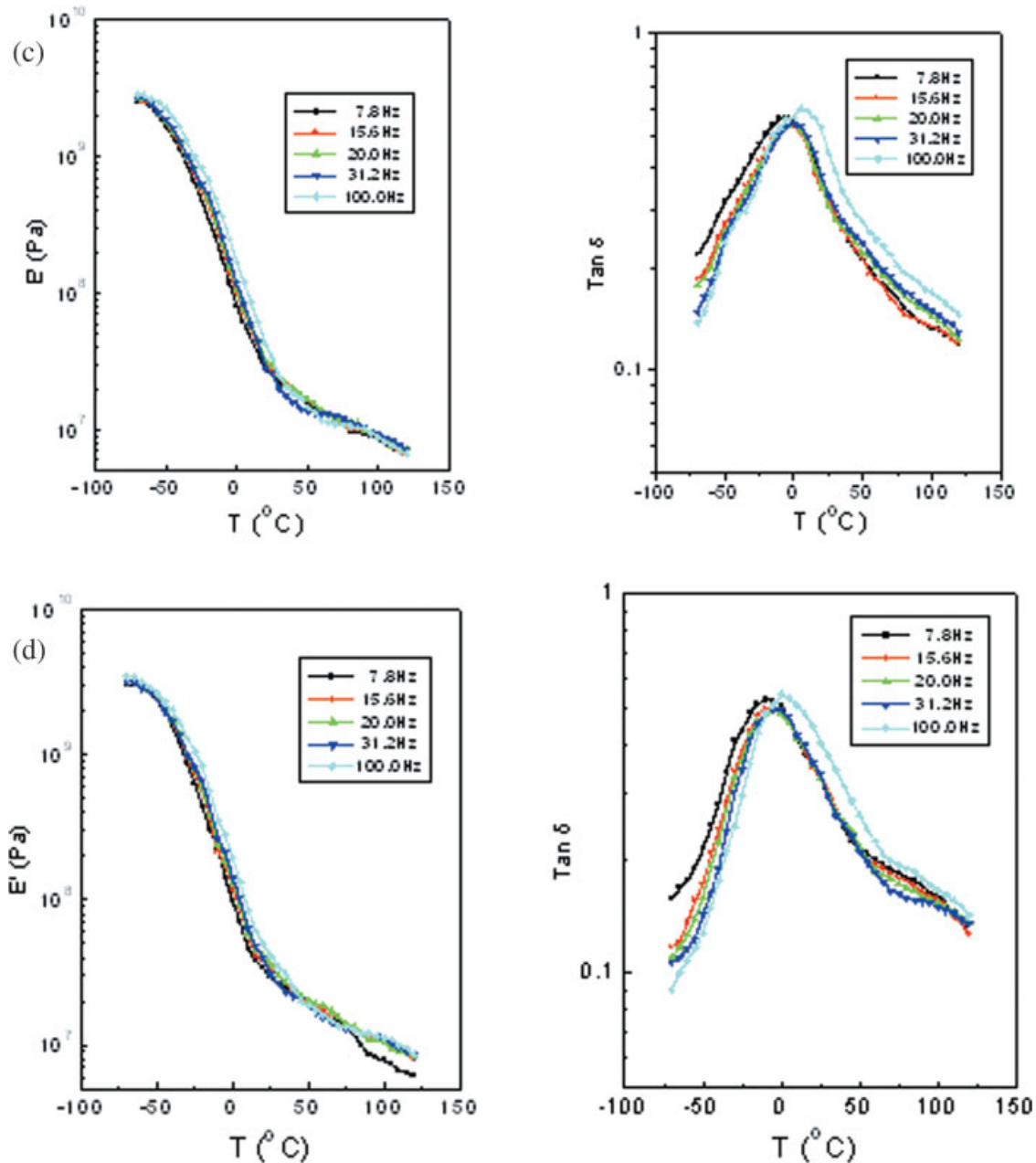
Figure 1 (*Continued from the previous page*)

exception made to this particular concentration. According to the previous work,[3] the α- and β-transitions can be assigned to the main and side chain glass transitions, respectively. In the case of Copolymer(60%EC)-LiClO$_4$ complexes, T_β remains almost constant within a wide concentration range of Li salt. When the LiClO$_4$ concentration is ≥1.06 mol/kg polymer, T_β increases to −40°C with increasing Li salt content. The variation of T_α with concentration of Li salt differs considerably from the dependence of T_β on content of Li salt. It can be seen that T_α of the Copolymer(60%EC)-LiClO$_4$ complex initially constant with increasing concentration of Li salt and then shows a minimum value in the concentration range

of Li salt from 0.4 to 1.0 mol/kg polymer. Compared with CBP-Li salt complexes based on methyl vinyl-ether/maleic anhydride alternating copolymer,[12] both the α- and β-transitions of the electrolytes are shifted considerably to the low temperature region, which indicates that, upon substituting the methoxy group with a plasticizer, not only does the softness of the macromolecule main chains increase, but also the mobility of the PEO side chains increase.

The master curve constructed for the gel electrolyte

It has been well established that the temperature dependence of the ion conductivity in SPEs scales with
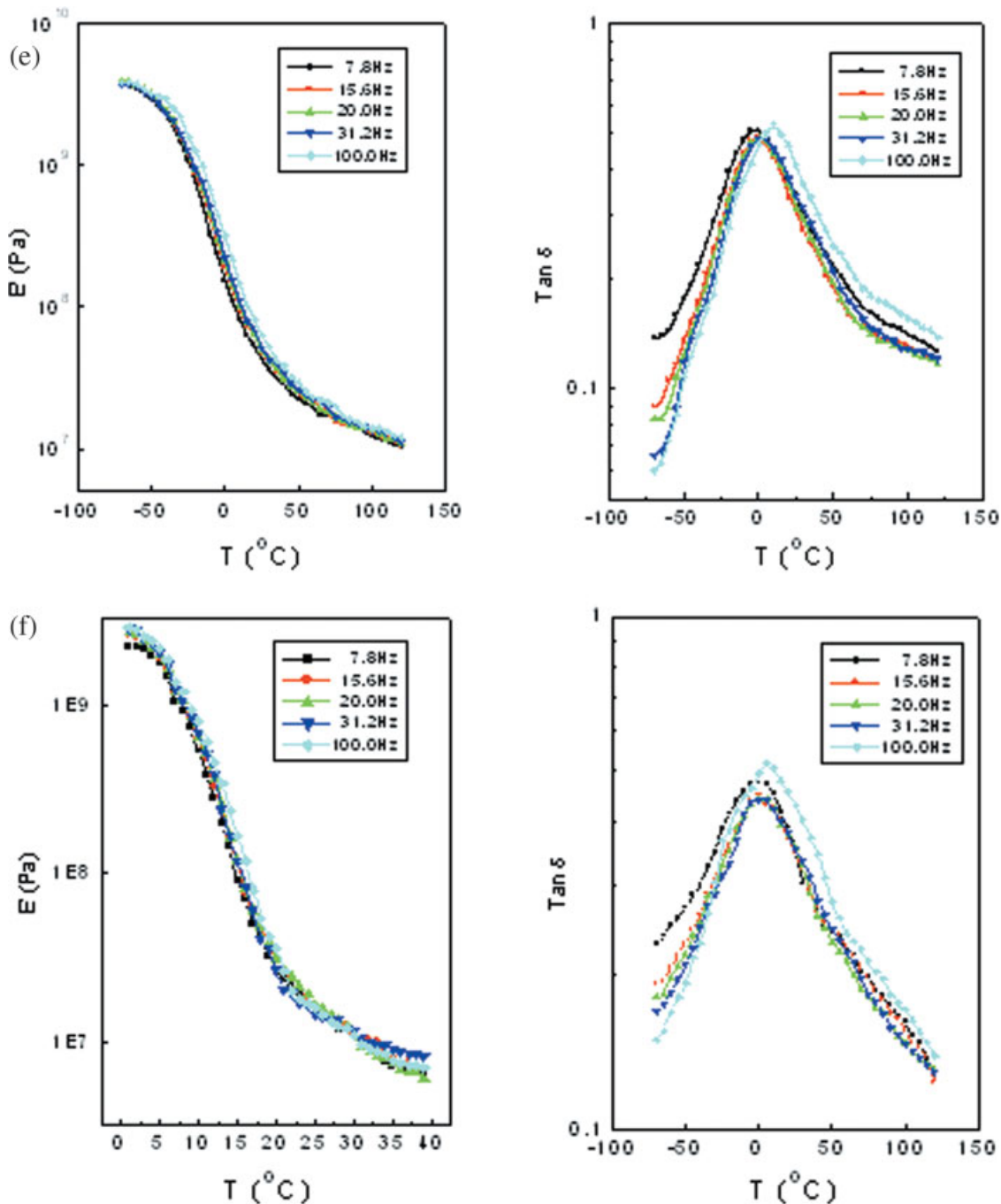
Figure 1 (*Continued from the previous page*)

the temperature dependence of the segmental motions.[4] Therefore, the temperature dependence of the ion conductivity, σ, can be described by the WLF equation:

$$- \log a_T = \log \sigma_T / \sigma_{T_g} = C_1(T - T_g)/C_2 + T - T_g \quad (1)$$

where a_T is the shift factor, T_g the glass-transition temperature, and C_1 and C_2 the WLF parameters.

And, thus the following WLF equation was adopted to treat the experimental data:

$$- \log a_T = \log \sigma_T / \sigma_{T_\alpha} = C_1(T - T_\alpha)/C_2 + T - T_\alpha \quad (2)$$

The storage modulus E' isotherms of the host polymer–Li salt gel electrolyte specimens at various temperatures were measured and superimposed to construct the master curve. To determine C_1 and C_2 in eq. (2), T_α, the main chain glass-transition temperature, was chosen as a reference temperature. The master curve constructed for the Copolymer(60%EC)-LiClO$_4$ gel electrolyte is shown in Figure 2. The shift factor, a_T, which is defined as the ratio of the relaxation time at T to T_α, can be obtained from the master curve. To transform eq. (2), one can obtain another form of the WLF equation:
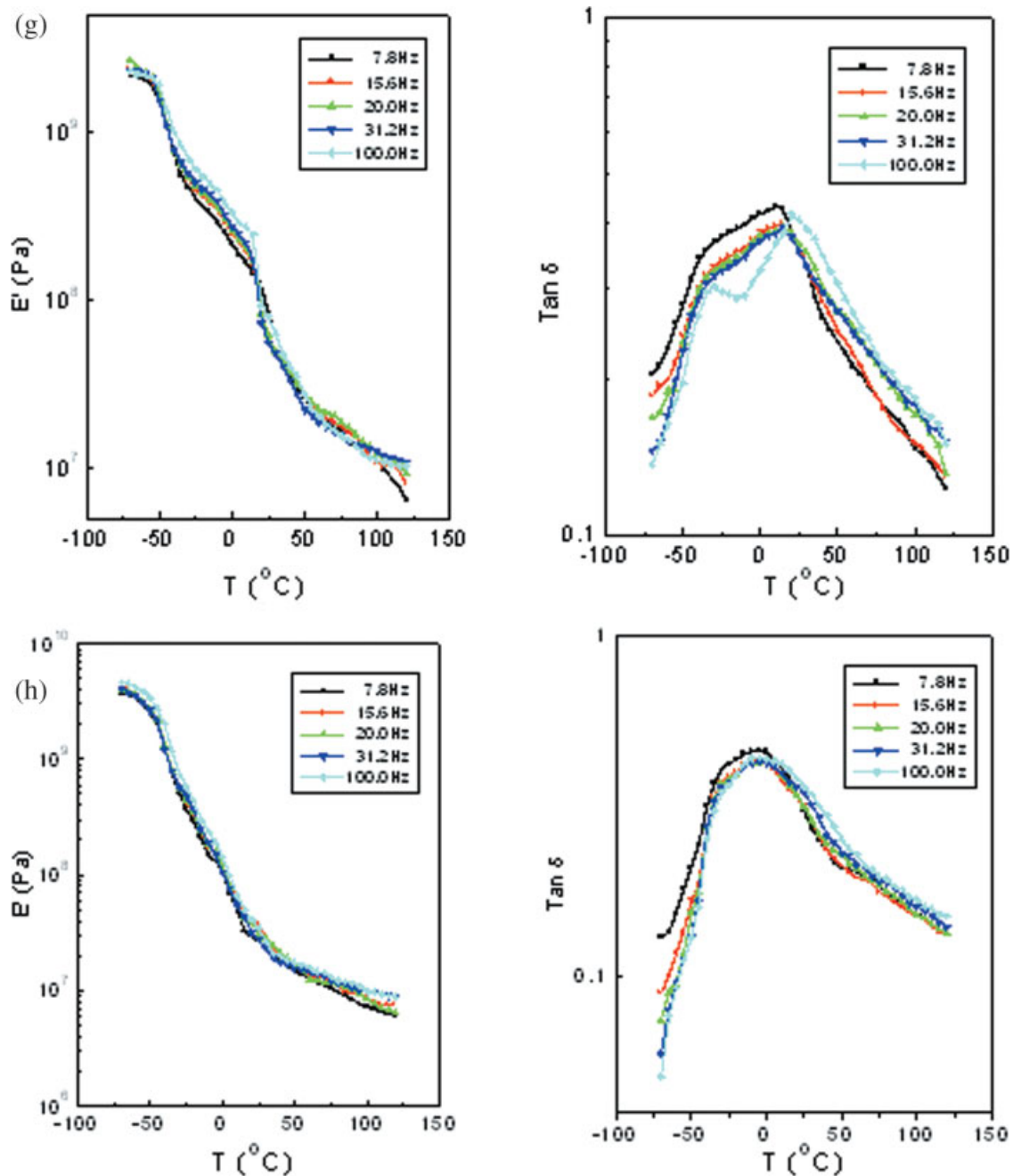
Figure 1 (*Continued from the previous page*)

$$-1/\log a_T = -/C_1 + C_2/C_1(T - T_\alpha) \qquad (3)$$

Plotting $-1/\log a_T$ versus $1/(T - T_\alpha)$ for the Copolymer(60%EC)-LiClO$_4$ (LiClO$_4$ = 2.005 mol/kg polymer) sample over a wide temperature range from -70 to $120°C$, a straight line is obtained (Fig. 3), which shows once again that the WLF equation holds very well.

Mobility of the macromolecular chain

As is known, the reciprocal of the relaxation time τ_T at temperature T can be taken as a measure of the macromolecular segment mobility. In an attempt to

evaluate the relaxation time τ_T, an alternative method for constructing the master curve was adopted. The master curves of the specimens were constructed by selecting a common reference temperature, $T_0 = 50°C$ (Fig. 4).

At the inflection point of the modulus (E') isotherm, the following relationship exists between the angular frequency ω and the relaxation time τ_T:[8]

$$\tau_T = 1/\omega \qquad (4)$$

Therefore, the average relaxation time of the specimens could be evaluated. First, the effect of Li salt concentration on the relaxation time was examined.
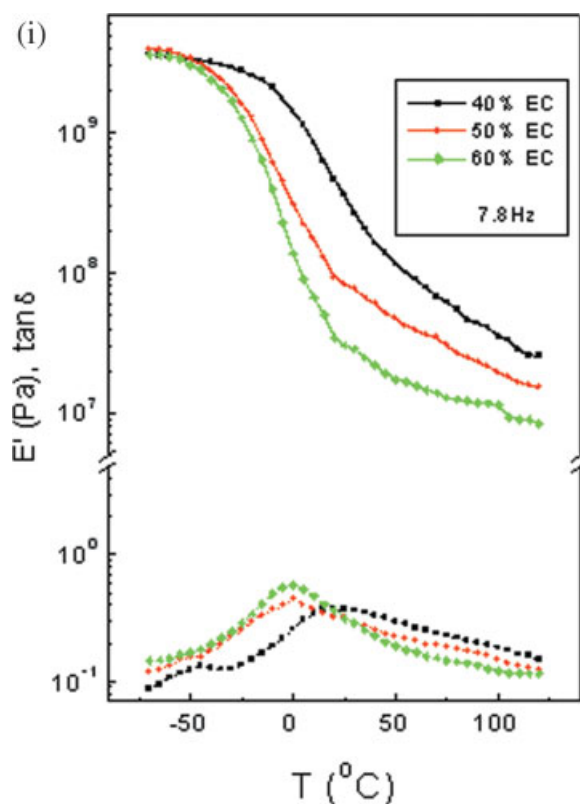
Figure 1 (*Continued from the previous page*)

The evaluated values of the average relaxation times for a series of specimens of Copolymer(60%EC)-LiClO$_4$ gel electrolytes having various LiClO$_4$ concentrations c are denoted τ_c and plotted against salt concentration c in Figure 5. The correlation between log τ_c and LiClO$_4$ salt concentration c was found to be linear (Fig. 5) and can be written as

$$\log \tau_c = -1.544 - 0.0808c \qquad (5)$$

with a correlation factor $r = 0.980$. It should be noted that the effect of the Li salt concentration on the relaxation time is tremendous, because eq. (5) has a rather large slope ($d \log \tau_c/dc = -0.0808$). From the

TABLE I
Transition Temperatures of the Comb-like Polymer and Its Li Salt Complexes

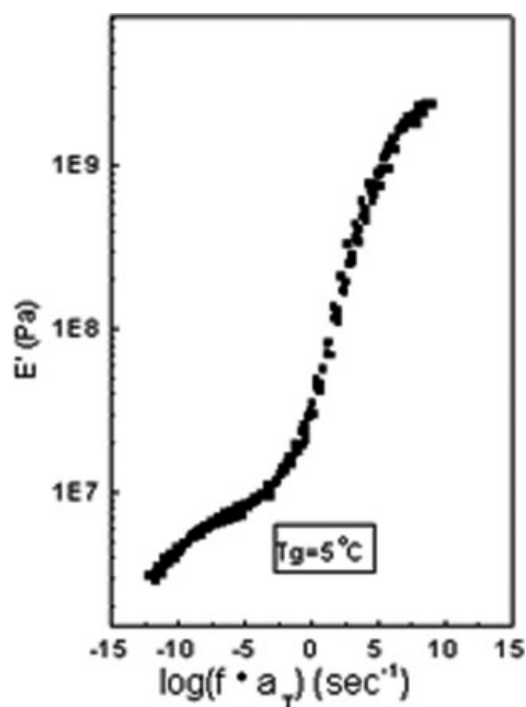|	[Li salt] (mol/kg polymer)	T_α (°C)	T_β (°C)
Copolymer(60%EC)-LiClO$_4$	0.401	−5	−45
Copolymer(60%EC)-LiClO$_4$	0.535	−10	−45
Copolymer(60%EC)-LiClO$_4$	1.069	−5	−40
Copolymer(60%EC)-LiClO$_4$	1.604	−5	−40
Copolymer(60%EC)-LiClO$_4$	2.005	−5	−40
Copolymer(60%EC)-LiBF$_4$	1.069	0	−45
Copolymer(60%EC)-LiCF$_3$SO$_3$	1.069	10	−35
Copolymer(60%EC)-NH$_4$ClO$_4$	1.069	−5	−50
Copolymer(60%EC)	0	0	−60
Copolymer(50%EC)	0	0	−50
Copolymer(40%EC)	0	20	−45

Figure 2 Master curve constructed for Copolymer(60%EC)-LiClO$_4$ gel electrolyte at $T_\alpha = 5$°C. [LiClO$_4$] = 2.005 mol/kg polymer.

viewpoint of gel system, raising the Li salt level in gel electrolytes always increases the ion concentration and the ionic conductivity within the range measured
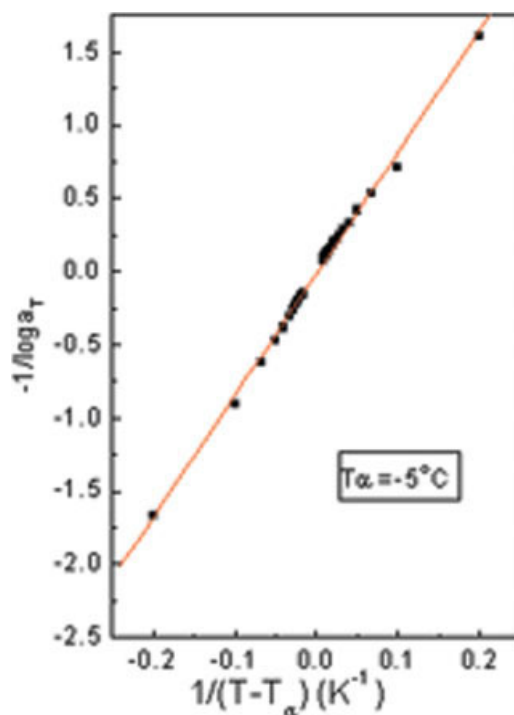

Figure 3 Plot of $-1/\log a_T$ versus $1/(T - T_\alpha)$ for Copolymer(60%EC)-LiClO$_4$. [LiClO$_4$] = 2.005 mol/kg polymer. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
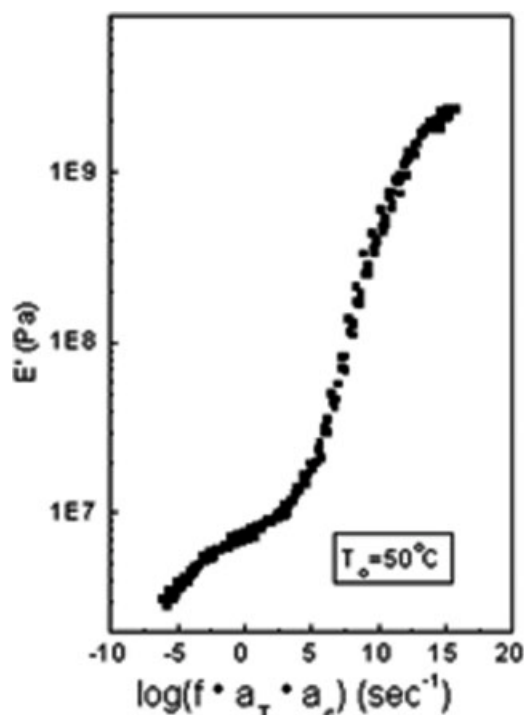
Figure 4 Double superimposed (frequency–temperature and frequency–concentration) master curve for Copolymer(60%EC)-LiClO$_4$ gel electrolyte at $T_0 = 50°C$. [LiClO$_4$] = 2.005 mol/kg polymer.

Figure 5 Relationship between relaxation time and salt content for Copolymer(60%EC)- LiClO$_4$. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

in the experiments. Second, the effect of the content of the plasticizer on the relaxation time τ_p was examined. The master curves constructed are displaced to higher frequency as the content of plasticizer. Their correlation is also linear (Fig. 6) and can be expressed as

$$- \log \tau_p = \log 1/\tau_p = 4.86 \times 10^{-3}(\text{EC\%}) + 1.491 \quad (6)$$

with a correlation factor of 0.999.

According to eq. (6), the larger the content of plasticizer, the greater is the mobility of the macromolecular segment. In other words, increasing the content of plasticizer tends to increase the ionic conductivity of the Copolymer(60%EC)-LiClO$_4$ gel electrolytes, except that crystallization of the side chain occurs. The effect of the kind of Li salt on the relaxation time was also examined. Data obtained for Copolymer(60%EC)-LiClO$_4$ gel electrolytes are shown in Table II. According to the magnitude of τ, the order of mobility of the macromolecular segment is LiBF$_4$ > LiClO$_4$ > LiCF$_3$SO$_3$. It is very interesting that this order is consistent with the order of conductivity observed for these four salts (Table II). Because NH$_4$ClO$_4$ is not Li salt, conductivity and relaxation cannot be compared with the Li salt. This salt also affect on the relaxation time of gel polymer electrolyte. So the system is a contrast with Li salt system. It shows that other salts on polymer electrolytes also affect on conductivity of the system.
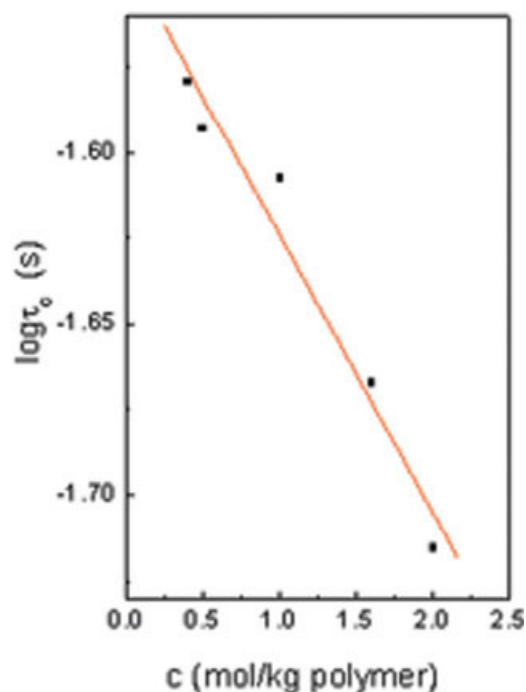
To sum up, the preceding findings indicate that all the three factor, i.e., LiClO$_4$ salt concentration, the content of the plasticizer, and the kind of Li salt
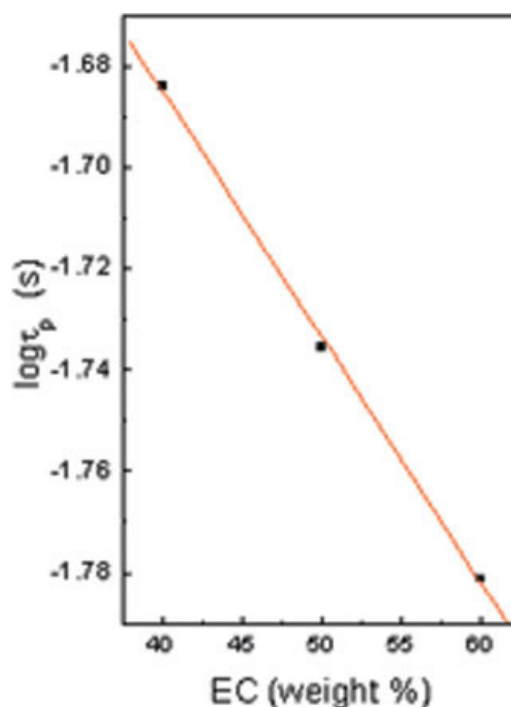

Figure 6 Effect of the content of plasticizer on relaxation time. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Salt	Log τ	τ (s)	Log σ (S/cm) (20°C)
Copolymer 60%EC-NH$_4$ClO$_4$	−1.663	0.0217	−4.69
Copolymer 60%EC-LiBF$_4$	−1.625	0.0237	−4.09
Copolymer 60%EC-LiClO$_4$	−1.608	0.0247	−4.29
Copolymer 60%EC-LiCF$_3$SO$_3$	−1.488	0.0325	−5.35

[Salt] = 1.069 mol/kg polymer.

have profound influence on the average relaxation times, which in turn affect the ionic conductivity of the system. Among the factor two have plasticizer-like and increasing the ion concentration action and lead to reduce the relaxation time. In the contrast, the latter, the kind of Li salt, also shows the same effect on the relaxation time. Based on the volume concept, all the effect arising from these factors could be attributed to the change in the free volume. It has been widely recognized that the ionic conductivity of a polymer electrolyte is governed by the product of the number of ionic carriers and their mobility, and that latter is closely concerned with the segmental motion of polymer. Since it is known that the reciprocal of the relaxation time is informative to characterize the backbone motion of a polymer electrolyte. As a consequence, a polymer with a low T_g would possess a high segmental mobility at any temperature T above T_g, and thus a high ionic conductivity. To be a useful gel polymer electrolyte, however, an adequate mechanical strength at least capable of self-supporting should be maintained. Thereby a compromise between T_g and the strength of the specimen must be taken into consideration.

Summary

1. The dynamic mechanical properties of these comb-like polymers (with AN and methacrylate as backbone and oligoethylene glycol monomethyl ethers as side chains) -Li salt gel electrolytes were investigated. The results showed that the gel polymer electrolytes possess two glass transitions: α-transition and β-transition. The α-transition is assigned to the main chain glass transition. The β-transition is assigned to the side chain glass transition and is also a function of the Li salt content.

2. By means of master curve construction, a linear relationship between $−1/\log a_T$ and $1/T − T_\alpha$ was obtained, indicating that eq. (2) can be used to treat data for the temperature dependence of segmental motion.

3. At temperatures above T_α (about 0°C), the main chains of the host polymer are mobilized. Therefore, the segmental motion observed is the motion of the main chains. The average relaxation time of the segmental motion was evaluated. It was found that log τ is not only a linear function of the Li salt content, but is also a linear function of the content of the plasticizer. The mobility of the segmental motion of the electrolyte is also dependent on the nature of the Li salt, and its order is LiBF$_4$ > LiClO$_4$ > LiCF$_3$SO$_3$.

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