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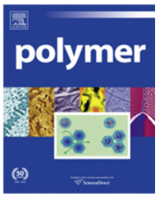

Polymer Communication

Alternating copolymers of carbon dioxide with glycidyl ethers for novel ion-conductive polymer electrolytes

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ABSTRACT

To overcome the low ionic conduction of existing poly(ethylene oxide)-based polymer electrolytes, we consider polycarbonates obtained from the copolymerization of CO_2 and epoxy monomers. We synthesized four types of polycarbonates possessing phenyl, *n*-butyl, *t*-butyl and methoxyethyl side groups using zinc glutarate, and measured the ionic conductivity of their electrolytes, including 10 mol% of LiTFSI. The electrolyte possessing methoxyethyl side groups had the highest conductivity, of the order of 10^{-6} S cm^{-1} at room temperature. The activation energy (E_a) for ionic conduction in the polycarbonate electrolytes was estimated from the VTF equation, and the E_a of the electrolyte possessing *n*-butyl side groups was almost the same with the polyether-based electrolytes. An interesting feature of our study is that the polycarbonate is a unique candidate for ion-conductive polymers because of its flexible and hydrophobic properties.

1. Introduction

Polymer electrolytes are soft materials that are notable as ionic conductors, since they have good safety characteristics (not flammable, no leakage), and their flexibility and light weight are particularly useful in solid-state lithium-ion secondary batteries [1,2]. Ionic conduction in poly(ethylene oxide) (PEO)-metal salt complexes was first discovered in the 1970s [3,4], and there have since been many studies of PEO-based electrolytes with a reduced degree of crystallinity and improved salt solubility [5–7]. Unfortunately, these electrolytes have relatively low conductivity, not exceeding 10^{-5} S cm^{-1} at room temperature. It is well known that the migration of ions in PEO can be realized by the local motion of oxyethylene chains in the amorphous region. The local structure that is crucial in the migration is believed to facilitate cation–dipole interaction [5]. In fact, this interaction sometimes inhibits fast migration, because of the strong cohesion of cations and dipoles, which increases the glass transition temperature, T_g. To overcome these problems, another candidate for the base matrix is needed, without an oxyethylene framework.

As one way to improve the conductivity, processing with CO_2 under subcritical and supercritical conditions has been reported for simple polyether-salt mixtures [8], organically modified ceramics as polymer electrolytes [9], and polyether-clay composites [10]. Our previous reports concluded that CO_2 molecules which permeated into the treated sample can promote the dissociation of ions in the local structure, and increase ionic mobility. In other words, introduction of CO_2 as a raw material into the base polymer can improve the conductivity of polymer electrolytes, so we accordingly focused on a CO_2/epoxide copolymer. CO_2/epoxide alternating copolymerization was first carried out in 1969 [11,12], and today there are numerous reports and reviews, mainly of the development of highly active catalysts [13,14] so as to yield the corresponding polymer efficiently. The copolymerization method is promising not only for the novel polymerization reaction, but also in view of the potential carbon source, in environmental terms. Studies involving polycarbonates have recently been carried out for novel functional materials, including biodegradable polymers [15], nanocomposites [16], and liquid crystalline complexes [17]. In the present study we synthesized alternating copolymers of CO_2 with glycidyl ether type-epoxide monomers, and used the polymers in preparing ion-conductive polymer electrolytes. Polycarbonate is a good candidate for novel ion-conductive polymers, because it has moderate polar groups on the main chain and is flexible, with a relatively low T_g. The polar carbonate groups are likely to dissolve

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salts without strong cohesion of cations, and carrier ions may migrate rapidly in the polycarbonates.

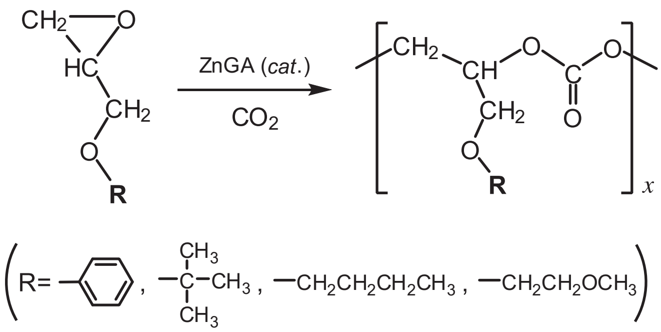
2. Experimental section

2.1. Preparation of monomers and catalyst

Zinc oxide (ZnO, 99%), glutaric acid (GA, 98%) and CO_2 (99.99%) were all used as received. Glycidyl ether (GE) monomers possessing phenyl (Phe, 98%), *tert*-butyl (*t*Bu, 99%) and *n*-butyl (*n*Bu, 95%) groups were purchased and were stored using 4 Å molecular sieves prior to copolymerization. A GE monomer possessing methoxyethyl (MeEt) group was synthesized from epichlorohydrin and 2-methoxyethanol in the presence of NaOH. As polymerization catalyst, zinc glutarate (ZnGA) was synthesized from ZnO and GA [18,19]. GA (0.99 mol) was dissolved in toluene (90 mL) in a flask equipped with a Dean–Stark trap with a reflex condenser and a drying tube. ZnO (1.00 mol) was added as a fine powder into the solution and stirred vigorously at 55 °C for 4 h, and the solution was then refluxed for 24 h. After cooling to room temperature, the mixture was filtered, washed three times with acetone, and dried under vacuum at 120 °C.

2.2. Copolymerization and characterization

Alternating copolymerization of CO_2 with GE monomer was undertaken in a stainless reactor (Taiatsu Techno Co.). The GE monomer was added with ZnGA (appl. 5 mol% to monomer) to the reactor in a dry Ar-filled glove box. The reaction conditions were fixed at 8.2 MPa and 60 °C for 24 h. In the case of polymerization using MeEt-GE monomer, the conditions were 5.0 MPa and 60 °C for 7 days. The polymerization process is summarized in Scheme 1. After polymerization the reactor was cooled to room temperature, and the resulting mixture was dissolved in chloroform. The chloroform solution was filtered in order to remove ZnGA, and was then concentrated to a proper volume using a rotary evaporator. The solution was dropped into excess methanol; this dropping process was carried out at least three times. The precipitated polymer, which is abbreviated as P(R-GEC), was dried under vacuum at 60 °C for 24 h. The ^{1}H and ^{13}C NMR spectra of all of the synthesized polycarbonates (see Figs. S1–S4 of Electronic Supplementary Material) were observed using a JEOL EX-400. Molecular weights and polydispersities of polycarbonates were estimated using a gel permeation chromatography (GPC) system (JASCO Co.), with two columns (TOSOH TSKgel GM_{HHR}-H) and chloroform (HPLC grade) as an eluent at a flow rate of 1.0 mL min^{-1} (calibrated by polystyrene standards).



Scheme 1. Copolymerization of CO_2 with GE monomers (side groups R = Phe, *t*Bu, *n*Bu and MeEt).

2.3. Measurements

Polycarbonate electrolytes were prepared using the simple casting method. The polycarbonate was dissolved in chloroform with lithium bis-(trifluoromethane sulfonyl) imide (LiTFSI, donated from Daiso Co.) at room temperature. LiTFSI was able to dissolve in chloroform, and the polymer/salt mixed solution was completely transparent. The LiTFSI content in the electrolyte was chosen to be 10 mol% to a monomer unit of each polycarbonate. The solution was cast onto the plastic dish and dried under vacuum at 60 °C for 24 h. Differential scanning calorimetry (DSC) measurements of all samples were made using a DSC120 (Seiko Inst.) from −100 °C to 300 °C at a heating rate of 10 °C min^{-1} under dry N_2 gas. The ionic conductivities of all electrolytes were measured by the complex impedance method, using an impedance/gain-phase analyzer 4194A (HP) in the frequency range from 100 Hz to 15 MHz. The temperature was reduced from 100 to 30 °C and the cell was held constant at 10 °C or 20 °C intervals for at least 30 min, after which each impedance measurement was carried out.

3. Results and discussion

3.1. Copolymerization of CO_2 with glycidyl ethers

The four polycarbonates were obtained as high molecular weight polymers (Table 1), but they differed in color and stiffness. P(Phe-GEC), P(*n*Bu-GEC) and P(MeEt-GEC) were transparent polymers, and P(*n*Bu-GEC) and P(MeEt-GEC) were jellylike rubbers and were much softer than P(Phe-GEC) at room temperature. P(*t*Bu-GEC) was a white fibrous solid. These electrolytes with 10 mol% LiTFSI included were all slightly opaque and were rubbery solids; no precipitation of the salt was observed. NMR measurements do not show any peaks in the range 3.4–3.9 ppm in the ^{1}H NMR spectra of the original polycarbonates (−CH_2CHO− main chain) which depend on the glycidyl ether homopolymer [19]. It follows that all polycarbonates are alternating copolymers of CO_2 and GE monomer. In addition, no NMR peaks of unreacted GE monomers were observed, only polycarbonate.

3.2. Thermal analysis

Fig. 1 shows DSC curves of the original polycarbonates and the electrolytes. The values of T_g for all samples are summarized in Table 1. For the original polymers, the values of T_g were significantly different because of the structure of their side groups (denoted by R in Scheme 1). For P(*n*Bu-GEC), T_g was 33 °C lower than for P(*t*Bu-GEC). This is due to the difference in mobility of the side groups, *n*- and *tert*-butyl, in the polycarbonates. Steric hindrance of the *tert*-butyl group should be very different from that of the *n*-butyl group, even though these groups have the same formula weight. For P(*t*Bu-GEC) there was a very weak glass transition, because of coexistence in small amounts of crystalline domains, which are related to the endothermic peak at 141 °C. P(Phe-GEC) is a glassy polymer because of its rigid side groups, with the highest T_g of all the polymers. P(MeEt-GEC) had the lowest T_g value of all the

Table 1
Characterization of synthesized polycarbonates.

P(R-GEC)	Yield[a]	$M_n \times 10^4$	M_w/M_n	T_g (°C)	T_g' (°C)[b]
R = Phe	0.44	1.5	4.5	45	41
*t*Bu	1.21	4.4	1.5	9	18
*n*Bu	1.35	19	2.3	−24	−20
MeEt	0.30	1.7	2.1	−45	−55

[a] Yield (g/g of cat.) of P(R-GEC) copolymers insoluble in methanol.
[b] T_g of polycarbonate/LiTFSI (10 mol%) electrolytes.

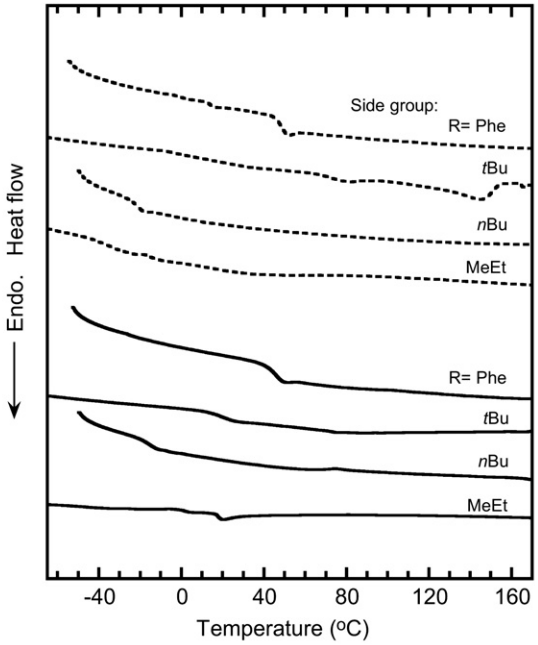


Fig. 1. DSC curves of P(R-GEC) originals (dashed lines) and P(R-GEC)$_{10}$LiTFSI electrolytes (solid lines). (side groups R = Phe, *t*Bu, *n*Bu and MeEt).

original polymers, but the transition was also very weak (see Fig. S5 of Electronic Supplementary Material). For P(*n*Bu-GEC) and P(*t*Bu-GEC), however, T_g clearly increased upon addition of LiTFSI. Morover the small endothermic peak of P(*t*Bu-GEC) disappeared, and these electrolytes became amorphous without any thermal peaks above T_g. These results indicate that the increase in T_g is due to increased cross-linking structures in amorphous regions, based on the weak interaction between cations or aggregated ions and polar groups in the polycarbonate. In other words, the added salt can dissolve, and the dissociated ions act as carrier ions in the polymer. Based on our study of the polar groups in polycarbonate, we believe that both ether oxygens of the side chain and the carbonate units of the main chain are involved in the interaction. The T_g values of P(Phe-GEC) and P(MeEt-GEC) changed in opposite senses upon addition of LiTFSI. The decrease for P(Phe-GEC) and P(MeEt-GEC) may be due to the plasticization effect of dissociated TFSI anions [20].

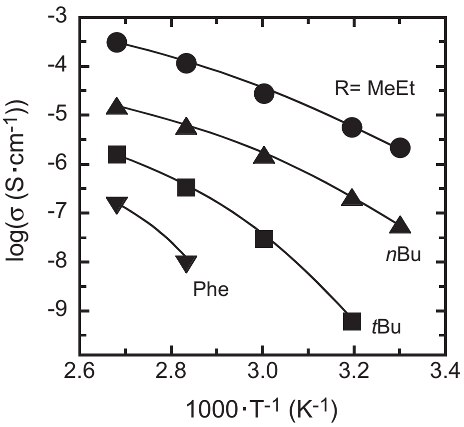


Fig. 2. Temperature dependence of ionic conductivity for P(R-GEC)$_{10}$LiTFSI electrolytes. (side groups R = Phe, *t*Bu, *n*Bu and MeEt).

3.3. Impedance measurement

The temperature dependence of the conductivity of polycarbonate/LiTFSI electrolytes is shown in Fig. 2. All polycarbonates gave typical Arrhenius plots, similar to polyether-based amorphous electrolytes, which are convex throughout the entire range of measurement temperature. The conductivity of P(Phe-GEC)/LiTFSI was the lowest of all polycarbonate electrolytes, approximately 10^{-8} S cm^{-1} at 80 °C, because its T_g was highest. The P(*t*Bu-GEC) electrolyte also had very low conductivity, of the order of 10^{-9} S cm^{-1} at 40 °C. The P(*n*Bu-GEC) electrolyte had good conductivity relative to P(Phe-GEC) and P(*t*Bu-GEC) electrolytes, because its T_g is low. Moreover, the P(MeEt-GEC) electrolyte had the greatest conductivity (2.2×10^{-6} S cm^{-1} at 30 °C) of all polycarbonate samples, and its value was only 10-times lower than typical polyether-based electrolytes such as poly[oligo(oxyethylene glycol) methacrylate] (PMEO)/LiTFSI (2.4×10^{-5} S cm^{-1} at 30 °C) [21]. The Arrhenius plots of P(*n*Bu-GEC) and P(MeEt-GEC) electrolytes in Fig. 2 have smaller gradient than for P(*t*Bu-GEC) and P(Phe-GEC), and have similar gradient to PMEO$_{10}$LiTFSI. This suggests that there is almost no difference, in the activation energy for ionic conduction, between the polycarbonate and PMEO. The temperature dependence of amorphous polymer electrolytes is known to follow the VTF empirical equation,

$$\sigma = A/T^{1/2} \cdot \exp[-E_a/R(T - T_0)] \tag{1}$$

where A (K$^{1/2}$ S cm^{-1}) is a constant that is proportional to the number of carrier ions, T_0 is an ideal T_g, R (J mol^{-1} K^{-1}) is the fundamental gas constant and E_a (kJ mol^{-1}) is an activation energy for ionic transport via segmental motion [7]. We took T_0 to be 50 °C lower than the value of T_g obtained from the DSC measurement [22]. Equation (1) can be rewritten by taking logarithms as

$$\ln\left(\sigma \cdot T^{1/2}\right) = -E_a/R(T - T_0) + \ln A \tag{2}$$

The parameters A and E_a can be estimated from the intercept and the gradient of each linear plot based on equation (2). VTF plots for P(*n*Bu-GEC), P(MeEt-GEC) and PMEO [21] electrolytes including LiTFSI are shown in Fig. 3. It is clear that the parameter A was lower for P(*n*Bu-GEC)$_{10}$LiTFSI (11.5 K$^{1/2}$ S cm^{-1}) than for PMEO$_{10}$LiTFSI (16.1 K$^{1/2}$ S cm^{-1}). This is because the non-polar (*n*-butyl) side group inhibits the smooth dissociation of ions. However, the value of E_a for P(*n*Bu-GEC)$_{10}$LiTFSI (11.6 kJ mol^{-1}) was almost the same as that for PMEO$_{10}$LiTFSI (11.4 kJ mol^{-1}). This indicates that there is no difference in the potential energy for ionic transport in P(*n*Bu-GEC) and in PMEO,

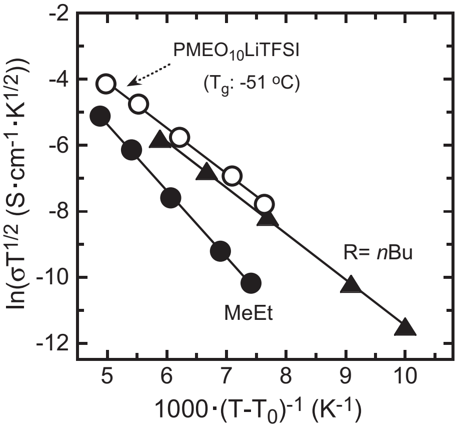


Fig. 3. VTF plots of P(R-GEC)$_{10}$LiTFSI (side groups R = MeEt and *n*Bu) and PMEO$_{10}$LiTFSI electrolytes. (RMS of all plots >0.99).

showing that carrier ions can migrate even in the polycarbonate. Shriver has argued that transport in a rigid polymer electrolyte possessing a carbonate unit is decoupled from the segmental motion in the polymer [23]. We believe that the decrease in the E_a of P(*n*Bu-GEC)$_{10}$LiTFSI observed in the present study is a result of a similar decoupling due to the weak ion–dipole interaction. The dependence for P(MeEt-GEC)$_{10}$LiTFSI also followed the VTF equation, but the parameters were significantly different ($A = 109\,\mathrm{K}^{1/2}\ \mathrm{S\ cm}^{-1}$, $E_a = 16.7\ \mathrm{kJ\ mol}^{-1}$). These unusual data are perhaps due to the decrease in T_g caused by the addition of LiTFSI. We consider that ionic migration in P(MeEt-GEC) is due not to the segmental motion of the main chain but mainly to the fast local motion of short side chains, such as γ-relaxation. A study of this is under way, and other side groups can be introduced to the polymer with high A and low E_a so as to increase the conductivity.

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Appendix. Supplementary data

Supplementary data associated with this article can be found in the on-line version, at doi:10.1016/j.polymer.2010.07.037.

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