New Type Polymer Electrolytes Based on Bis-Oxetane Monomer with Oligo(ethylene oxide) Units

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ABSTRACT: A new procedure for preparing of polymer electrolytes based on ring-opening polymerization of bis-oxetane derivatives [1,9-bis(3-ethyl-3-oxetanyl)-2,5,8-trioxanonane (DDOE), 1,12-bis(3-ethyl-3-oxetanyl)-2,5,8,11-tetraoxadodecane (TrDOE), and 1,15-bis(3-ethyl-3-oxetanyl)-2,5,8,11,14-hexaoxapentadecane (TeDOE)] having oligo-ethylene oxide (EO) chain was carried out with lithium salts [$LiPF_6$, $LiBF_4$, and $LiN(C_2F_5SO_3)_2$] as a polymerization catalyst. Addition of a polar solvent such as acetone or acetonitrile ("retarding" solvent) to the monomer-lithium salt mixture was effective in regulating the polymerization rate. The polymer electrolytes were characterized by infrared spectroscopy, differential scanning calorimetry (DSC), dynamic mechanical spectroscopy, X-Ray diffraction measurement, and alternating current impedance spectroscopy. The polymer electrolytes obtained with $LiBF_4$ were free-standing and dimensionally stable films and indicated high conductivity (2.8×10^{-5} S cm^{-1} at 30°C) as solvent-free polymer electrolytes. Conductivity of the poly(oxetane)–$LiBF_4$ complexes was found to depend on the amount of $LiBF_4$, the kind of "retarding" solvent (acetone or acetonitrile) and length of oligo-EO chain in the bis-oxetane monomer. Maximum conductivity of the complexes acquired from the $LiBF_4$–acetone solution of DDOE, TrDOE, and TeDOE revealed 2.7×10^{-5}, 2.0×10^{-5}, and 1.8×10^{-5} S cm^{-1} at 30°C, and from $LiBF_4$–acetonitrile solution, 7.6×10^{-7}, 1.6×10^{-6}, and 2.8×10^{-5} S cm^{-1} at 30°C, respectively. DSC and dynamic mechanical spectroscopy of the polymer electrolytes suggested that the network structures in the electrolytes were influenced by the polar solvent.
KEY WORDS Ring-Opening Polymerization / Polymer Electrolyte / Lithium Salts / Oxetane /

The need for light-weight and high-energy rechargeable batteries has been increasing for electronic devices and electric vehicles.[1,2] In particular, lithium rechargeable batteries have high energy density compared to other conventional secondary cells such as nickel–cadmium and nickel–hydrogen. Application of polymer electrolytes to the secondary lithium batteries has been extensively studied due to their good mechanical, chemical, and electrochemical stability. Polymer batteries were prepared by interposing polymer electrolyte membranes between anode and cathode for lithium salt dissolution and lithium ions transfer as well as the electrode separator. Polymer cells provide shape in desirable design and safety in mechanical and thermal shock.

To obtain polymer electrolytes with high conductivity, investigation on polymer electrolytes having large segmental motion and facile ion transport has been extensively carried out.[3–5] A number of studies has been devoted particularly to poly(ethylene oxide) (PEO) with desirable coordination of the lithium ion to the ether oxygen atom in oligo-ethylene oxide (EO) chain. With a PEO-based electrolyte, a semicrystalline material and the crystalline complex with lithium salt shows decreased ionic conductivity, and insufficient flexibility of polymer backbone for lithium ion mobility at ambient temperature.[6–9] To suppress crystallinity and increase segmental mobility of the ethylene oxide chain, PEO-based compounds with polysiloxane[6] or polyurethane[10] and branched[11] or hyperbranched ether chain[12,13] and with cross-linked networks[14,15] have been studied. These polymers need to eliminate byproducts produced in polymerization or catalysts used for polymerization which have adverse effect on their electrochemical properties. Purification is not so facial because of the removal of impurities from high-molecular-weight compound.

This paper shows a new procedure of preparation of polymer electrolytes having networks consisting of 2-ethyltrimethylene oxide and oligo-EO chains as shown in Figure 1. These electrolytes were prepared without further purification after cationic polymerization of bis-oxetane monomers containing oligo-EO chains with lithium salts. Polymerization of the bis-oxetane monomer is initiated by the addition of lithium salts and the polymerization rate is regulated by addition of a polar solvent ("retarding" solvent), such as acetone or acetonitrile. The lithium salt and "retarding" solvent affected the network structures in the electrolytes and

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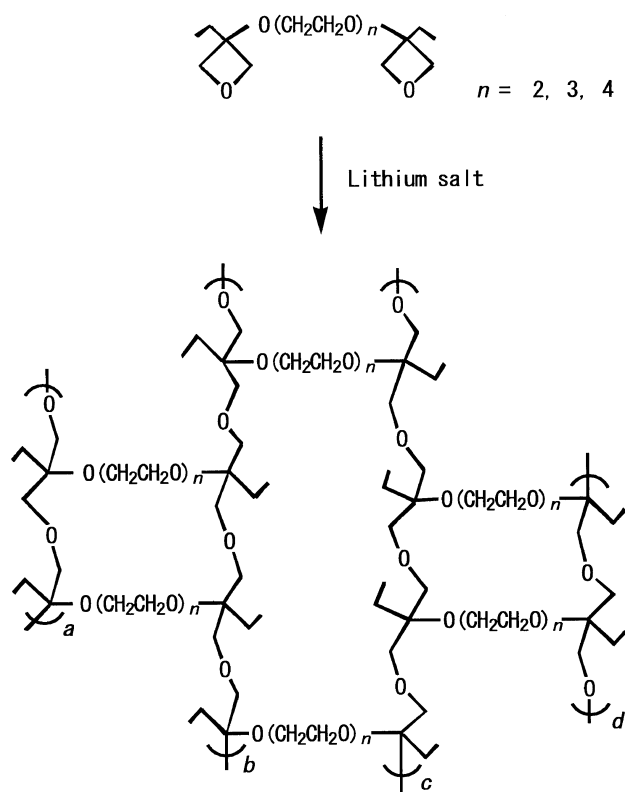†To whom correspondence should be addressed.

Figure 1. Structures of bis-oxetane monomers and schematic presentation of the polymer network based on the monomer.

conductivity.

EXPERIMENTAL

Materials

Reagent grade acetone, tetrahydrofuran, and acetonitrile were purchased from Katayama Chem., Japan, and purified by standard procedures. Lithium-battery-grade $LiBF_4$ and $LiPF_6$ were obtained from Morita Chem., Japan, and used without further purification. $LiN(C_2F_5SO_2)_2$ was obtained from 3 M, USA, and employed after drying at $130°C$ for $13\,h$ under vacuum. DDOE, TrDOE, and TeDOE were prepared by procedures described previously.[16]

Measurements

Differential scanning calorimetory measurements were carried out with a Shimadzu thermal analyzer DSC-50 instrument at a heating rate of $10°C\,min^{-1}$ under helium. An indium standard was used to calibrate the instrument. Dynamic mechanical spectroscopy was performed with a solid analyzer viscoelastometer (RSA II, Rheometric Scientific). The measurements were carried out at a frequency of $1\,Hz$, at -150 to $250°C$ in a nitrogen atmosphere at a heating rate of $3°C\,min^{-1}$. The storage modulus (E') and loss tangent ($\tan\delta$) of the electrolytes were determined. X-Ray diffraction patterns were recorded on a Rigaku diffractionmeter

RINT2500 instrument using Cu-K_α radiation between 5 and $60°$ at $30\,kV$. Conductivity measurements were made using a Model 263 A Potentiostat/Galvanostat and a Model 1025 AC Impedance of EG&G Princeton Applied Research over a frequency range of $1\,Hz$ to $100\,Hz$ at $30°C$. Polymer electrolyte films were sandwiched between the two stainless steel electrodes having an average surface area of $1.33\,cm^2$ and placed in a sealed cell under dry conditions for conductivity study.

Sample Preparation

Sample preparation procedures were similar to those described previously.[16] Network formation was induced by ring-opening polymerization of oxetane derivatives, using lithium salts as initiator, in acetone (AT), acetonitrile (AN), or tetrahydrofuran (THF) solution, respectively. Typical preparation of the polymer electrolyte was as follow: 1,9-bis(3-ethyl-3-oxetanyl)-2,5,8-trioxanonane (DDOE) ($0.60\,g$, $2.0\,mmol$) was added to acetonitrile solution with $LiPF_6$ ($0.032\,g$, $0.2\,mmol$). The solution (ca. $40\,wt\%$) was cast onto an aluminum foil dish and heated at $50°C$ under dry nitrogen atmosphere for $1\,h$, followed by under high vacuum for a further $2\,h$ at $90°C$. The oxetane–$LiBF_4$–AT and –AN systems cast onto an aluminum foil dish were treated under high vacuum for a further $5\,h$ at $70°C$ after heated at $50°C$ under dry nitrogen atmosphere for $1\,h$. The oxetane–$LiN(C_2F_5SO_2)_2$–THF system was heated at $100°C$ for $2\,h$. "PolyDDOE–$LiBF_4$–AT" is an abbreviation for the polymer electrolyte prepared from the acetone solution containing DDOE and $LiBF_4$.

Extraction of Polymer Electrolyte with THF

To analysis of the polymer networks in polyDDOE–$LiBF_4$ complexes, the polymer electrolyte films were stirred in THF to remove THF-soluble polymers for $24\,h$ at room temperature. The weight of residue of the extracted polyDDOE–$LiBF_4$ complex was compensated by the loaded weight of $LiBF_4$. The weight ratio of the residue to the original film was estimated from compensated weight.

RESULTS AND DISCUSSION

Structures and Thermal Properties of Poly(oxetane)–LiX (X = BF$_4$, PF$_6$, and N(C$_2$F$_5$SO$_2$)$_2$) Complexes

Poly(oxetane)–LiX complexes with oligo-EO networks were prepared by ring-opening polymerization of oxetane derivative (DDOE, 1,12-bis(3-ethyl-3-oxetanyl)-2,5,8,11-tetraoxadodecane (TrDOE), or 1,15-bis(3-ethyl-3-oxetanyl)-2,5,8,11,14-hexaoxapentadecane (TeDOE)) with lithium salt ($LiBF_4$, $LiPF_6$, or $LiN(C_2F_5SO_2)_2$) as catalyst. Our previous paper

on the polymerization of the oxetane derivatives showed the following results:[16] Lithium salts initiate polymerization of the oxetane monomers. The order of catalytic activity to polymerization of the oxetanes is $LiPF_6 > LiBF_4 \gg LiN(C_2F_5SO_2)_2$. $LiPF_6$ and $LiBF_4$ have strong activity and polymerize the oxetane monomers immediately. Addition of a polar solvent such as acetone or acetonitrile ("retarding" solvent) to the oxetane–$LiPF_6$ or –$LiBF_4$ mixture retards the beginning of polymerization of the bis-oxetane by the lithium salt. Removing the added solvent starts the polymerization of the oxetanes. The disappearance of the oxetane rings in the poly(oxetane)–LiX complexes confirmed by their IR spectra.

The estimated network structure of the poly(oxetane) is shown in Figure 1. The polymer network consists of 2-ethyltrimethylene oxide and oligo-EO chains. The network structures of poly(oxetane)–LiX complexes depended on anion (X) of lithium salt and concentration of LiX. The optimum concentration of LiX to form free-standing films was Li/O mol ratio = 0.005–0.04 for $LiPF_6$, 0.15–0.54 for $LiBF_4$, and 0.10–0.20 for $LiN(C_2F_5SO_2)_2$.

Figure 2 shows DSC thermograms of polyTeDOE–LiX complexes cured as described in the Experimental section. Figure 3 illustrates the relationships between glass transition temperature (T_g) and lithium salt concentration in the complexes. Melting peaks appearing in the DSC curves of the polyTeDOE–$LiBF_4$ and –$LiN(C_2F_5SO_2)_2$ complexes are associated with the crystallinity of the polymer-salt complex.[17–19] No endothermic peak was observed in the polyTeDOE–$LiPF_6$ complex due to lower salt concentration.

T_g of polyTeDOE–complexes obtained with $LiPF_6$, $LiBF_4$, and $LiN(C_2F_5SO_2)_2$ are presented at −34– −20°C (Li/O mol ratio = 0.005–0.04), around −65°C (0.30–0.54), and −40– −32°C (0.10–0.20), respectively. T_g of the complex with $LiPF_6$ increased with $LiPF_6$ concentration. It was difficult to add much $LiPF_6$ to the matrix based polyTeDOE because of high catalytic activity. T_g of the $LiN(C_2F_5SO_2)_2$–complex decreased with increase in $LiN(C_2F_5SO_2)_2$. T_g of the polyTeDOE–$LiBF_4$ complexes were at *ca.* −66°C. T_g are 26–36°C lower than those of the polyTeDOE–$LiPF_6$ and –$LiN(C_2F_5SO_2)_2$ complexes. Thus the chain mobility in the polyTeDOE–$LiBF_4$ complexes may be higher than that in the other TeDOE complexes at room temperature.

Salt Dependence of Conductivity of Poly(oxetane)–LiX (X = BF_4, PF_6, and $N(C_2F_5SO_2)_2$) Complexes

Figure 4 shows conductivity at 30°C of polyTeDOE–lithium salt complexes stated above as a function of

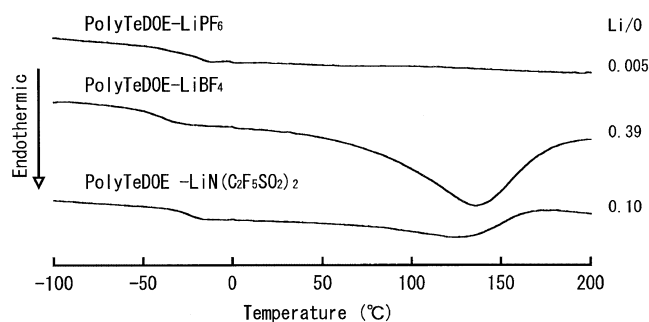**Figure 2.** DSC curves for samples of polyTeDOE containing different lithium salts. PolyTeDOE–$LiPF_6$, –$LiBF_4$, and –$LiN(C_2F_5SO_2)_2$ complex were prepared from acetonitrile, acetone, and THF solution containing TeDOE and lithium salt, respectively.
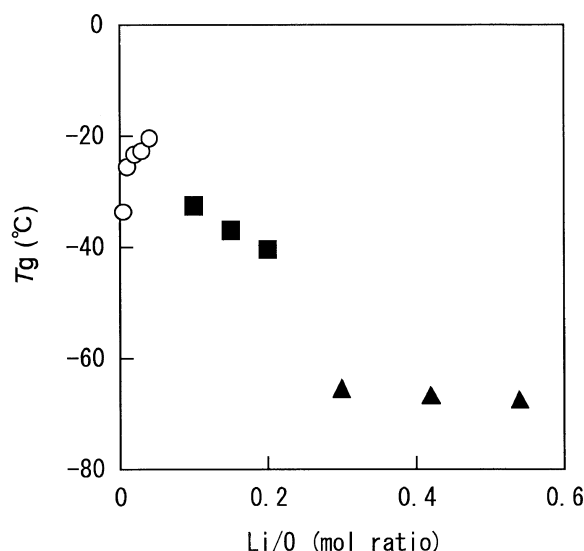

Figure 3. T_g of polyTeDOE–lithium salt complexes as a function of Li/O mol ratio. PolyTeDOE–$LiPF_6$ (○), –$LiBF_4$ (▲), and –$LiN(C_2F_5SO_2)_2$ complexes (■), prepared from acetonitrile, acetone and THF solutions containing TeDOE and lithium salt, respectively.

Li/O mol ratio. Conductivity, as well as T_g (see Figure 3), depend on the lithium salt used to polymerize TeDOE monomer. Conductivity for polyTeDOE–$LiPF_6$ (Li/O mol ratio = 0.005) complex was 3.9×10^{-7} S cm^{-1}. Conductivity of $LiPF_6$–complexes decreased extremely with increase in the Li/O mol ratio. The conductivity for the complex (Li/O mol ratio = 0.04) is two orders of magnitude lower than that of the complex (Li/O mol ratio = 0.005). High reactivity of $LiPF_6$ for polymerization of TeDOE would form highly cross-linked networks with high T_g and the networks prevent rapid ion transportation in the matrix. The polyTeDOE–$LiN(C_2F_5SO_2)_2$ complexes had the same order of conductivity, 10^{-6} S cm^{-1}. In the case of polyTeDOE–$LiBF_4$ complexes, conductivity increased gradually with addition of its salt and after attaining a maximum, falls off. The complex (Li/O mol ratio
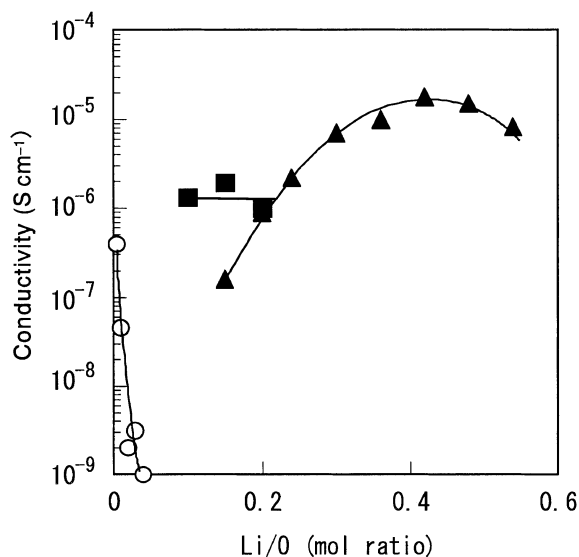
Figure 4. Conductivity at 30°C of polyTeDOE–lithium salt complexes as a function of Li/O mol ratio. PolyTeDOE–LiPF$_6$ (○), –LiBF$_4$, (▲), and –LiN(C$_2$F$_5$SO$_2$)$_2$ complexes (■), prepared from acetonitrile, acetone and THF solutions containing TeDOE and lithium salt, respectively.
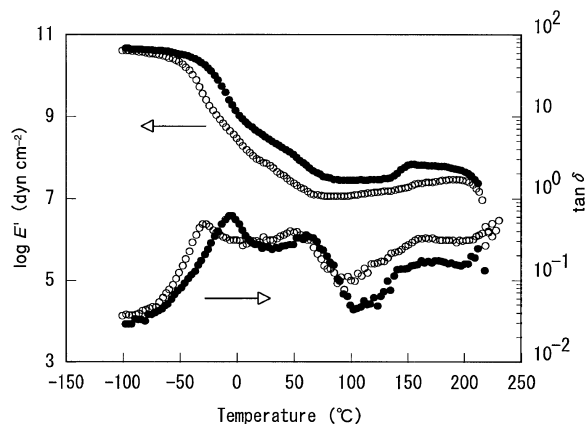

Figure 5. Dynamic mechanical analysis plots of polyDDOE–LiBF$_4$ (Li/O mol ratio =0.39) complexes prepared from acetone (○) and acetonitrile solution (●) containing DDOE and LiBF$_4$, respectively.

= 0.42) shows a maximum conductivity of 1.8×10^{-5} S cm^{-1}, which is in the range of the Li/O mol ratio where a constant T_g appears (Figure 3). Complexes with LiBF$_4$ showed good conductivity and good mechanical strength.

Effects of Solvent ("Retarding" Solvent) Used to Prepare Poly(oxetane)–LiBF$_4$ Complexes on Their Matrix Structures

As described above, the addition of a polar solvent ("retarding" solvents) to oxetane-lithium salt mixture prevents the beginning of polymerization of oxetane monomer. We confirmed the effect of the "retarding" solvent on structures of the poly(oxetane)–LiBF$_4$ complexes. Figure 5 shows the temperature dependence of the elastic modulus (E') and loss tangent (tan δ) for polyDDOE–LiBF$_4$–AT (Li/O mol ratio = 0.39) and polyDDOE–LiBF$_4$–AN (Li/O mol ratio = 0.39) complex between −100 and 250°C. The temperature at tan δ peaks was related to T_g. The tan δ peak (−30°C) of polyDDOE–LiBF$_4$–AN complex shifts toward higher temperature than that of polyDDOE–LiBF$_4$–AT one. Both spectra of E' show a transition region caused by the glass transition of the rubbery, plateau above 90°C, and finally the decomposition region where their E' begins to take a sharp drop at 220°C. E' decreases at ambient temperature and the complexes are obtained as rubber-like materials having E' values of 10^7–10^9 dyn cm^{-2}.

E' of polyDDOE–LiBF$_4$–AN complex is larger than that of polyDDOE–LiBF$_4$–AT except at below −50°C.

There is a slight rise of E' of polyDDOE–LiBF$_4$–AT complex from 90 to 200°C, while E' of polyDDOE–LiBF$_4$–AN complex increases clearly between 137 and 162°C, followed by gradual decrease of E' over 162°C. The increase of E' of polyDDOE–LiBF$_4$ complexes suggests that cross-linking of the networks in the matrix developed during the dynamic mechanical spectroscopy measurements. However, residual amounts of oxetane groups would be extremely small since no IR absorption spectra of oxetanes (data not shown) and no exhothemic peak corresponding to ring-opening polymerization of oxetane was measured in the complexes (see Figure 2). The solvents, added to control the polymerization reaction of oxetanes in the oxetane-lithium salt system, affected the network structures of the resulting polymer electrolytes.

Characteristics of polyDDOE–LiBF$_4$–AT and polyDDOE–LiBF$_4$–AN complexes prepared from acetone or acetonitrile solution with DDOE–LiBF$_4$ (Li/O mol ratio = 0.39), respectively, are listed in Table I. T_g of polyDDOE–LiBF$_4$–AT and polyDDOE–LiBF$_4$–AN complexes are −46.0 and −25.7°C, respectively. T_g of the former complex is about 10°C lower than that of the latter. This indicates that there are some differences of structures in the polyDDOE–LiBF$_4$ complexes obtained using acetone or acetonitrile as "retarding" solvent.

To investigate the preperties of the polyDDOE network, LiBF$_4$ and some THF-soluble polymers in the complexes were removed by extraction of the complexes with THF. The weight ratio of the residue was 86.4% for polyDDOE–LiBF$_4$–AT and 93.8% for the polyDDOE–LiBF$_4$–AN complex, (the values were compensated by the loaded weight of LiBF$_4$). The former complex contained larger amounts of THF-soluble polymers than the latter. T_g of the residues

Table I. Characteristics of samples before and after extraction of polyDDOE–LiBF$_4$ complexes prepared from different solvents (acetone or acetonitrile)

Sample	Extraction[a]	T_g / °C	Residue of polymer / %	Conductivity / S cm^{-1} at 30°C
PolyDDOE–LiBF$_4$–AT[b]	Before	−46.0	–	3.7×10^{-5}
	After	−14.6	86.4	–
PolyDDOE–LiBF$_4$–AN[b]	Before	−25.7	–	6.8×10^{-7}
	After	−17.2	93.8	–

[a]Extracted with THF for 24 h at room temperature. [b]Li/O mol ratio = 0.39.

was similar, −14.6°C (polyDDOE–LiBF$_4$–AT) and −17.2°C (polyDDOE–LiBF$_4$–AN complex). Therefore, THF-soluble polymers in the networks increased the flexibility of the networks, and decreased T_g of the polyDDOE–LiBF$_4$ complexes. Significantly higher conductivity (3.7×10^{-5} S cm^{-1}) was observed in the complexes obtained from an acetone solution than in those (6.8×10^{-7} S cm^{-1}) from an acetonitrile one.

Effects of Monomer Structure and "Retarding" Solvent on Conductivity of Poly(oxetane)–LiBF$_4$ Complexes

The "retarding" solvent affects the conductivity of poly(oxetane)–LiBF$_4$ complexes. Figure 6 shows variation of conductivities for the complexes with LiBF$_4$ prepared from acetone or acetonitrile solution as a function of the Li/O mol ratio. As shown in Figure 6A, salt concentration dependence of conductivity for poly(oxetane)–LiBF$_4$ complexes prepared from the acetone solutions is independent of the structures of the oxetane monomers. Maximum conductivity of all the poly(oxetane)–AT complexes was about 2×10^{-5} S cm^{-1} at Li/O mol ratio = 0.45. Conductivity of the complexes prepared from the acetonitrile solution depended on the structure of the oxetane monomer as shown Figure 6B. Maximum conductivity of the polyDDOE–, polyTrDOE–, and polyTeDOE–acetonitrile complex was 7.6×10^{-7} (Li/O mol ratio = 0.40), 1.6×10^{-6} (0.30 and 0.34), and 2.8×10^{-5} S cm^{-1} (0.39), respectively. The difference of conductivity between the poly(oxetane)–AT and poly(oxetane)–AN complexes is presumably caused by low molecular weight materials as described before. As listed in Table II, this phenomenon is also explained by the fact that the poly(oxetane)–AT complexes show lower T_g than the corresponding poly(oxetane)–AN. The conductivity of the poly(oxetane)–AT complexes is mainly govern by the content of THF-soluble polymers.

For poly(oxetane)–AN complexes, variation of conductivity and T_g is caused by differences of structure of the oxetane monomer and salt content. The dependence of conductivities and T_g on the structure of the oxetane monomer is explained as follows: The complex prepared from the monomer having a longer length

Table II. T_g of poly(oxetane)–LiBF$_4$ complexes prepared from different solutions

Acetone		Acetonitrile	
Li/O	T_g / °C	Li/O	T_g / °C
polyDDOE			
0.32	−34.4	0.30	−31.6
0.39	−46.0	0.40	−27.5
0.45	−49.5	0.50	−32.2
polyTrDOE			
0.31	−58.7	0.23	−36.4
0.43	−60.5	0.34	−45.1
0.55	−60.9	0.46	−56.5
polyTeDOE			
0.30	−65.3	0.26	−44.3
0.42	−66.1	0.39	−49.2
0.54	−67.6	0.52	−60.5

Li/O : mol ratio.

of oligo(ethylene oxide) chain gave lower T_g (Table II) and high conductivity at Li/O mol ratio = 0.2–0.4 (Figure 6B). This is because the long chains give low degree of cross-linked points and large segmental mobility. The dependence of conductivity and T_g on salt concentration is elucidated as follows: T_g decreases with increasing salt concentration as shown in Table II. The increase in salt content provides polymers with the lower polymerization as the salt acts as catalyst of polymerization of oxetanes, and consequently reduces T_g. The complex with high salt content gives good conductivity due to low T_g and the large number of charge carriers. However, beyond appropriate addition of lithium salt, conductivity decreases as shown Figure 6B. Further addition of salts (Li/O mol ratio > *ca*. 0.6, Figure 6B) gives gel-like and no free standing films.

Figures 7 and 8 show X-Ray diffraction patterns of poly(oxetane)–LiBF$_4$–AN complexes. Increase in salt concentration (from Li/O mol ratio = 0.1 to 0.38) in the poly(oxetane) complexes enhanced conductivity. As shown in Figure 7, X-Ray diffraction patterns of the complexes suggests that the complexes (Li/O mol ratio < *ca*. 0.4) are amorphous and LiBF$_4$ is dissolved into the matrixes. However, further addition of LiBF$_4$ to the matrixes decreased conductivity. X-Ray diffraction patterns of the complexes with high LiBF$_4$ concentra-
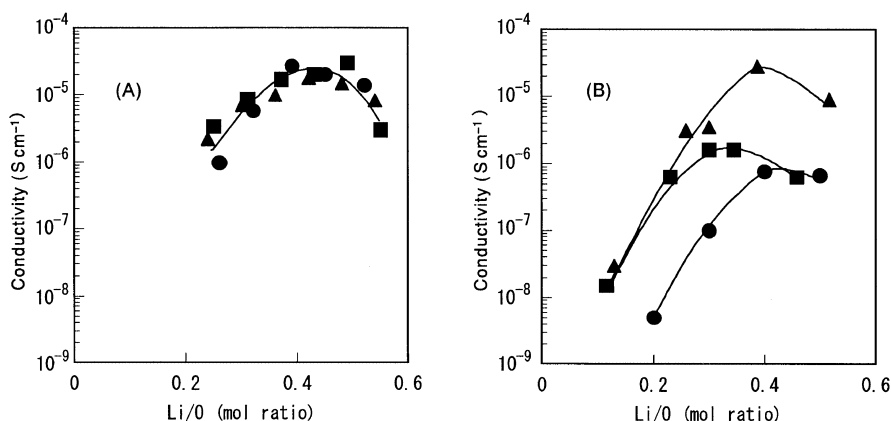
Figure 6. Conductivity at 30°C of poly(bis-oxetane)–LiBF$_4$ complexes as a function of Li/O mol ratio. PolyDDOE– (●), polyTrDOE– (■), and polyTeDOE–LiBF$_4$ complexes (▲), prepared from acetone (A) and acetonitrile solutions (B) containing bis-oxetane and LiBF$_4$, respectively.

CONCLUSIONS

New poly(oxetane)-based electrolytes with oligo(ethylene oxide) networks were prepared from bis-oxetane and lithium salt mixtures. The electrolytes were prepared directly from cationic polymerization of oxetane derivatives with lithium salts as catalyst. A polar solvent, such as acetone or acetonitrile, retarded the beginning of polymerization of the bis-oxetane by lithium salt. The "retarding" solvents affected the structures of the resulting polymer networks. T_g and conductivity of the acetonitrile system-based complexes were influenced by the length of oligo(ethylene oxide) chains in bis-oxetanes, but those of acetone system-based complexes were not done by it due to the presence of low molecular weight materials. Lithium salts make different contribution to the formation of the polymer networks. In particular, LiBF$_4$-based polymer electrolytes showed low T_g, high conductivity, and no deposition of LiBF$_4$ at the maximum conductivity.
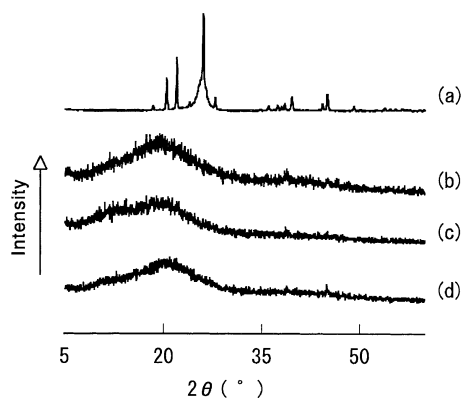

Figure 7. X-Ray diffraction patterns of (a) LiBF$_4$, and (b) polyDDOE (0.40), (c) polyTrDOE (0.34) and (d) polyTeDOE (0.39), prepared from acetonitrile solution containing bis-oxetane and LiBF$_4$. The figure in the brackets is Li/O mol ratio.
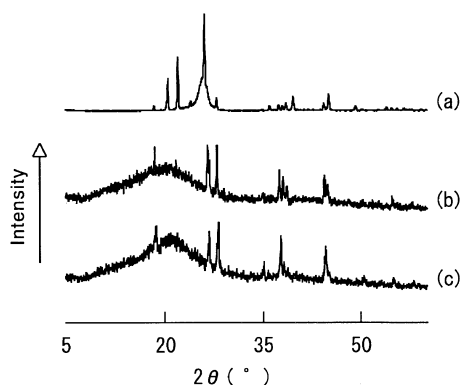

Figure 8. X-Ray diffraction patterns of (a) LiBF$_4$, and (b) polyTrDOE (0.46) and (c) polyTeDOE (0.52), prepared from acetonitrile solution containing bis-oxetane and LiBF$_4$. The figure in the brackets is Li/O mol ratio.

tion (Li/O mol ratio $< ca.$ 0.4) indicate increased crystallinity and existence of undissolved LiBF$_4$ (see Figure 8). Reduction of conductivity is considered to be due to undissolved LiBF$_4$.

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