

ETHYLENE OXIDE—ETHYLENE TEREPHTHALATE SEGMENTED COPOLYMER SOLID ELECTROLYTE*

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ABSTRACT

A series of ethylene oxide-ethylene terephthalate segmented copolymers (EOET) were synthesized and complexed with LiClO_4 to form some new polymer electrolytes. The EOET— LiClO_4 electrolytes exhibit not only high ionic conductivity, but also good mechanical strength and toughness. The EOET 3400—25— LiClO_4 complex possesses the highest conductivity ($4.65 \times 10^{-5} \text{ s} \cdot \text{cm}^{-1}$) at room temperature when the ratio $[\text{Li}^+]/[\text{EO}]$ equals 1/16.

The structures of these electrolytes were examined with FTIR analysis, X-ray diffraction and DSC thermograms, and the results of high ionic conductivity of the segmented copolymers were discussed.

A continuously growing interest is devoted to polymer electrolytes because of their promising applications in versatile and high-energy batteries^[1-3]. Moreover, ionic conducting polymers appear now to be important in electrochemical displays and sensors^[4,5]. So far, the majority of the studies are focused on complexes between poly (ethylene oxide) (PEO) and lithium salts^[6,7], which reveal high conductivities.

Pure poly (ethylene oxide) possesses the general advantages of polymers, such as plasticity, low-cost and ease to form thin films. Many experimental results have proved that polymer electrolyte can keep high ionic conductivity in amorphous phases with low glass transition temperatures. However, for polymer electrolytes, good mechanical and thermal properties are also necessary. Precisely because of this, many researches aimed at modifications of PEO-based ionic conductive systems were carried out by crosslinking, copolymerizing, introducing various kinds of additives.

This work deals with the ethylene oxide-ethylene terephthalate segmented copolymers (EOET) in view of their good mechanical strength and toughness. The lithium perchlorate (LiClO_4)-EOET segmented copolymer system exhibits high ionic conductivity which changes regularly with different conditions.

EXPERIMENTAL

Ethylene oxide-ethylene terephthalate segmented copolymers were synthesized via two steps^[8]: the first involves the ester exchange between dimethyl terephthalate and ethylene glycol and poly (ethylene oxide) with hydroxy end groups. The second step is the polycondensation in the presence of catalyst. A series of EOET segmented copolymers and their PEO molecular weight M_n , intrinsic viscosities $[\eta]$, glass transition temperatures T_g and PET content are listed in Table 1. The PET contents in

Table 1 Poly(ethylene oxide-co-ethylene terephthalate) segmented copolymers used in for study

Segmented copolymers No.	Acronym No.	PEO Molecular weight	PET Content (calculated)	PET Content (NMR)	$[\eta]$ (dl/g)	T_g (°C)
1	EOET600-45	600	45%	44.1%	1.19	-13
2	EOET600-40	600	40%	40.2%	0.82	
3	EOET600-35	600	35%	36.4%	0.83	-21
4	EOET1000-35	1000	35%	37.5%	0.92	-24
5	EQET1540-35	1540	35%	36.4%	0.78	-23
6	EOET3400-35	3400	35%	35.6%	1.11	-15
7	EOET3400-30	3400	30%	30.5%	1.05	-17
8	EOET3400-25	3400	25%	26.0%	1.15	-18

EOET segmented copolymers were measured by an EM-360L NMR spectrometer. Tetramethylsilane was used as standard. A typical proton spectrum is shown in Fig. 1.

The electrolyte films were prepared by conventional solution casting technique, but the preparation of anhydrous EOET- LiClO_4 complexes is very carefull. Generally the lithium perchlorate is only available as a hydrate which usually contains three water molecules per formula unit. LiClO_4 was

heated first in an oven to remove water, then in a vacuum oven at 180°C. All the solvents used in this work were predried.

The electrical conductivity of the films was measured by an AC bridge in the frequency range between 12Hz and 100KHz and by a complex impedance method using a ZL5

analyzer. All the procedures described above were carried out under a nitrogen atmosphere. The film was sandwiched between two Nickel (Ni) electrodes in an oil bath with a temperature controller for conductivity measurement.

The DSC measurements were conducted by a Perkin-Elmer DSC-2C apparatus equipped with a TADS microcomputer, calibrated with ultrapure indium. The glass transition temperature (T_g) was recorded at the half-height of the corresponding heat capacity jump. In the DSC apparatus the first temperature scan was carried out from 30°C to 200°C at a rate of 40°C/min and the sample was maintained at that temperature for 3 min, then quenched to -65°C and kept at that temperature for 1 min. The samples were finally reheated to 200°C. The first thermogram reflects the real state of the aggregate in EOET-LiClO₄ electrolyte, and the second one represents the real glass transition for each sample and the ability of crystallization.

FTIR measurements were made with a Nicolet 170 SX spectrometer. Thin films were cast onto NaCl plate from 5% (w/v) chloroform solutions. After evaporation of most of the solvent, the films were transferred into a vacuum oven to remove the residual solvent. The spectra were obtained at room temperature with a resolution of 2 cm⁻¹ and were signal-averaged with 200 scans. The films used in this study were sufficiently thin to obey the Beer-Lambert law.

The X-ray diffraction patterns for EOET segmented copolymers and their electrolytes at room temperature were obtained by a Rigaku D/max-rA diffractometer with rotation target. The experimental parameters were

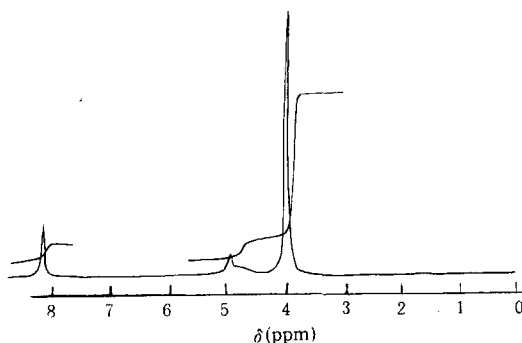


Fig. 1 60MHz proton of EOET segmented copolymer.
The solvent is trifluoroacetic acid

40KV and 100mA, Nickel filter was used for $\text{CuK}\alpha$ radiation.

RESULTS AND DISCUSSION

1. Crystallization behavior of EOET segmented copolymers

Since the crystallization of polymer electrolytes has great important influence on their conductivity, it is necessary to check the macromolecular aggregate state of pure EOET segmented copolymers. Thermograms of the films cast from the solution of EOET segmented copolymers are shown in Fig. 2. These curves demonstrate that the crystallization behavior changes with the molecular weight of soft segments (PEO) and the content of hard segments (PET). When the contents of hard segments are the same (35%) and soft segments have the molecular weight of $M_n = 3400$, the soft segments crystallize evidently, but the hard segments almost not crystallize. In another case, when EOET segmented copolymer with soft segments $M_n = 600$ and content of hard segments (35%), the soft segments almost do not crystallize, but the hard segments crystallize evidently. Such experimental facts suggest that the crystallization behaviors of hard segments and soft segments affect each other.

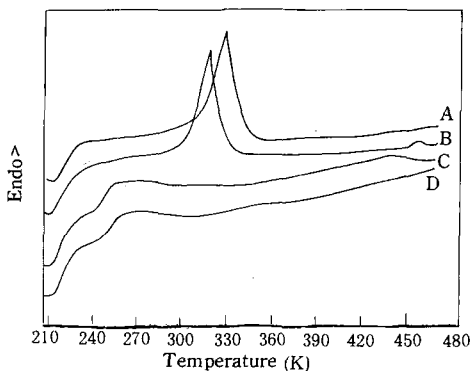


Fig. 2 DSC thermograms of EOET segmented copolymers with content of hard segments (35%) and soft segments of different molecular weight.

A. EOET3400-35; B. EOET1540-35;
C. EOET1000-35; D. EOET600-35

After the first scan and quenching, the DSC samples of EOET copolymers were reheated. In Fig. 3, the thermograms show that for the quenched samples with the soft segments of $M_n = 3400$ or 1540, the soft segments crystallize in quenching, while others do not. But hard segments of all the samples almost weakly or do not crystallize.

The X-ray diffraction curves of EOET3400-25 segmented copolymer and its LiClO_4 complexes do not exhibit sharp diffraction peaks as shown in Fig. 4. Such results indicate that perfect crystals with suitable size could not form, despite some DSC thermograms have endothermic peaks.

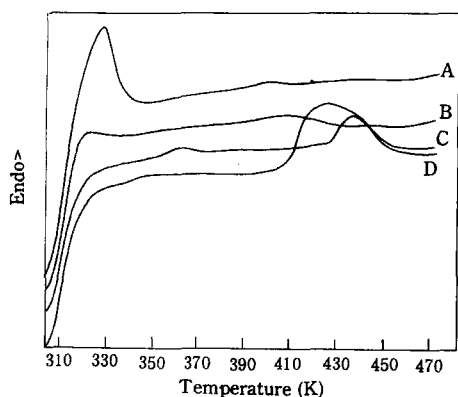


Fig. 3 DSC thermograms of the quenched EOET segmented copolymers
The same copolymers samples as in Fig. 2

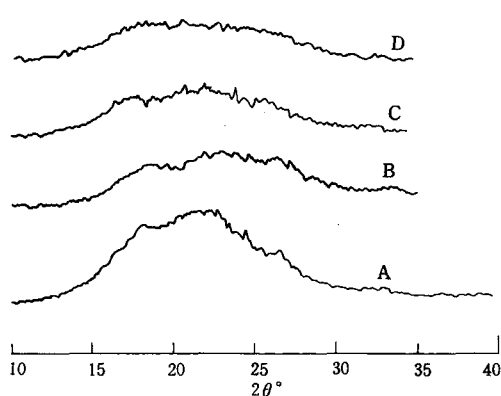


Fig. 4 X ray diffraction curves of EOET3400-25 copolymer and its complexes with LiClO_4
A. EOET3400-25; B. EOET3400-25(1 : 8);
C. EOET3400-25(1 : 16); D. EOET3400-25(1 : 32)

2. Conductivity of ionic complexes of EOET segmented copolymers with lithium perchlorate

The data of conductivity for ionic complexes of EOET segmented copolymers with lithium perchlorate at room temperature are given in Table 2.

Table 2 Conductivity of EOET- LiClO_4 electrolytes $\sigma \times 10^5 (\text{s} \cdot \text{cm}^{-2})$

Segmented copolymers \ [Li ⁺]/[EO]	1 : 4	1 : 8	1 : 12	1 : 16	1 : 32
EOET3400-25	4.40	3.39	3.40	4.65	0.60
EOET3400-30	2.53	2.62	3.43	4.08	1.72
EOET3400-35	1.17	1.61	2.04	2.83	2.82
EOET1540-35	0.53	1.00	1.14	2.76	2.58
EOET1000-35		0.77	1.13	2.66	1.97
EOET600-35		0.58	0.83	1.24	1.92
EOET600-40	0.28	0.51	0.74	1.61	1.44
EOET600-45	0.24	0.27	0.32	0.38	0.33

From these numeral results, it is evident that the conductivity of EOET- LiClO_4 electrolytes generally decreases with increasing of the content of hard segments. The dependence of the conductivity of EOET- LiClO_4

electrolytes on the ratio $[\text{Li}^+]/[\text{EO}]$ shows that when $[\text{Li}^+]/[\text{EO}]$ equals 1/16, the conductivity gets maximum. From the latter listed data of thermal analysis we can understand the reasons of such phenomenon. Such results are also plotted in Figs. 5 and 6. The curves demonstrate the same tendency

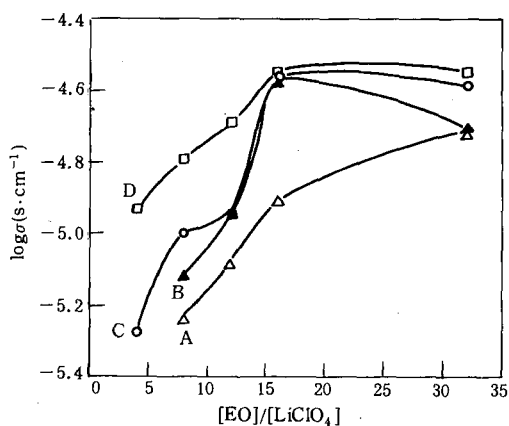


Fig. 5 Dependence of the conductivity of EOET - LiClO_4 complexes on the salt concentration (M. W. of soft segments are different)

- A. EOET600-35- LiClO_4
- B. EOET1000-35- LiClO_4
- C. EOET1540-35- LiClO_4
- D. EOET3400-35- LiClO_4

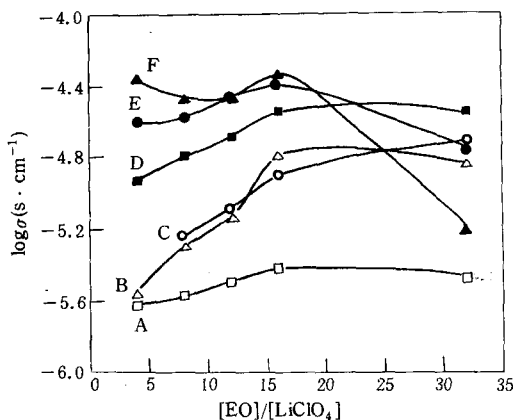


Fig. 6 Dependence of the conductivity of EOET- LiClO_4 complexes on salt concentration (contents of hard segments are different)

- A. EOET600-45- LiClO_4
- B. EOET600-40- LiClO_4
- C. EOET600-30- LiClO_4
- D. EOET3400-35- LiClO_4
- E. EOET3400-30- LiClO_4
- F. EOET3400-25- LiClO_4

about the conductivity. Only one point should be noticed: Why does the conductivity of EOET- LiClO_4 complexes become higher when the molecular weight of soft segments equals 3400. The longer the PEO molecular chain, the soft segments crystallize easily. However, crystallization of PEO segments is unfavorable for high conductivity. It is necessary to reveal the aggregate structure of EOET- LiClO_4 complexes in order to give the answer to the question put forward here.

3. FTIR spectroscopic analysis of EOET- LiClO_4 complexes

Fig. 7 shows the spectra of EOET3400-25 copolymer and its complex with LiClO_4 . It is known that the spectrum of lithium perchlorate has mainly two bands at 623cm^{-1} and 1100cm^{-1} , which are connected with stretching vibration of ClO_4^- . And the symmetric stretching vibration band of ether

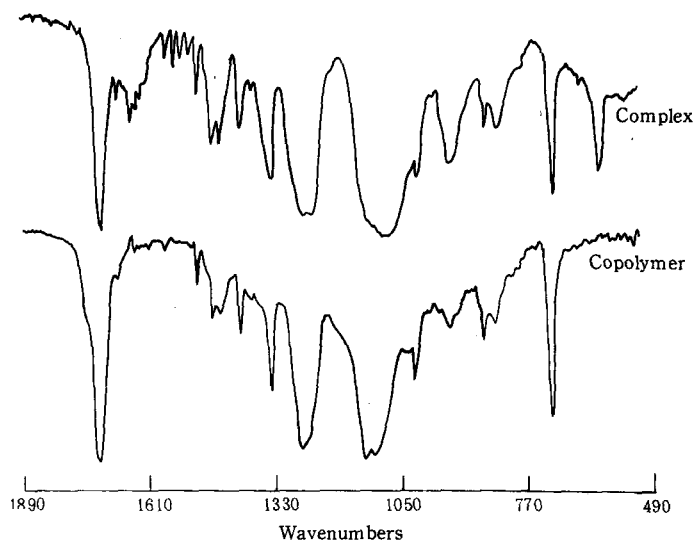


Fig. 7 FTIR spectra of EOET segmented copolymer and corresponding complex with LiClO_4

also occurs at 1100cm^{-1} . In comparison of the bands at 1100 cm^{-1} in the spectra of EOET copolymer to its complex with LiClO_4 , it indicates that the evident widening of the band at 1100 cm^{-1} should be related to the complexing of Li^+ ion with the ether oxygen. In Fig. 8 the shifts of the

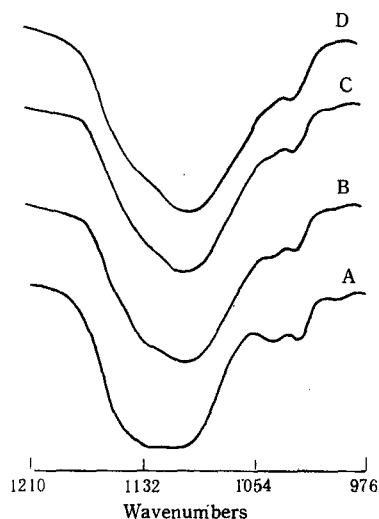


Fig. 8 Shifts of the band at 1100cm^{-1} for EOET3400-25 copolymer and its complexes

- A. EOET3400-25; B. EOET3400-25(1 : 32);
C. EOET3400-25(1 : 16); D. EOET3400-25(1 : 8)

band at 1100 cm^{-1} are shown for EOET3400—25 copolymer and its

complexes. The shift increases with the increasing amount of LiClO_4 in complexes. This confirms the existence of the complexing interaction.

4. Aggregate structure of EOET-LiClO_4 complexes

The DSC thermograms of all the EOET-LiClO_4 complexes were measured by two scans. All the thermograms of the cast films of the complexes from solution were obtained by the first scans and all those of quenched samples by the second scans. Typical DSC curves of complexes EOET3400-30 with different LiClO_4 contents by the first scan are shown in Fig. 9, and the curves of the corresponding quenched samples are shown in Fig. 10. From these two kinds of DSC curves we can carry out the following analysis:

Firstly, for the cast films with increasing LiClO_4 contents, the endothermic peak around $50\text{--}60^\circ\text{C}$ becomes weaker or disappears. This means that the soft segments become weakly crystallizable or non-crystallizable.

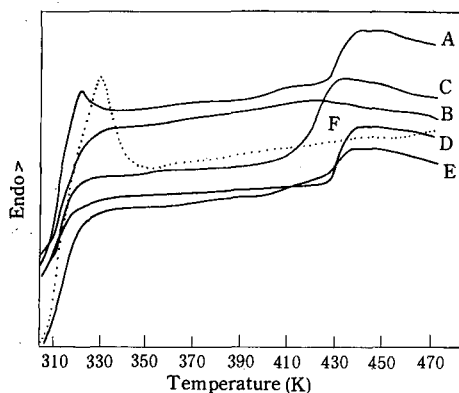


Fig. 9 DSC thermograms of complexes of EOET-30 copolymer with different amount of LiClO_4
 A. $\text{EOET3400-30}(1:32)$
 B. $\text{EOET3400-30}(1:16)$
 C. $\text{EOET3400-30}(1:12)$
 D. $\text{EOET3400-30}(1:18)$

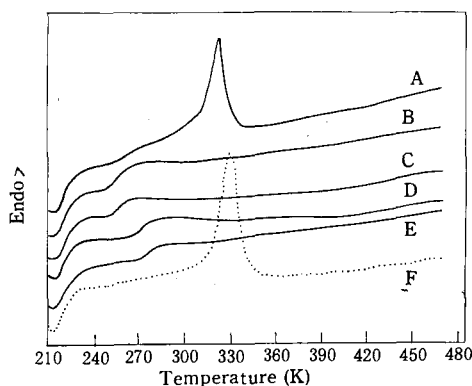


Fig. 10 DSC thermograms quenched samples of the same complexes of EOET-30 copolymers as in Fig. 9

Secondly, the DSC curves of the cast films exhibit a large and wide endothermic peak at high temperature. This means that, at least, after complexing of EOET copolymer with LiClO_4 , some ordered structure forms, which does not exclude the formation of some crystals, of course.

If the ester oxygen group can be complexed with LiClO_4 , then such

complexes also contribute to the wide endothermic peak.

It is very interesting that in the curve of EOET — LiClO₄ complex $\{[Li^+]/[EO]=1/16\}$, not only endothermic peak at low temperature disappears but also endothermic peak at high temperature becomes the weakest. Such experimental fact has just explained why this kind of complexes has the highest conductivity.

Thirdly, the DSC curves of both the cast complexes and the quenched samples all demonstrate that complexing of LiClO₄ with EOET copolymer plays a role in restraining crystallization of both soft and hard segments. Moreover, when $[Li^+]/[EO]=1/16$, the amount of some ordered structure also becomes the lowest. In the quenched sample of EOET3400-30-LiClO₄ complex $\{[Li^+]/[EO]=1/32\}$ the soft segments crystallized even in quenching.

Fourthly, for the quenched samples, the DSC curves exhibit that the complexing of LiClO₄ with EOET copolymer makes the glass transition temperature gradually higher. Moreover, the less the hard segment content and the shorter the soft segment are, the greater the influence of complexing of LiClO₄ on the glass transition temperature has.

In summary, the maximum conductivity at the ratio $[Li^+]/[EO]=1/16$ can also be explained by the effect of the following two factors: one is that with the increasing amount of LiClO₄, the quantity of charge carriers increases. This is a favorable factor for conductivity. The other is that increasing the amount of LiClO₄ makes both the glass transition temperature and the free volume decrease. This is an unfavorable factor for ionic transport. Such two factors determine the optimum ratio $[Li^+]/[EO]$. So as to the fact that complexes with soft segment $M_n=3400$ have higher conductivity, we can give such explanation that although soft segments of EOET3400 copolymer can crystallize easily, complexing of LiClO₄ can restrain their crystallization as effectively as it does for EOET600 copolymer.

5. Temperature dependence of conductivity

Many works about PEO-LiClO₄ system have shown that the conductivity increases with the increasing of measuring temperature. For EOET-LiClO₄ electrolytes the conductivity has been measured from 25—90°C. The data are listed in Table 3. If we plot $\lg \sigma$ against $1000/T$, we can find

Table 3 Conductivity of EOET3400-25-LiClO₄ electrolyte ([Li⁺]/[EO]=1/8)

Temperature (°C)	Conductivity $\sigma \cdot (\text{s} \cdot \text{cm}^{-1})$	Temperature (°C)	Conductivity $\sigma \cdot (\text{s} \cdot \text{cm}^{-1})$
25	1.63×10^{-5}	60	4.96×10^{-4}
30	3.38×10^{-5}	65	6.37×10^{-4}
35	7.12×10^{-5}	70	7.52×10^{-4}
40	1.13×10^{-4}	75	8.65×10^{-4}
45	1.78×10^{-4}	80	1.03×10^{-3}
50	2.72×10^{-4}	85	1.23×10^{-3}
55	3.82×10^{-4}	90	1.35×10^{-3}

that the curve (not straight line) is obtained as shown in Fig. 11. This means that the Arrhenius equation is not suitable for this system. However,

$$\sigma T^{1/2} = \sigma_0 \exp[-E_a/(T - T_g)]$$

if we use VTF equation in which σ is conductivity, T_g is glass transition temperature, and $\lg \sigma T^{1/2}$ is plotted vs. $1000/(T - T_g)$, we get straight line as shown in Fig. 12. From the slope of the straight line can be obtained the apparent activation energy $E_a = 6.64$ KJ/mole.

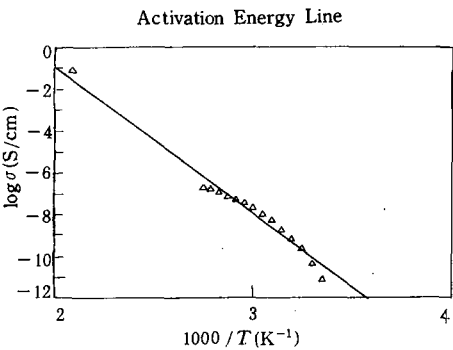


Fig. 11 Temperature dependence of conductivity plotted by Arrhenius equation

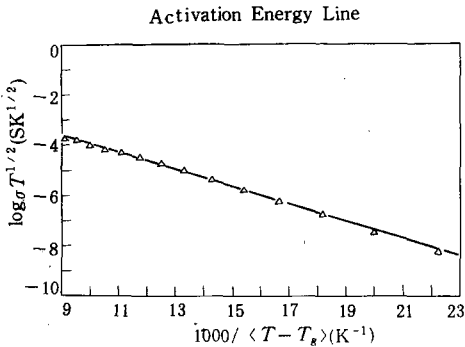


Fig. 12 Temperature dependence of conductivity plotted by VTF equation.

Keywords:

Ionically conducting polymer; Polymer electrolyte; Ethylene oxide-ethylene terephthalate; Segmented copolymer

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