Ion Conduction of Poly[Methoxy Oligo (oxyethylene) Propylene] Synthesized by the Et(Ind)₂ZrCl₂-MAO Catalyst

S. W. HU, W. D. YAN, S. B. FANG*

Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100080, PRC

Received 15 September 1998; accepted 2 November 1998

ABSTRACT: Poly[methoxy oligo (oxyethylene) propylene] was synthesized by means of the Et(Ind)₂ZrCl₂-MAO catalyst. The ionic conductivity of poly[methoxy oligo (oxyethylene) propylene] with the lithium salt depends on the content of the lithium salt. The temperature dependence of conductivity was determined and the Vogel–Tammann/ Hesser–Fulcher (VTF) plot agreed well with theoretical values, confirming the influence of the polymer segmental motion on conductivity. The ionic conductivity as high as $10^{-4.7}$ s/cm can be obtained at room temperature, and this can be increased one or two orders of magnitude by blending the polyelectrolyte with hydroxyl-containing additives such as tetraethylene glycol. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1397–1400, 1999

Key words: polymer electrolyte; conductivity; comblike polymer; $Et(Ind)_2ZrCl_2-MAO$; VTF equation

INTRODUCTION

Since the early work of Armand and Wright on the transport of ions in solid state complexes of alkali-metal salts and poly(ethylene oxide) (PEO),¹⁻³ a number of studies have been published on the synthesis and properties of ion conducting solvent-free polymer electrolytes.⁴⁻⁶ However, some investigations have demonstrated that the ionic conductivity occurs only in the amorphous regions of the PEO⁷, while a high proportion of the crystalline regions will greatly reduce the total conductivity. In view of that, there have been a number of works on synthesizing polymer hosts for the sake of giving fully amorphous polymer electrolytes.⁸

One method of solving this problem is to prepare a comblike polymer with short PEO chains as side groups attached to a large polymer backbone. Many synthetic strategies have been developed to prepare comblike polymer structures such as polyphosphazenes, polysiloxanes, and polymethacrylates as the

Correspondence to: S. B. Fang.

Journal of Applied Polymer Science, Vol. 73, 1397-1400 (1999)

backbone and oligo (oxyethylene) as the side group.^{9–11} However, the comblike polymers with methoxy oligo (oxyethylene) side chains anchored on polypropylene have not been reported. This polar monomer could not be polymerized with Ziegler–Natta catalysts by us, probably because the catalyst will chelate with some of the monomer, which leads to loss of the catalytic activity. As the $Et(Ind)_2ZrCl_2$ -MAO catalyst has higher activity than that of the usual Ziegler–Natta catalyst, it was selected for use in the polymerization.

In this paper, the polar monomer methoxy oligo (oxyethylene) propylene intended for solid state electrolyte was successfully polymerized by means of the Et(Ind)₂ZrCl₂-MAO catalyst, and activity of polymerization as high as 9.4×10^4 g/mol Zr \cdot h could be obtained. The ion conduction of the complexes of this polymer with lithium methoxy oligo (oxyethylene) sulfonate was investigated.

EXPERIMENTAL

Materials

The synthesis of the lithium methoxy oligo (oxyethylene) sulfonate (LiSEO₇ was followed accord-

^{© 1999} John Wiley & Sons, Inc. CCC 0021-8995/99/081397-04

ing to Ref 12. Methoxy oligo (oxyethylenes) (M_w = 350, 550, 750) were Aldrich reagents (AR) and used without further purification. Allyl chloride (AR) was distilled before use. Toluene (AR) was distilled over sodium under nitrogen atmosphere. The Et(Ind)₂ZrCl₂ and MAO was purchased from Wittico Co. and used without further purification.

Synthesis of Poly[Methoxy Oligo (oxyethylene) Propylene]

Poly[methoxy oligo (oxyethylene) propylene] was synthesized as follows:

$$\begin{array}{c} \mathrm{H}(\mathrm{OCH}_{2}\mathrm{CH}_{2})_{n}\mathrm{OCH}_{3} \xrightarrow{\mathrm{CH}_{2}=\mathrm{CHCH}_{2}\mathrm{CI}} \\ \mathrm{CH}_{2}=\mathrm{CHCH}_{2}\mathrm{O}(\mathrm{CH}_{2}\mathrm{CH}_{2}\mathrm{O})_{n}\mathrm{CH}_{3} \xrightarrow{\mathrm{Et}\,(\mathrm{Ind})_{2}\mathrm{ZrCl}_{2}\cdot\mathrm{MAO}} \\ \xrightarrow{\left(-\mathrm{CH}_{2}\mathrm{CH}\right)_{m}} \\ \xrightarrow{\left(-\mathrm{CH}_{2}\mathrm{CH}\right)_{m}} \\ \mathrm{CH}_{2}\mathrm{O}(\mathrm{CH}_{2}\mathrm{CH}_{2}\mathrm{O})_{n}\mathrm{CH}_{3} \end{array}$$

The monomer was prepared by etherification of methoxy oligo (oxyethylene) with allyl chloride with a modified procedure. To a well-stirred mixture solution of methoxy oligo (oxyethylene) (take $M_w = 350, n = 7$ as example) 35 g (0.1mol), 0.2 g tetrabutylammoiumiodide, and aqueous 50% (w/w) sodium hydroxide 10 g (0.125 mol NaOH), allyl chloride 38 g (0.5mol) was added at 70°C within 1 h. After the reaction was completed, the mixtures were extracted by ether until the oil phase become colorless. The organic extracts were dried over anhydrous magnesium sulfate, and 35.2 g liquid methoxy oligo (oxyethylene) propylene (MO₇P) was obtained. Yield: 90.2%. The IR spectrum of the monomer showed no -OH peak (ca. 3430 cm^{-1}) and C—Cl peak (ca. 760 cm^{-1}), but exhibited the characteristic peak of "CH₂=CH" (1640 cm $^{-1}$).

¹H-NMR (CDCl₃, δ , ppm): 5.9 (1H, CH₂=<u>CH</u>—), 5.2 (2H,<u>CH2</u>=CH—), 4.12 (2H, =CH—CH₂O), 3.6–3.8 (28H, —<u>CH₂CH₂</u>—O), 3.40 (s,3H, —O<u>CH₃</u>).

The polymerization was carried out in a 100 mL glass flask thermostated at 60°C under nitrogen atmosphere. The amount of 7.2 g (0.02 mL) of MO₇P, 4.5 mL of 3*M* MAO, and 0.4 mL toluene solution of ethylene bis(1-indenyl) zirconium dichloride (13 μ *M*) were introduced respectively. After 2 h, the reaction mixture was poured into 100 mL of acidified alcohol. The polymerized solid product recovered by washed with methanol and

dried. The amount of 3.7g PMO₇P was obtained. The IR spectrum showed no peak for the carbon double bond (ca.1640 cm⁻¹), but showed the characteristic peak of —(CH₂CH)—_n (2927 cm⁻¹, 2903 cm⁻¹). $M_w = 5.3 \times 10^4$, $M_n = 2.5 \times 10^4$ $M_w/M_n = 2.12$.

¹H-NMR (DMSO, δ , ppm): 1.3 [2H, -(<u>CH</u>₂CH)-_n], 1.6 [1H,-(CH₂<u>CH</u>)-_n], 3.6-3.8 (30H, -<u>CH</u>₂<u>CH</u>₂-O), 3.4 (s,3H, -O<u>CH</u>₃).

Measurements

The thermal properties of the polymer were studied on a Perkin-Elmer DSC-4 differential scanning calorimeter at a heating rate of 20°C/ min. ¹H-NMR spectra were obtained on a BRUKER DMX-300 spectrometer. The conductivities were measured using HIOKI LCR 3520 Hi TESTER over 1KHZ. The experimental procedure is described as follows: after the electrolyte was dried under vacuum at 100°C for 48 h, the cylindrical disk samples were sandwiched between two platinum electrodes and sealed in a test tube filled with dry nitrogen. Before each measurement was made, the sample was kept at constant temperature for at least 30 min. A Waters ALC/GPC 224 column was used to analyze gel permeation chromatograms with the calibration of standard poly(oxyethylene) ether sample.

RESULTS AND DISCUSSION

Polymer Synthesis

The phase transfer catalyst was used for preparing the monomer. The most important condition was that the amount of ally chloride used was excessive. No residual —OH group could be detected by ¹H-NMR and IR in the product, indicating that its formation from methoxy oligo (oxyethylene) was complete.

From the results listed in Table I, although the activity of the polymerization of the methoxy oligo (oxyethylene) propylene was much lower than that of the ethylene ($A = 10^6-10^7$ g/mol Zr · h), activity of the polymerization as high as 5.5×10^4 g/mol Zr · h can be obtained. It can also be found that the side-chain length of the monomer affects the activity of the polymerization. With the increasing unit size of oligo (oxyethylene), the activity of polymerization decreased. For example, when the repeat unit of PEO was 7, the activity of

n ^a	$ m Zr^b$	$A_1/\mathrm{Zr^c}$	<i>T</i> (°C)	<i>t</i> (h)	$A \; (\text{g/mol Zr} \cdot \mathbf{h})$
7	5.3	1200	60	1	$9.4 imes10^4$
12	5.3	1200	60	1	$5.5 imes10^4$
17	5.3	1200	60	1	$5.7 imes10^4$

Table I Polymerization of MOP with Et(Ind)₂ZrCl₂/MAO as Catalyst

^a *n*: Number of units of oxyethylene in the monomer.

^b Zr: molar content of $Et(Ind)_2 ZrCl_2$ in the polymerization in μ mol.

 $^{c}A_{1}/\text{Zr}$: molar ratio of MAO to $\text{Et}(\text{Ind})_{2}\text{Zr}\hat{\text{Cl}}_{2}$ in the polymerization. A: activity of the polymerization in gram of polymer per molar zirconium and hour.

the polymerization was 9.4×10^4 g/mol Zr \cdot h, compared with 5.5×10^4 g/mol Zr \cdot h when the repeat unit of PEO was 12. However, as the unit of the PEO increased further, the catalytic activity did not change obviously. Further research of the polymerization is in progress.

Ionic Conduction of the PMOP/LiSEO₇ System

As is well known, candidate electrolytes for lithium batteries should pursue a high Li^+ ionic transference number. The effective method is to anchor anions in a macromolecular chain through covalent bonds¹²; thus the lithium salt LiSEO₇, with big anions, was selected due to its low dissociation energy and good compatibility with the polymer.

Conductivity (σ) is determined by ionic mobility (μ), carrier number (n), and charge (e), as eq.(1) shows:

$$\sigma = n e \mu \tag{1}$$

For poly[methoxy oligo (oxyethylene) propylene] (abbreviated as PMO_7P) (the following discussion takes PMO_7P as example)/LiSEO₇ system, *e* is



Figure 1 Isothermal conductivity as a function of the composition of the PMOP/LiSEO₇ system at 25° C.

constant while ionic mobility and carrier number varies with the composition, as shown in Figure 1. The addition of salt provides the complex with a carrier ion as it dissociates in the polar media. With increasing salt concentration, conductivity increases because the carrier number increases rapidly. However, the dissociating degree drops with increasing salt content as the salt becomes crowded. Meanwhile, much salt mainly exists as ion pairs or ion clusters that even hinder segmental motion by chelating the ether oxygen atoms. As a result, the maximum conductivity of the $PMO_7P/LiSEO_7$ system appears at O:Li = 33. The following discussions are based on maximum conductivity composition.

Figure 2 gives the temperature dependence of conductivity for the complex of the $PMO_7P/$ LiSEO₇ (O:Li = 36) system. It can be seen that the plots of $\log \sigma$ vs 1/T is a curved line rather than a linear one, which suggests that the ionic conduction mechanism should be of the WLF type.¹³ In this viscous matrix transference, the properties are described by the VTF equation¹⁴:



Figure 2 Arrhenius plots of the conductivities for the $PMOP/LiSEO_7$ (O : Li = 36) system.

$$\sigma = AT^{-1/2} \exp(-B/T - T_0)$$
(2)

where A and B are constants, T is absolute temperature, and T_0 is a temperature related to the T_g ($T_g = 225$ K). According to Gibbs configurational entropy model, the T_0 is regarded as 50°C below the measured T_g . It can be inferred from eq. (2) that it should vary linearly with $(T - T_0)^{-1}$, which is proved by the good linear relationship of VTF plots in Figure 3, when the data of Figure 2 is applied. That is to say, ionic conductivity is considerably affected by the segmental motion of polymer chains in the amorphous region of the electrolytes.¹⁵

The effect of additives such as tetraethylene glycol (TEG) on the conductivity of the PMOP/LiSEO₇ (O : Li = 36) system was examined. Figure 4 shows the relationship between the content of the additive and the conductivity for the PMOP/LiSEO₇ (O : Li = 36) system. Addition of 20% of TEG rapidly increases ionic conductivity from $10^{-4.7}$ to $10^{-4.2}$ s/cm at room temperature, while when 50% of TEG is added the ionic conductivity drastically increases to $10^{-3.4}$ s/cm at the same temperature. It is apparent that the additives lower the microviscosity of the ion-conducting material, which improves segmental mobility of the polymer chains and further enhances the conductivity.¹⁶

Here a new type of poly[methyoxy oligo (oxyethylene) propylene] was synthesized by metallocene /MAO catalyst. The ion conduction of the resulting polymer with LiSEO₇ was examined. The ionic conductivity of the PMOP/LiSEO₇ system as high as $10^{-4.7}$ s/cm can be obtained at



Figure 3 Vogel–Tammann/Hesse–Fulcher plots for the PMOP/LiSEO₇ (O : Li = 36) system.



Figure 4 Arrhenius plots of the conductivities for the (A) PMOP/LiSEO₇, (B) PMOP/LiSEO₇/20% TEG, and (C) PMOP/LiSEO₇/50% TEG (O : Li = 36) system, respectively.

room temperature, which is one of the highest $(\sim 10^{-4.5} \text{ s/cm})$ ever reported in the literature.

The authors acknowledge many helpful exchanges of information and discussions with Prof. You-huai Wang and You-liang Hu.

REFERENCES

- Armand, B.; Chabagho, J.; Duciot, M. Fast Ion Transport in Solids; North Holland Publishing Co., 1979; p 131.
- 2. Fenton, D.; Parker, J.; Wright, P. Polymer 1973, 14, 589.
- 3. Wright, P.Br. Polym J 1975, 7, 319.
- 4. Zheng, Y.; Wan, G. J Appl Poly Sci 1995, 57, 623.
- 5. Itaya, K. J Appl Phys 1982, 53, 804.
- Akahoshi, H.; Toshima, S. J Phys Chem 1981, 35, 818.
- 7. K.; Kaneto, K. Yoshino, J Appl Phys 1983, 22, 412.
- 8. Fang, S.; Jiang, Y. Polym Bull 1988, 19, 81.
- 9. Percec, V.; Hsu, C. Polym Bull 1990, 23, 463.
- Hardy, L; Shriver, D. J Am Chem Soc 1985, 107, 3823.
- Bannister, D.; Davies, G.; Mcintyre, J. Polymer 1984, 25, 1291.
- Zheng, Y.; Wan, G. JMS Pure Appl Chem A, 1993, 30, 365.
- Williams, M.; Landel, R.; Ferry, J. J Am Chem Soc 1955, 77, 3701.
- 14. Fulcher, G. J Am Chem Soc 1925, 8, 339.
- 15. Adam, G.; Gibbs, J. J Chem Phys 1965, 43, 139.
- Hardy, L.; Shriver, D. J Am Chem Soc 1985, 107, 3823.