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Effect of Molecular Weight of Polymeric Solvent on Ion Conductive Behavior in Poly(propylene oxide) Solution of $LiClO_4$

Masayoshi WATANABE, Junko IKEDA, and Isao SHINOHARA

Department of Polymer Chemistry, Waseda University,
Ohkubo, Shinjuku-ku, Tokyo 160, Japan

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ABSTRACT: Ion conductive behavior of $LiClO_4$ in poly(propylene oxide) (PPO) was studied. PPO solutions of $LiClO_4$ had ionic conductivity of 10^{-4}—10^{-6} S cm^{-1} at [$LiClO_4$]/[PO unit] = 0.01—0.1. The concentration dependence of conductivity showed a maximum at [$LiClO_4$]/[PO unit] = 0.04. The increase in the molecular weight of PPO lowered the conductivity. The viscosity of the electrolyte solution increased enormously with an increase in [$LiClO_4$]/[PO unit], and was higher for higher molecular weight of PPO. The increase in viscosity results from solvation of the polar and flexible PPO main chain to $LiClO_4$, which acts as transient crosslinking points between PO units. The equivalent conductance was influenced not only by the viscosity but also by the molecular weight of PPO. At low viscosity ($<10^4$ cP), the equivalent conductance decreased with an increase in the molecular weight of PPO. With an increase in viscosity ($>10^4$ cP), the dependence of the equivalent conductance on the molecular weight of PPO diminished.

KEY WORDS Polymeric Solvent / Poly(propylene oxide) (PPO) / $LiClO_4$ / Ionic Conductivity / Viscosity / Equivalent Conductance /

It is generally recognized that low electrical conductivity of usual polymers at low electric fields is due to ionic impurities, absorbed moisture, and decomposition products in the polymers. If a large amount of carrier ions can be generated and the carriers can have high mobility in polymers, polymeric ion conductors will be obtained. Such conductors will have a wide range of applications[1] in such areas as solid-state batteries,[2] fuel cells, electrochemical displays, and chemical sensors. In order to design a polymeric ion conductor, it is important to investigate the mechanisms of carrier generation and carrier migration in the polymer. However, because of the extremely low conduction current in usual polymers, these mechanisms have not as yet been clarified.

The most popular ionic conductors are electrolyte solutions, in which low molecular weight compounds are used as solvents. However, some kinds of polymers dissolve inorganic salts to form electrolyte solutions.[3-5] Relatively low molecular weight polyethers such as poly(ethylene oxide),[3] poly(propylene oxide) (PPO),[4,5] and poly(tetramethylene oxide)[5] are in the liquid state at room temperature, and dissolve many kinds of inorganic salts up to a high concentration. Electrolyte solutions formed with such polymeric solvents are useful in order to investigate the ion conductive behavior in polymeric materials.

We found[6] that PPO solutions of $LiClO_4$ have ionic conductivity of 10^{-4}—10^{-6} S cm^{-1} at room temperature and that films of these solutions prepared by block copolymerization give a polymeric solid electrolyte. The work described in this paper is concerned with the effect of molecular weight on the ion conductive behavior of $LiClO_4$ in PPO.

EXPERIMENTAL

Materials

Four PPO samples having different molecular weights were used for the present study. PPO 400 (mol. wt. = 420) and PPO 3000 (mol. wt. = 2880) were obtained from Asahi Denka Industry Co. Ltd., and PPO 1000 (mol. wt. = 1160) and PPO 2000 (mol. wt. = 2020) were purchased from Kishida

Kagaku Co. Ltd. Volatile compounds in these PPO samples were allowed to evaporate under reduced pressure at 80°C for 5 h. Anhydrous $LiClO_4$ was purchased from Mitsuwa Kagaku Co. Ltd., and dried under reduced pressure at 150°C for 15 h. Methanol was purified by distillation over calcium chloride and then over magnesium.

$LiClO_4$ is soluble directly in PPO, though the dissolution takes a long time at an elevated temperature (*ca.* 150°C). In this study, each electrolyte solution was prepared as follows. A pre-weighed amount of $LiClO_4$ was dissolved completely in methanol, and then a pre-weighed amount of PPO was added to that solution. The solution was stirred till it became homogeneous, and methanol was evaporated completely from it under reduced pressure at 80°C for 5 h. The electrolyte solution obtained was transparent and viscous. The concentration of $LiClO_4$ in the electrolyte solutions was expressed as the molar ratio of $LiClO_4$ to the repeating unit of PPO ($[LiClO_4]/[PO\ unit]$).

Conductivity Measurement

The conductivity of a given electrolyte solution was measured with a Toa-Electronics CM-20A digital conductometer at 50 Hz. The temperature of the solution was maintained at 25 ± 0.1°C by a thermoregulator. The cell constant was measured, using a standard 0.1 N KCl aqueous solution ($1.286 \times 10^{-2}\ S\ cm^{-1}$).

Viscosity Measurement

The viscosity of a given electrolyte solution of PPO was measured with a Shibaura Systems Vismetron VSA-L viscometer at 25 ± 0.1°C. The viscosity of a given electrolyte solution of methanol was measured with a Ubbelohde-type viscometer at 25 ± 0.1°C. The viscosity (η) was calculated from

$$\eta = \eta_0 (td/t_0 d_0) \qquad (1)$$

where t and t_0 are the flow times of the electrolyte solution and methanol, respectively, d and d_0 are the densities of the electrolyte solution and methanol ($0.789\ g\,cm^{-3}$), respectively, and η_0 is the viscosity of methanol (0.545 cP).

Specific Volume Measurement

The specific volume of each electrolyte solution was measured with a pycnometer at 25 ± 0.1°C.

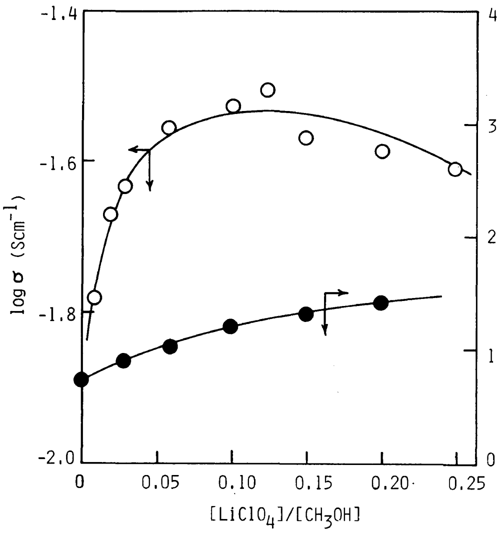

Figure 1. Concentration dependence of conductivity (σ) and viscosity (η) in methanol solution of $LiClO_4$ at 25°C.

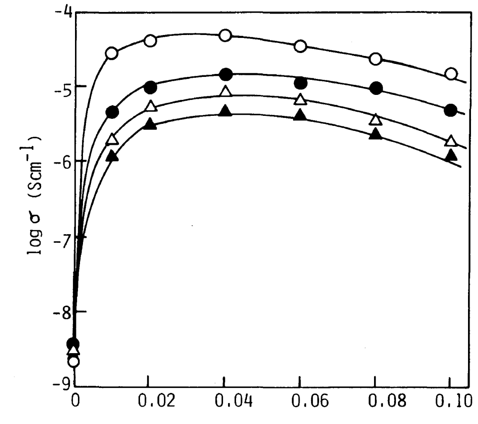

Figure 2. Relation between $[LiClO_4]/[PO\ unit]$ and conductivity (σ) in PPO solution of $LiClO_4$ at 25°C: ○, PPO 400; ●, PPO 1000; △, PPO 2000; ▲, PPO 3000.

RESULTS

As a model of low molecular weight solvent, methanol was used. Figure 1 shows the dependence of conductivity (σ) and viscosity (η) of methanol solutions of $LiClO_4$ at 25°C on $[LiClO_4]/[CH_3OH]$. The concentration region ($[LiClO_4]/[CH_3OH] = 0.01$—$0.20$) was converted to the molarity region

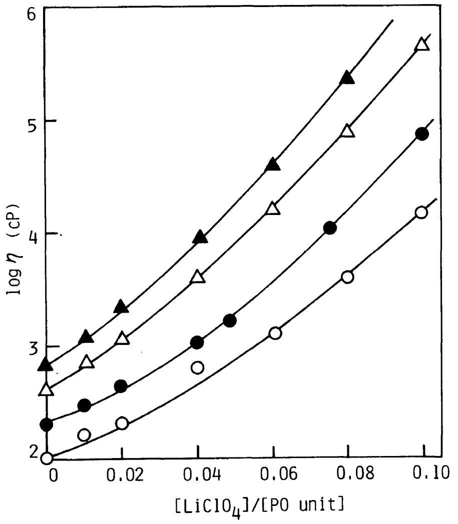

Figure 3. Relation between [$LiClO_4$]/[PO unit] and viscosity (η) in PPO solution of $LiClO_4$ at 25°C: ○, PPO 400; ●, PPO 1000; △, PPO 2000; ▲, PPO 3000.

from 0.24 to 4.2 mol/l. The σ of the electrolyte solution increased with an increase in [$LiClO_4$]/[CH_3OH], reached a maximum at [$LiClO_4$]/[CH_3OH] = 0.1—0.15, and then gradually decreased. The σ in the measured concentration range was of the order of 10^{-2} S cm^{-1}. The η of the electrolyte solution increased gradually with an increase in [$LiClO_4$]/[CH_3OH].

Figure 2 shows the relation between σ and [$LiClO_4$]/[PO unit] in the PPO solution of $LiClO_4$ at 25°C. The concentration region ([$LiClO_4$]/[PO unit] = 0.01—0.1) was converted to the molality region from 0.17 to 1.7 mol l^{-1}. The σ of PPO in the absence of $LiClO_4$ was of the order of 10^{-9} S cm^{-1}. The σ of the electrolyte solution increased with an increase in [$LiClO_4$]/[PO unit], and reached 10^{-4}—10^{-6} S cm^{-1} at [$LiClO_4$]/[PO unit] = 0.01—0.1. When a comparison is made between the σ values at the same [$LiClO_4$]/[PO unit], the electrolyte solution containing a higher molecular weight PPO had a lower σ. For instance, σ of the PPO 400 solution of $LiClO_4$ ([$LiClO_4$]/[PO unit] = 0.04) was 4.85×10^{-5} S cm^{-1}, whereas that of the PPO 3000 solution of $LiClO_4$ ([$LiClO_4$]/[PO unit] = 0.04) was 4.64×10^{-6} S cm^{-1}. The σ had a maximum value at [$LiClO_4$]/[PO unit] = 0.04, and then gradually decreased. The concentration for the maximum in the PPO solution of $LiClO_4$ was considerably lower than that in the methanol solution of $LiClO_4$.

Figure 3 shows the relation between η and [$LiClO_4$]/[PO unit] at 25°C. The dissolution of $LiClO_4$in PPO increased η enormously. Thus, η at [$LiClO_4$]/[PO unit] = 0.1 was 10^4—10^6 cP, while η of PPO in the absence of $LiClO_4$ was of the order of 10^2 cP. This enormous increase in η was not found in the methanol solution of $LiClO_4$. The increase in η with [$LiClO_4$]/[PO unit] became more pronounced as the molecular weight of PPO was increased.

DISCUSSION

Conductivity and Viscosity Behavior

Ion conduction in a solution consisting of a monomeric solvent and a salt is caused by dissociation of the salt and by migration of the generated ionic carriers against the viscosity of the solution. It can be seen from Figure 2 that σ of the PPO solution of $LiClO_4$ is considerably higher than that of PPO in the absence of $LiClO_4$. This indicates that $LiClO_4$ in PPO dissociates to generate carrier ions. The polar and flexible PPO main chain easily solvate $LiClO_4$ and dissociate $LiClO_4$. The increase in σ is due to migration of the generated carriers in PPO, as in usual monomeric solvents. The σ values of PPO solutions of $LiClO_4$ are lower than those of the methanol solution of $LiClO_4$. This difference may be due to a higher viscosity of PPO than that of methanol. The appearance of a maximum σ in both methanol and PPO soluiton of $LiClO_4$ (see Figures 1 and 2) may be explained as a combinated effect of the ion association and the decrease in carrier mobility due to viscosity increase.

There is a large difference in viscosity behavior between the methanol and PPO solutions of $LiClO_4$. The viscosity of electrolyte solution increases mainly as a result of ion-ion interaction and ion-solvent interaction. When methanol dissolves $LiClO_4$, part of methanol molecules interacts with ions. This interaction may reduce the mobility of the methanol molecules which solvate ions. However, in such monomeric solvents as methanol, one solvent molecule has usually one polar group which solvates ions. Therefore, the methanol molecules which do not solvate ions can move around independently of the methanol molecules which solvate ions. Thus, the ion-solvent interaction does not greatly increase η of the electrolyte solution. On the other hand, when PPO is used as the solvent, one PPO molecule has many polar ether oxygen atoms which are linked with each other by covalent bonds. These ether oxygen atoms solvate ions. Thus, the interaction between ions and PO segments seems to reduce the segmental mobility of PPO molecules, and act as transient crosslinking points. The number of such crosslinking points increases with an increase in [LiClO$_4$]/[PO unit]. As a result, an enormous increase in the η may result. The fluidity of the electrolyte solution is brought about by the fact that the interaction between ions and PO segments is not permanent but transient.

The enormous increase in η greatly lowers carrier mobility. Therefore, the salt concentration for the maximum σ of the PPO solution of LiClO$_4$ is considerably lower than that of the methanol solution of LiClO$_4$.

Correlation between Viscosity and Equivalent Conductance

In order to clarify the effect of η on ion conductive behavior, the relation between η and equivalent conductance (μ) was investigated. In this study, μ was defined by

$$\mu = \sigma / ne \tag{2}$$

where n is the number of ions per unit volume, and e is the charge of an ion. n was calculated by

$$n = \frac{2N[\mathrm{LiClO_4}]/[\mathrm{PO\ unit}]}{([\mathrm{LiClO_4}]/[\mathrm{PO\ unit}]M_\mathrm{L} + M_\mathrm{P})V} \tag{3}$$

where N is the Avogadro constant, V is the specific volume of the electrolyte solution, and M_L and M_P are the molecular weights of LiClO$_4$ and PO unit, respectively. If LiClO$_4$ undergoes complete dissociation in the electrolyte solutions, the μ values estimated from eq 2 and 3 agree with the carrier mobilities, and hence give a lower limit of the carrier mobilities.

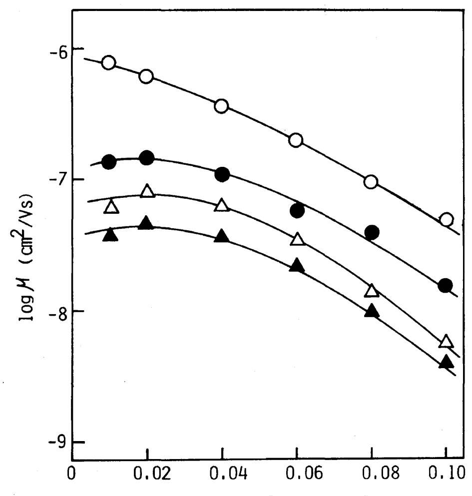

Figure 4. Relation between [LiClO$_4$]/[PO unit] and equivalent conductance (μ) in PPO solution of LiClO$_4$ at 25°C: ○, PPO 400; ●, PPO 1000; △, PPO 2000; ▲, PPO 3000.

Figure 4 shows the relation between μ and [LiClO$_4$]/[PO unit]. With an increase in [LiClO$_4$]/[PO unit], μ is decreased. Lower μ values were obtained for higher molecular weight of PPO. These decreases in μ nearly correspond to the increase in η.

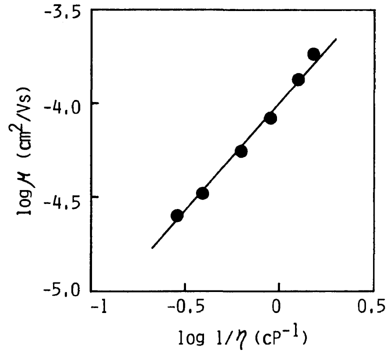

Figure 5. Relation between reciprocal of viscosity ($1/\eta$) and equivalent conductance (μ) in methanol solution of LiClO$_4$ at 25°C.

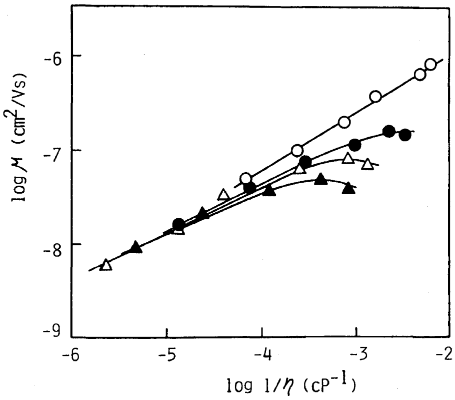

Figure 6. Relation between reciprocal of viscosity ($1/\eta$) and equivalent conductance (μ) in PPO solution of LiClO$_4$ at 25°C: ○, PPO 400; ●, PPO 1000; △, PPO 2000; ▲, PPO 3000.

However, the magnitude of decrease in μ with an increase in [$LiClO_4$]/[PO unit] is similar in all the PPO solutions of $LiClO_4$, although the increase in η became more pronounced as the molecular weight of PPO was increased.

Figure 5 shows the relation between μ and the reciprocal of η in the methanol solution of $LiClO_4$. The μ values were calculated by the same method as for the PPO solution of $LiClO_4$. The relation between $\log 1/\eta$ and $\log \mu$ was linear, and its slope was about 1.0, indicating that μ is proportional to the reciprocal of η, *i.e.*, the empirical Walden's rule[7] is obeyed.

When PPO was used as the solvent, the relation between $\log 1/\eta$ and $\log \mu$ was considerably different from that for the methanol solution, as shown in Figure 6. The observed relations were nearly linear, except in the region of low salt concentration, but their slopes were smaller than 1.0. This difference in slope between the methanol and PPO solutions of $LiClO_4$ indicates that the influence of η on μ is different in these two solutions. The increase in η with the salt concentration does not decrease μ of the PPO solution of $LiClO_4$ as much as it does in the methanol solution of $LiClO_4$.

The slope of the relation between $\log 1/\eta$ and $\log \mu$ decreased with an increase in the molecular weight of PPO. In the low viscosity region ($<10^4$ cP), μ decreased with an increase in the molecular weight of PPO. With the viscosity increase ($>10^4$ cP), the dependence of μ on the molecular weight of PPO diminished. Thus, μ is influenced not only by η but also by the molecular weight of PPO. Further study of this effect is in progress.

CONCLUSIONS

PPO solutions of $LiClO_4$ had ionic conductivity of 10^{-4}—10^{-6} $S\,cm^{-1}$ at room temperature. $LiClO_4$ dissolved in PPO dissociates to generate carrier ions. The generation of the carriers is due to the solvation of the polar and flexible PPO main chain to $LiClO_4$. Dissolution of $LiClO_4$ in PPO enhances enormously the viscosity of the solution, forming transient crosslinking points between PO units. The equivalent conductance is influenced not only by viscosity but also by the molecular weight of PPO.

The electrolyte solutions studied in this work may be utilized as an electrolyte for batteries, because of the advantages of their extremely low vapor pressure and high viscosity. Further, films of these electrolyte solutions prepared by block copolymerization,[6] or crosslinking, or blending will give polymeric solid electrolytes.

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