Ionic Conductive Polymers Based on Polymethylsiloxane Graft-crosslinked with Oligo(ethylene oxide)

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ABSTRACT

Polymethylsiloxane graft-crosslinked with oligo(ethylene oxide) (EO) was synthesized and characterized. The polymer was an elastic solid and stable to hydrolysis. Polymer/salt complexes were formed on mixing with lithium trifluoromethane-sulfonate($LiCF_3SO_3$). The ionic conductivity of the complexes was measured by complex impedance method and the conductivity reached 6×10^{-5} S cm^{-1} at 25°C and 1.5×10^{-4} S cm^{-1} at 40°C. The effect of salt concentration, crosslinking, length of EO units and moisture content on the conductivity were investigated. Glass transition temperature and thermal stability of the polymer and the polymer/salt complexes were determined by differential scanning calorimeter and thermogravimetric analysis measurements.

KEYWORDS: Lithium ion conductors, Methylsiloxane-ethylene oxide graft polymer, Ionic conductivity measurement

INTRODUCTION

Solvent-free polymer electrolytes have generated much interest because of their potential applications in such areas as high energy density batteries [1], solid state electrochromic displays [2], and photo-electrochemical cells [3]. Early investigations were

FIGURE 1. Chemical structure of polymer (I) (polymethylsiloxane graft-cross linked with oligo(ethylene oxide)) *(top)* and block copolymer of phenylsiloxane and ethylene oxide polymer (II) *(bottom)*.

focused on alkali metal ion conduction in poly(ethylene oxide) (PEO) and poly(propylene oxide) (PPO) [4]. Recent work has utilized various polymers such as poly(ethylene imine) [5] and poly(ethylene succinate) [6] as well as macromolecules with pendant methoxyoligo(oxyethylene) chains anchored to polymethacrylate [7], polyphosphazene [8], and polymethylsiloxane [9,10] backbones.

Polysiloxane has long been used as a flexible hydrophobic polymeric material with low glass transition temperature ($T_g \sim -120$°C), high thermal stability and low dielectric constant [11].

The block copolymer of phenylsiloxane and ethylene oxide [11] has been synthesized and the complex with lithium salt showed high ionic conductivity at room temperature [12]. However, the polymers are readily hydrolyzed in air. Thus, in order to improve the hydrolytic and thermal stability of siloxane polymers, we synthesized polymethylsiloxane graft-crosslinked with oligo (ethylene oxide) (1) (Fig. 1). In

this paper, we report the synthesis and properties, as well as ionic conductivity, of the polymer/lithium salt complexes.

EXPERIMENTAL

Synthesis

Graft-crosslinked polymers (I) were synthesized through hydrosilation reaction of polymethylhydrosiloxane with allyl ethylene oxide monomethylether and diallyl ethylene oxide. The general synthesis route is shown in Fig. 2.

The typical synthesis of this copolymer is as following: to a 250 ml three neck flask equipped with condenser, thermometer, stirrer, dropping funnel, dry nitrogen inlet and outlet was charged 100 ml of anhydrous tetrahydrofuran (THF) and 30 g (0.147 mol) of allylmethoxytriethylene oxide (AMOEO, $m = 3$), which were prepared by the reaction of methoxytriethyleneglycol–Na salt with allylchloride. After the charge it was warmed to 50°C and three drops(~ 0.1 ml) of the catalyst (chloroplatinic acid/1,2-dimethoxyethane solution) was added

into the flask under nitrogen atmosphere. Subsequently 12.6 g (0.21 mole) of polyhmethyl-hydrosiloxane (PMHS, purchased from Petrach, $(CH_3)SiO$—$(Si(CH_3)(H)O)_n$—$Si(CH_3)_3)$ were added dropwise. In the course of addition the temperature was kept at 50–55°C. After all the PMHS had been added, the system was stirred for one hour at 50°C to complete the graft-hydrosilation. Then, 8.6 g (0.031 mole) of diallyltetraethylene oxide (DAOEO, $n = 4$) prepared from the reaction of tetraethyleneglycol-disodium salt with allylchloride were added into the flask dropwise. Two more drops of catalyst were added after all of the DAOEO had been added. The reaction mixture was kept at 50–55°C until gelation occured. The gel was poured out into a beaker, washed three times with water and subsequently treated with THF. The resulting polymer was dried in a vacuum oven at 60°C for 20 h.

These reaction steps were monitored by analyzing the IR and NMR spectra. IR spectra of the polymer showed the disappearance of Si–H (2200 cm^{-1}) and C=C (1650 cm^{-1}) bonding and the formation of Si–C–C (1220 cm^{-1}) bonding. NMR peaks for Si–H and C=C were used to confirm the
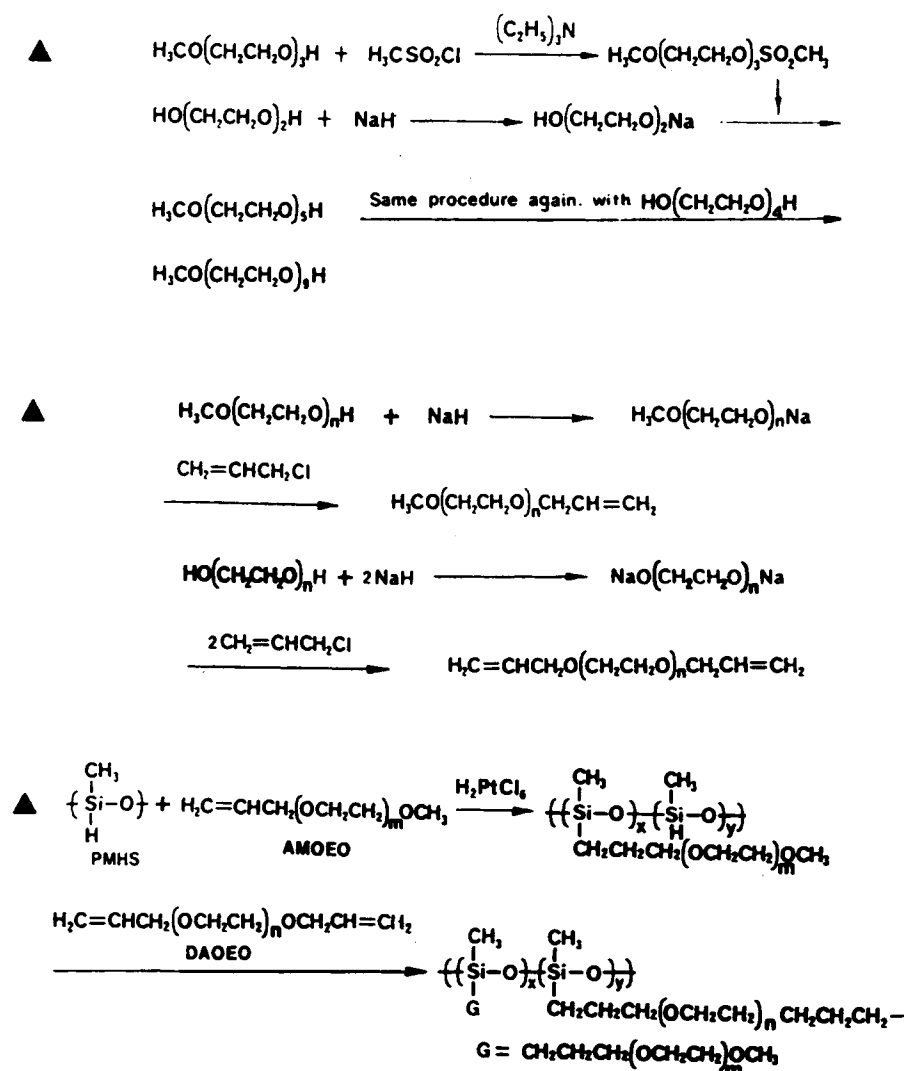
FIGURE 2. Scheme of the synthesis of polymer (I).

completion of grafting. After completion of grafting, the NMR spectra showed that the $C=C$ peaks (δ 5.2 and 5.9) had disappeared and the Si–H peak (δ 4.7) had reduced to 30% of its original. This indicates the completion of the grafting reaction and excludes the possible self-polymerization of the allyl monomer. After grafting was complete, diallyl oligo(ethylene oxide) was added for crosslinking. Since the cross-linked polymer was no longer dissolved in organic solvent, only IR spectra were used to confirm the completion of crosslinking.

Mixing with Salt

The crosslinked polymers are not soluble in solvent but can be swollen. The mixing of polymer with $LiCF_3SO_3$ salt was pursued in the following way: purified polymer with a calculated amount of lithium salt were put in a mortar and ground. Then the mixture was put into a flask. Anhydrous THF was added and the polymer was swollen for four days. The polymer was dried under vacuum at 60–70°C for 24 hr. When all solvent was removed, polymer/salt complex was obtained.

Thermal Analysis

Thermal analysis of the polymers and polymer/salt complexes were performed using a Du Pont 1090 thermal analyzer connected to a DuPont 9120 differential scanning calorimeter (DSC) and a Du Pont 951 Thermogravimetric Analyzer (TGA). The heating rate was 10°C per minute for DSC and 20°C per minute for TGA measurements. All the thermal characterizations were run in a nitrogen atmosphere.

Ionic Conductivity Measurement

The sample of polymer/salt complex must be dried under high vacuum (10^{-3} torr) and at 70°C for at least 24 hr. A dried sample was put into a glove box under a nitrogen atmosphere. A dried polymer/salt complex was transferred into a cell consisting of glass, Teflon® and stainless steel plates and electrodes for the measurement of conductivity. The transfer was also done in the glove box. When the specimen was well installed in the cell, the whole cell was removed from the glove box and put in a temperature-controlled cabinet.

Before the start of measurement, the sample must be heated to 80–90°C, annealed for at least 30 min. Then the screw caps of the cell were tightened and the sample was squeezed to ensure an intimate contact between the sample and the two electrodes. The cell is cooled down to room temperature and the measurement starts. When heating the sample up and cooling it down, the conductivities of the sample at the same temperature were recorded twice (one was on heating, the other one was on cooling). The two values should be the same or very close (relative deviation less than 5%), otherwise the sample must be re-dried. The measurement was usually from room temperature to about 100°C with
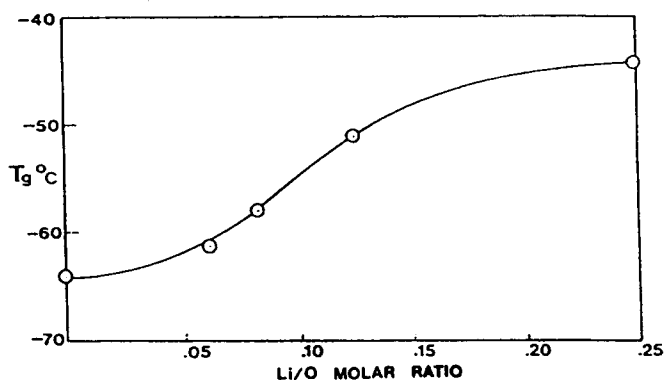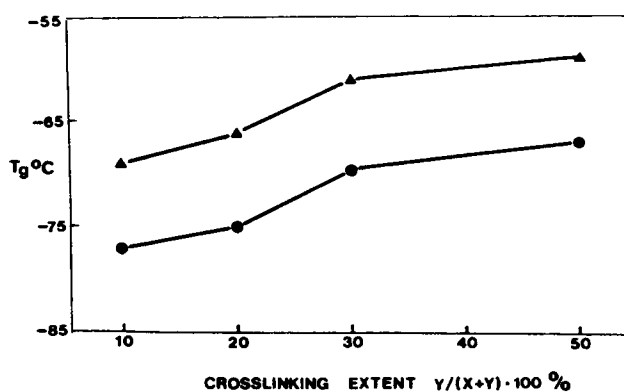
FIGURE 3. Glass transition temperature T_g vs concentration of $LiCF_3SO_3$ for the polymer (I)/salt complexes with $m=3$, $n=4$ and $x:y=9:1$.

an interval of around 15°C. A Hewlett-Packard 4192A impedance analyzer controlled by a PC was used for the measurement.

RESULTS AND DISCUSSION

The graft-crosslinked PMHS-ethylene oxide copolymers are transparent colorless elastic materials which are not soluble in but can swell in ether, THF, chloroform and many other organic solvents.

The motion of lithium ions in polymers in solid state is coupled to the local segmental motion of the polymer chain which assists the migration of ions through the solid. The conductivity is directly proportional to the mobility of the ions [13]. Therefore, the glass transition temperature, T_g, becomes a critically important parameter for ionic conductivity. The range of the T_g of polymer (I) in this study is from $-65°C$ to $-80°C$. Fig. 3 shows that T_g increases with the addition of lithium salt. The glass transition temperature also increases when the extent of cross-linking increases (Fig. 4). T_g was found to increase when the length of the EO units in the graft side chain increased (Fig. 5). Fig. 6 shows that the T_g decreases with the increase of the length of EO units in the crosslinking segment.

FIGURE 4. Glass transition temperature T_g as a function of extent of crosslinking for polymer (I)/$LiCF_3SO_3$ complexes with $m=7$, $n=9$ and $O/Li=12$. (▲, $O/Li=12$; ●, no salt).
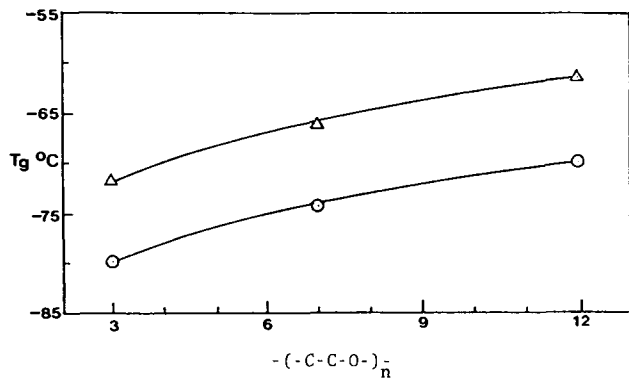
FIGURE 5. Glass transition temperature T_g vs :EO) unit length m in the graft side chain of polymer (I) with $n=9$ and x:y $=9:1$. ($\triangle$, O/Li $=12$; O, no salt).
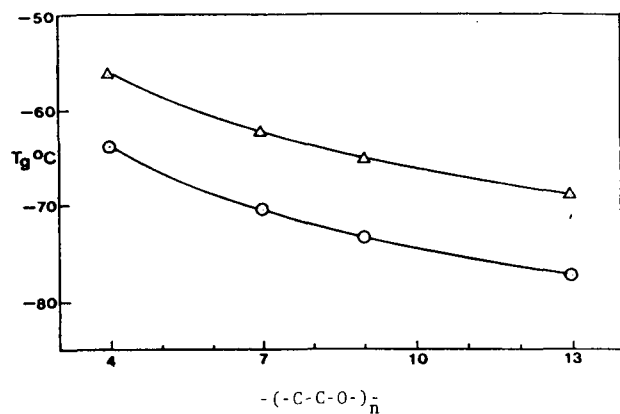

FIGURE 6. Glass transition temperature T_g vs (EO) unit length n in the crosslinking segment of polymer (I) with $m=7$ and x:y $=9:1$. ($\triangle$, O/Li $=12$; O, no salt).

Thermally stable polymers are desirable in order to withstand elevated temperatures in battery applications. Thermal gravimetric analysis (TGA) was used to investigate the thermal stability of the polymers of this study. Fig. 7 shows how the degradation temperature, T_d, increased with the extent of crosslinking of the polymer. Figs 8 and 9 show the
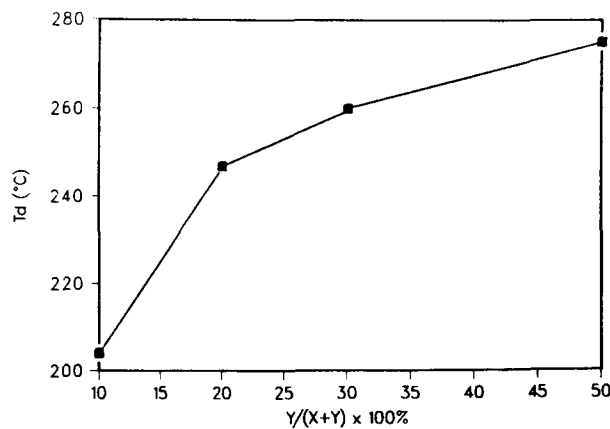
FIGURE 7. Degradation temperature T_d as a function of crosslinking extent for polymer (I) with $m=7$ and $n=9$.
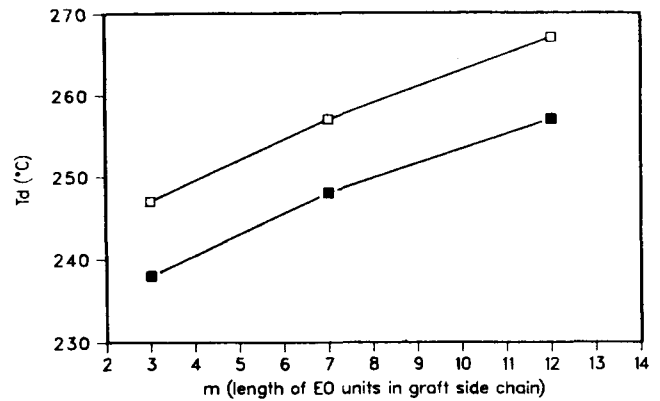
FIGURE 8. Degradation temperature T_d as a function of (EO) unit length m in the graft side chain for polymer (I) with $n=9$ and x:y $=8:2$. ($\blacksquare$, no salt; $\square$, O/Li $=12$).
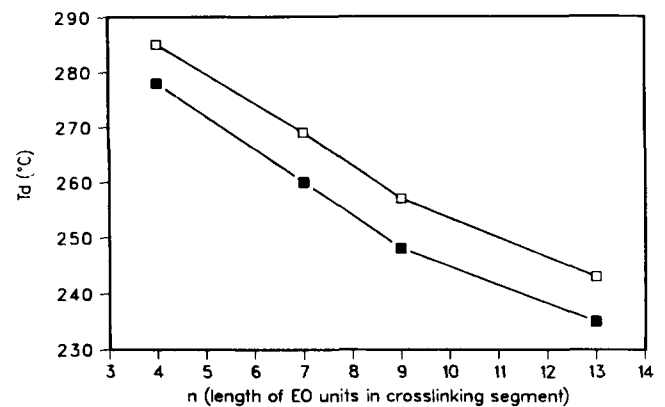
FIGURE 9. Degradation temperature T_d as a function of (EO) unit length n in the crosslinking segment for polymer (I) with $m=7$ and x:y $=8:2$. ($\blacksquare$, no salt; $\square$, O/Li $=12$).

change in T_d as a function of the length of EO units in both allyl and diallyl agents. The T_d increases when the EO units become longer in the allyl agent; on the other hand, T_d decreases with an increase of the length of the EO units in the diallyl agent. This tendency is the same as for T_g. Fig. 10 shows that the T_d increases with increasing amount of lithium salt.
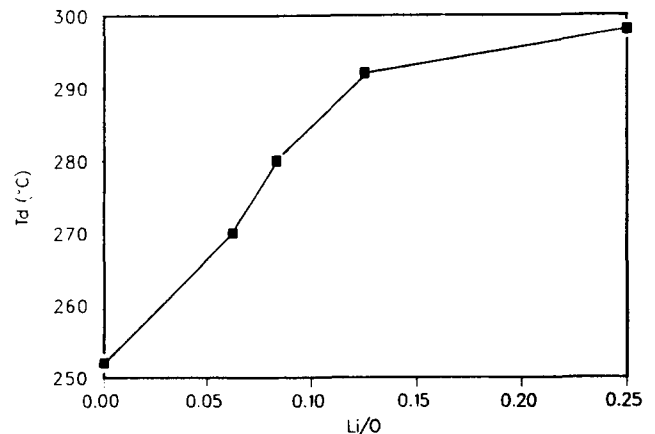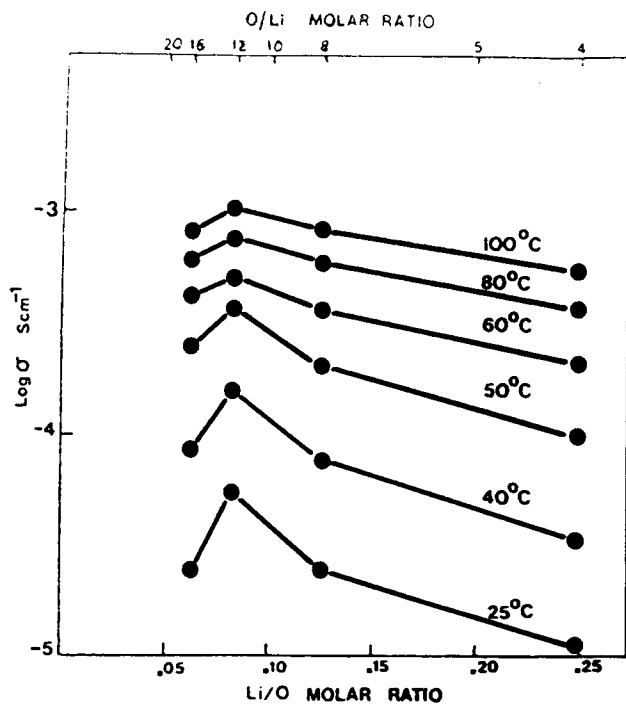

FIGURE 10. Degradation temperature T_d vs concentration of LiCF$_3$SO3 for polymer(I)/salt complexes with $m=3$, $n=4$ and x:y $=7:3$.
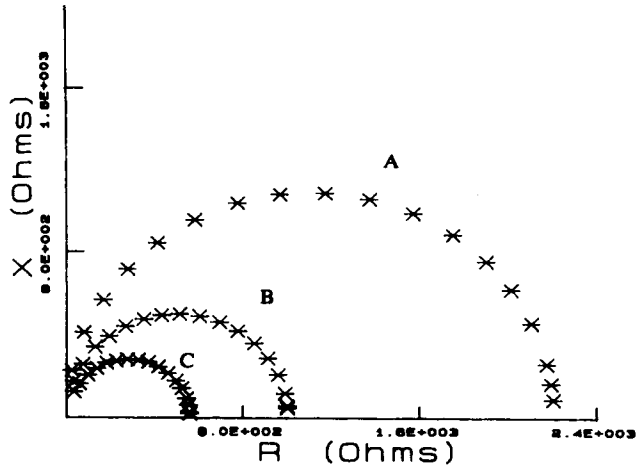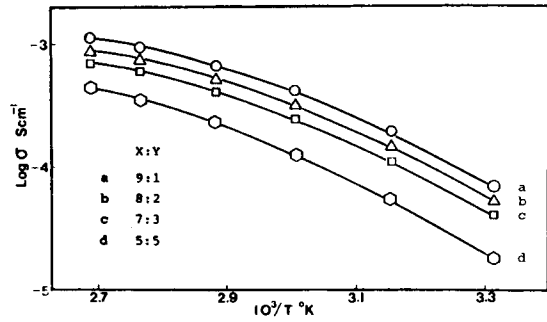
FIGURE 11. Impedance diagrams for the conductivity measurement of polymer(I)/LiCF₃SO₃ complexes.


FIGURE 13. Ionic conductivity as a function of crosslinking extent for polymer(I)/LiCF₃SO₃ complexes with $m=7$, $n=9$ and O/Li = 12.

Since both EO and lithium salts are hygroscopic, the stability of the polymer to hydrolysis becomes an important chemical property for the ionic conductive polymers. It was found that Si–C–C bonded polymer (I) lost only 0.5% of the weight when it was put in 25°C water for 7 days, but Si–O–C bonded polymer (II) lost 25% of the weight under the same conditions.

The most interesting property of the polymer/ salt complex is the ionic conductivity, especially at ambient temperature. Many factors, such as the chemical structure and morphology of the polymer, the nature of the salt and its concentration, the

sample drying and the condition of measurement, affect the ionic conductivity.

Fig. 11 shows complex impedance diagrams of a polymer(I)/LiCF₃SO₃ complex at three different temperatures. In all the cases typical half cycle diagrams were obtained. This indicates that all the polymers in this study have normal resistor–capacitor behavior and the complex impedance method gives reliable bulk conductivity measurement.

Fig. 12 shows the relationship between conductivity and the concentration of lithium salt in the polymer. Conductivity increases with the temperature and is also a function of the lithium salt concentration. Samples with molar ratio O/Li = 12 (EO unit/Li) were found having the highest conductivity at all temperatures. The increasing conductivity in the low salt concentration region might be attributed to the increase in the number of charge carriers. On the other hand, at higher salt concentrations the conductivity becomes nearly constant and then decreases sharply. This behaviour is due to the decrease in charge carrier mobility [13]. There is, therefore, an optimum concentration which yields the highest conductivity values.

Fig. 13 shows the ionic conductivity as a function of crosslinking extent for the graft-crosslinked

FIGURE 12. Ionic conductivity as a function of salt concentration for polymer(I)/LiCF₃SO₃ complexes with $m=7$, $n=9$ and x:y = 9:1.
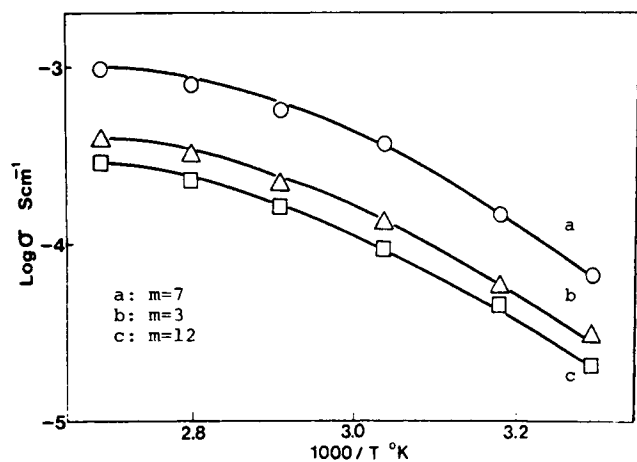
FIGURE 14. Conductivity vs (EO) unit length in graft side chain m for polymer(I)/LiCF₃SO₃ complexes with $n=9$, x:y = 9:1 and O/Li = 12.
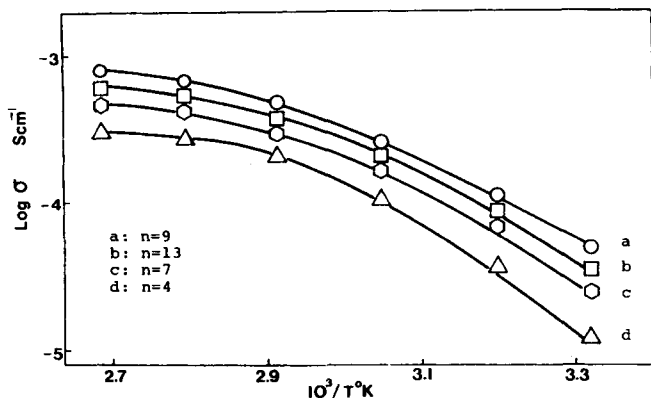
FIGURE 15. Conductivity vs (EO) unit length in crosslinking segment n for polymer(I)/LiCF$_3$SO$_3$ complexes with $m = 7$, x:y = 9:1 and O/Li = 12.
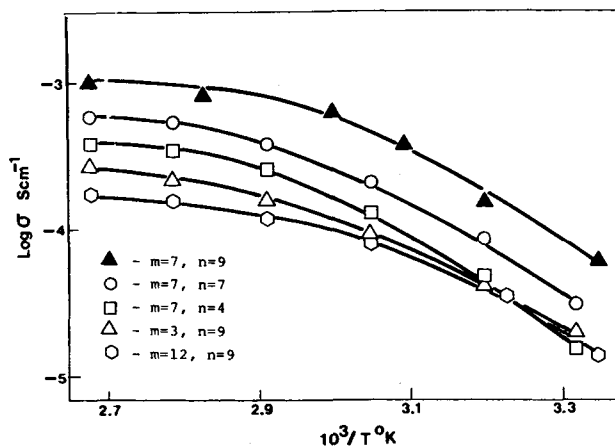
PMHS–EO polymer/LiCF$_3$SO$_3$ complexes with O/Li = 12. The ionic conductivity decreases with increasing extent of crosslinking. At the lower level of crosslinking, the change in conductivity is moderate. At high levels of crosslinking, a significant decrease in conductivity is observed.

Figs 14 and 15 show the conductivity changes as a function of EO unit length in both the graft and the crosslinking segment. A polymer complex with $m = 7$ in the graft side chain and $n = 9$ in the crosslinking segment with the least crosslinking extent (x:y = 9:1) and O/Li = 12 reaches the highest conductivity at room temperature, 6×10^{-5} S cm^{-1} at 25°C and 1.5×10^{-4} S cm^{-1} at 40°C. Those samples having the EO units in the crosslinking network longer than the EO units in the graft side chain (i.e., $n > m$) showed the highest conductivities. Both m and n should be less than 10 because of the potential of crystallization when EO units are longer.

The ionic conductivity varies as the moisture content changes, as shown in Fig. 16. For the highly dried sample with $m = 7$, $n = 9$, x:y = 9:1 and O/Li = 12, the conductivity at 25°C was 6×10^{-5} S cm^{-1}. When the same sample is exposed to 100% humidity for 4 hr, the conductivity increases to $2 \times$
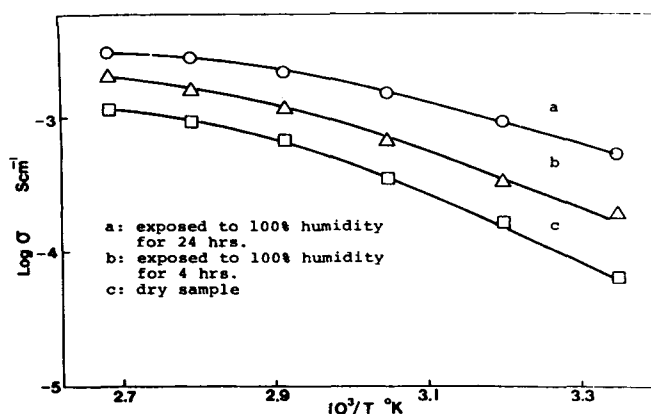
FIGURE 16. Conductivity as a function of moisture content for polymer(I)/salt complexes with $m = 7$, $n = 9$, x:y = 9:1 and O/Li = 12.

FIGURE 17. Conductivity (log σ) vs temperature (10^3/T °K) for polymer(I)/LiCF$_3$SO$_3$ complexes with different values of m and n (all with O/Li = 12 and x:y = 9:1).

10^{-4} S cm^{-1}, approximately a factor of three increase. When the sample is exposed to 100% humidity for 24 hrs, its conductivity increases further and reaches a maximum approximately eight times that of the dry sample. Water plays a role not only as a plasticizer but also in solvating the lithium ions, thereby increasing the salt dissociation. Both factors improve the mobility of the lithium ions, resulting in enhanced conductivity.

Fig. 17 shows the temperature dependence of ionic conductivity for the polymer(I)/LiCF$_3$SO$_3$ complexes. The plots of log σ vs 1000/T are not straight lines. This indicates that the ions migrate through the amorphous phase of the polymer.

CONCLUSIONS

Copolymers based on polymethylsiloxane graft-crosslinked with oligo(ethylene oxide) were synthesized and characterized. The materials have low glass transition temperatures, good thermal stability and strong resistance to hydrolysis.

High ionic conductivities were observed for these polymers complexed with LiCF$_3$SO$_3$. The highest value reached 6×10^{-5} S cm^{-1} at 25°C and 1.5×10^{-4} S cm^{-1} at 40°C.

The ionic conductivity was a function of the concentration of lithium salt in the complex. The highest conductivity is reached with a molar ratio EO unit/Li = 12.

The ionic conductivity of the polymer/salt complexes depends on the length of EO units both in the grafting side chain and in the crosslinking segment. The highest value of conductivity was observed with the EO uinits $m = 7$ in the graft side chain and the EO units $m = 7$ in the graft side chain and the EO units $n = 9$ in the crosslinking segment.

ACKNOWLEDGEMENT

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