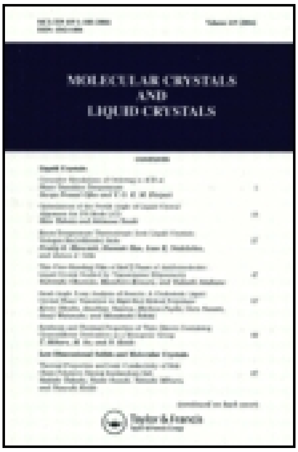

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Ionic Conductive Polymers Based on Crosslinked Elastic Siloxane-Ethylene Oxide Copolymers

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Ionic Conductive Polymers Based on Crosslinked Elastic Siloxane-Ethylene Oxide Copolymers

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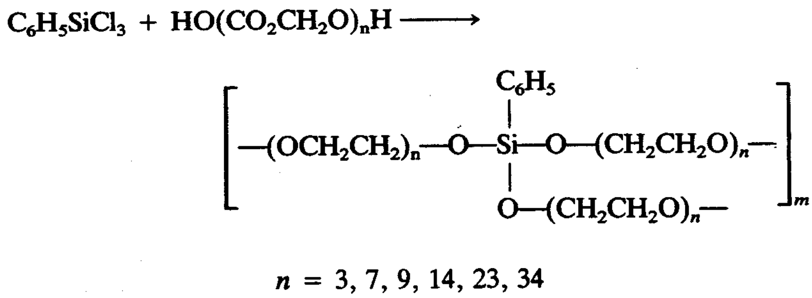
INTRODUCTION

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 display,[2] photoelectrochemical cells.[3] Early investigations were 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(ethylenimine)[5] and poly(ethylene succinate)[6] as well as macromolecules with pendant methoxy-oligo(oxyethylene) chains anchored to polymethacrylate,[7] polyphosphazene,[8] and methylsiloxane[9] backbones.

Siloxane-ethylene oxide copolymers are one of the most attractive polyelectrolytes because of their flexible main chain and low glass transition temperature.[10]

In this paper, we report on our recent work concering flexible elastic polymers which were synthesized by crosslinking copolymerization of phenyltrichlorosilane and poly(ethylene glycol) (Scheme 1). These polymers are excellent ion conductors when complexed with CF_3SO_3Li. Ionic conductivities of the order of 10^{-5} S/cm at room temperature were obtained.



SCHEME 1 The Synthesis of Crosslinked Elastic Siloxane-Ethylene Oxide Copolymers

EXPERIMENTAL

The crosslinked polymers were prepared by condensation polymerization from phenyltrichlorosilane purchased from Petrarch and poly(ethylene glycol) purchased from Aldrich. The product was identified by IR and NMR spectroscopy. An appropriate portion of the tetrahydrofuran (THF) solution of the polymer was mixed with the THF solution of CF_3SO_3Li. After the solvent was removed under vacuum at 70°C a rubber-like elastic material was obtained. The polymer/salt complex was completely dried at 5×10^{-2} torr at 60°C for 24 hrs. The complex was placed in a sealed cell for the conductivity measurements. Sample transfer was performed in a nitrogen atmosphere dry box. Ionic conductivity measurements were taken with a Hewlett-Packard 4192A Impedance Analyzer. Thermal analysis was performed using a DuPont 910 DSC and 951 TGA with a DuPont 1090 Analyzer.

RESULTS & DISCUSSION

Typical DSC thermograms for the uncomplexed polymer and complexed polymer are shown in Figures 1 and 2. A single T_g between −63°C and −40°C was observed for the uncomplexed polymer and polymer/salt complexes. As the lithium salt content increases, T_g increases sharply for low concentrations of lithium salt and then moderately with the increase of lithium salt content at higher concentra-

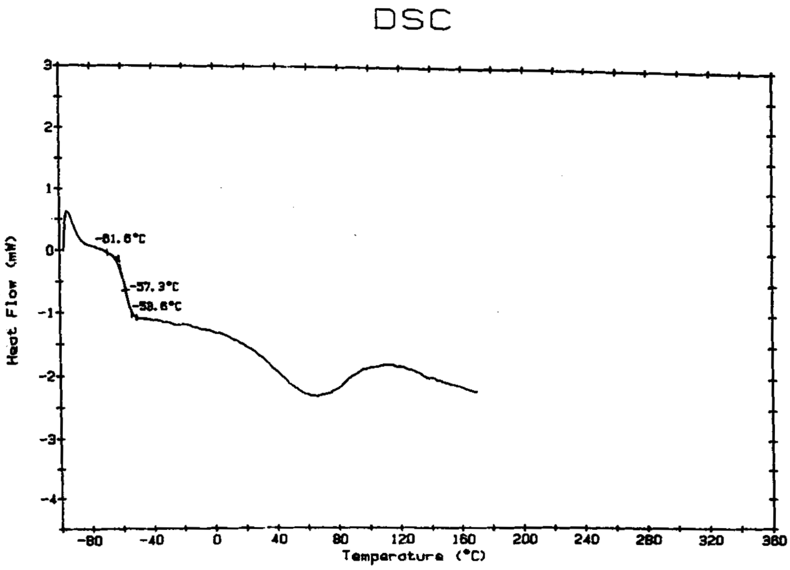


FIGURE 1 DSC thermogram of poly(phenylsiloxane-ethylene oxide) with the number of EO units $n = 7$.

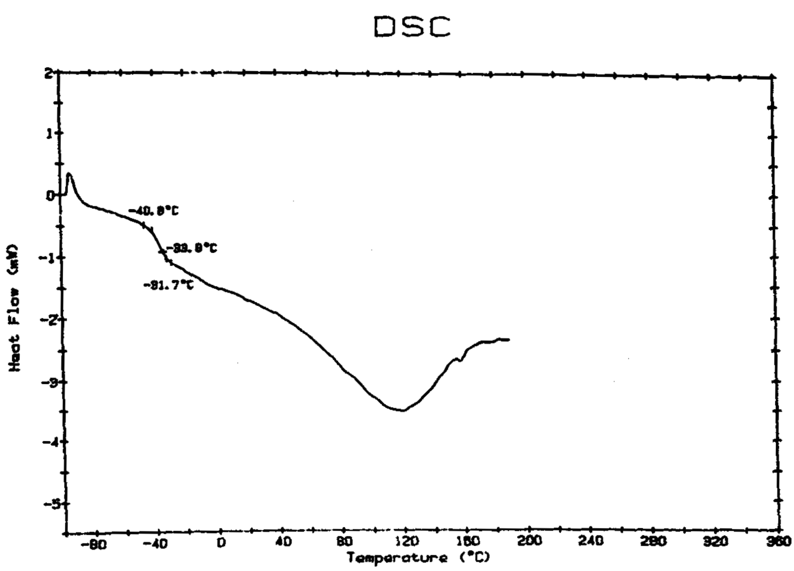


FIGURE 2 DSC thermogram of poly(phenylsiloxane-ethylene oxide)/CF_3SO_3Li with the number of EO units $n = 7$ and O/Li = 4.

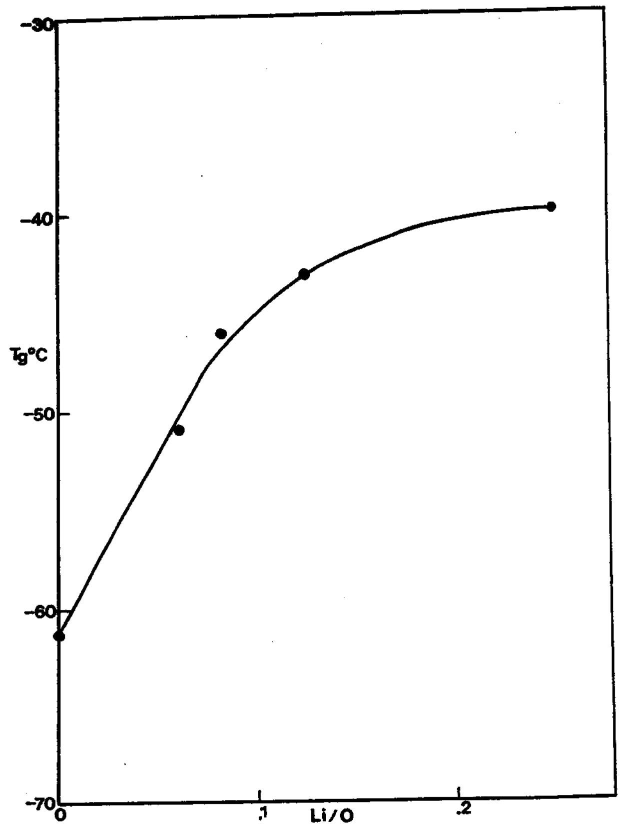


FIGURE 3 Glass transition temperature vs. molar ratios for complexes of poly(phenylsiloxane-ethylene oxide)/CF_3SO_3Li with $n = 7$.

tion (Figure 3). There are no sharp T_m peaks for either the uncomplexed polymer or the polymer/salt complexes indicative of an amorphous nature of the crosslinked network. A broad endothermic peak at around 60°C was observed for the uncomplexed polymer. Upon the complexation with lithium salt, the peak was shifted to higher temperature around 120°C. The TGA thermogram (Figures 4 and 5) show that the thermal stability of polymer increases after complexing with lithium salt.

Table I shows the ionic conductivities of polymer/salt complexes measured by A. C. complex impedance method. The highest conductivity of the complexes was 1.5×10^{-5} S/cm at 25°C and 2.7 ×

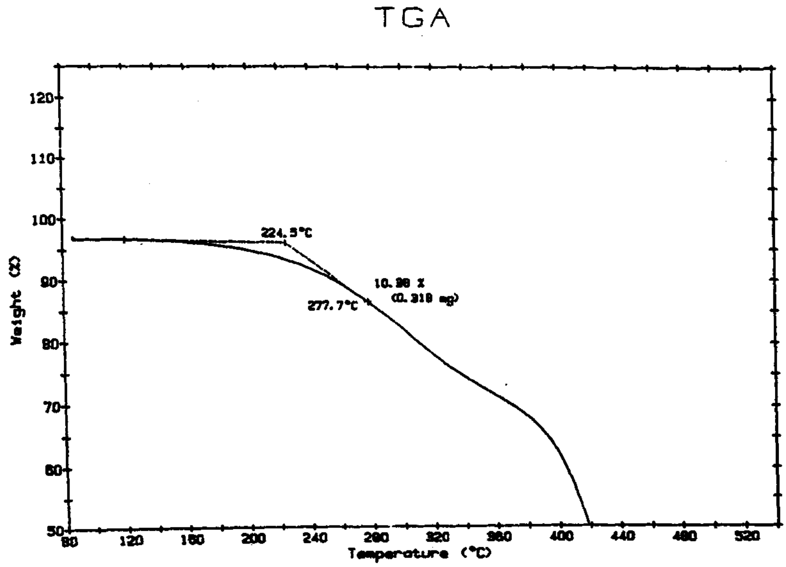


FIGURE 4 TGA thermogram of poly(phenylsiloxane-ethylene oxide) with the number of EO units $n = 7$.

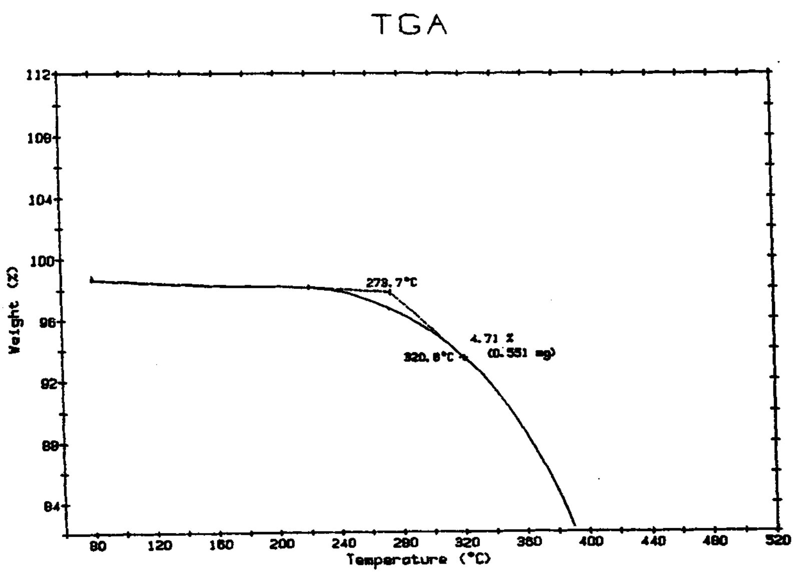


FIGURE 5 TGA thermogram of poly(phenylsiloxane-ethylene oxide)/CF_3SO_3Li with $n = 7$ and O/Li = 8.

TABLE I

Relationship among ionic conductivity,[a] O/Li ratio and number of EO unit

	EO unit n					
O/Li ratio	3	7	9	14	23	34
8:1	—	3.1	—	—	—	—
12:1	6.9	15.0	4.2	3.1	1.4	1.2
16:1	—	11.2	—	—	—	—

[a]Ionic conductivity (10^{-6} S/cm) at 25°C.

10^{-4} S/cm at 63°C for the complex having seven ethylene oxide units and O/Li = 12 (Figures 6, 7, and 8). The conductivity decreases as the number of the EO unit in the copolymer increases. When the number of EO unit is low (n = 3, 7, 9 and 14) the temperature dependence of the ionic conductivity follows Vogel-Tamman-Fulcher (VTF) behavior. For polymers with a high number of EO (n = 23 and 34) the temperature dependence shows a straight line when plotted with Arrhenius coordinates. This may be due to the crystalline structure of the ethylene oxide moiety of the polymer. Both VTF and Arrhenius straight line behavior have a change in slope at around

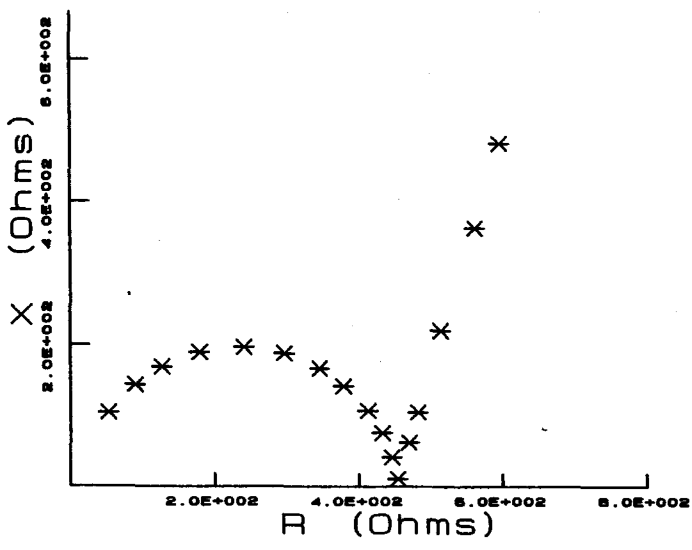


FIGURE 6 Complex impedance diagram for a sample of poly(phenylsiloxane-ethylene oxide)/CF_3SO_3Li.

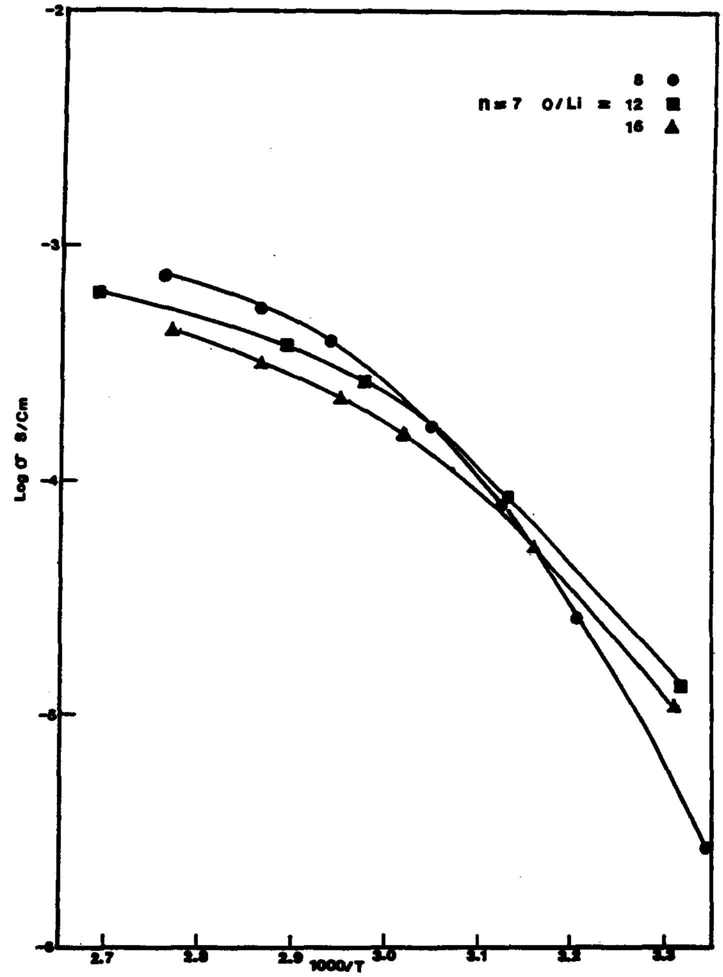


FIGURE 7 Ionic conductivity vs. temperature for poly/(phenylsiloxane-ethylene oxide)/CF_3Li with $n = 7$ and different O/Li ratios.

60–70°C. This may be due to the change of the coordination number between lithium and oxygen.[11]

CONCLUSIONS

Rubber-like elastic materials of poly(phenylsiloxane-ethylene oxide) crosslinked copolymers were synthesized and complexes with CF_3SO_3Li

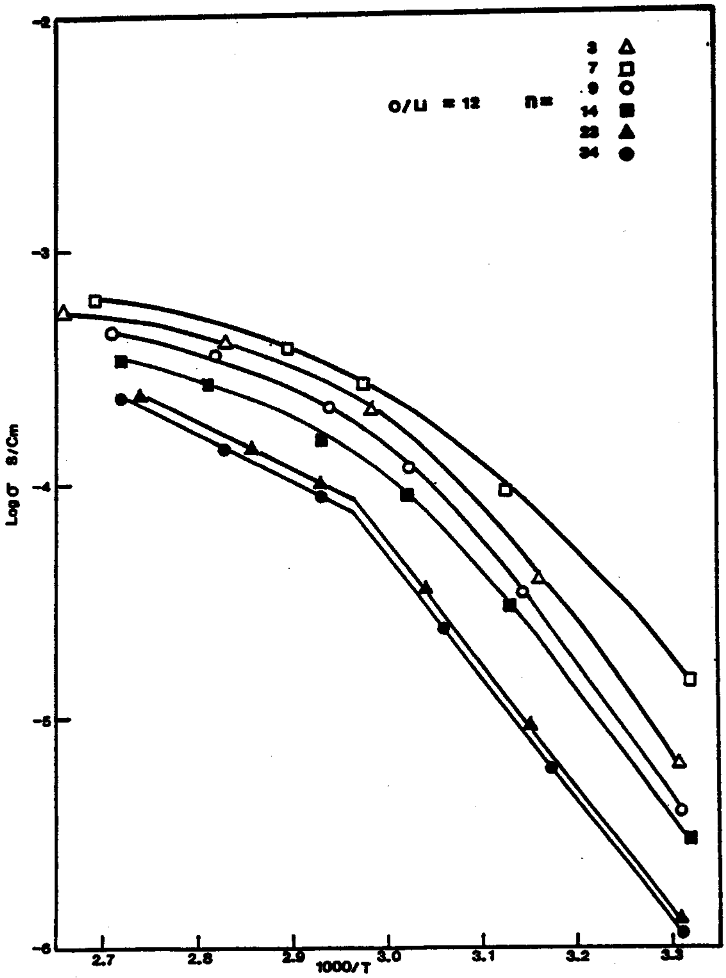


FIGURE 8 Ionic conductivity vs. temperature for poly(phenylsiloxane-ethylene oxide)/CF_3SO_3Li with O/LI = 12 and different EO unit lengths.

were made. The highest ionic conductivity was observed for the polymer/salt complex with the number of EO unit $n = 7$ and O/Li = 12. The room temperature conductivity is considerably higher than that of PEO-alkali metal salt complexes.[12]

Both Arrhenius (n = 23 and 34) and VTF (n = 3, 7, 9 and 14) type behavior for the temperature dependence of the conductivity were observed.

These systems were found to be thermally stable in dry condition up to at least 225°C.

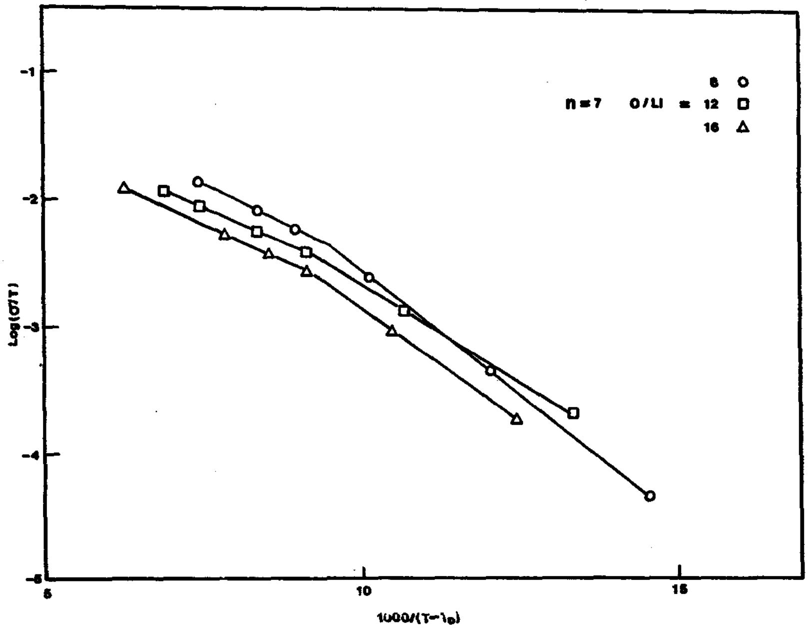


FIGURE 9 Log($\sigma\sqrt{T}$) vs. ($T - T_0$) for poly(phenylsiloxane-ethylene oxide)/CF_3SO_3Li with the number of EO units $n = 7$ and different O/Li ratios.

Acknowledgment

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