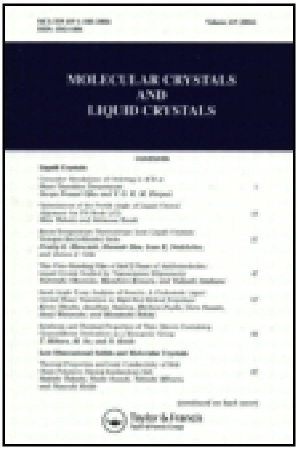

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Fluorenyllithium Salt Containing Polymers as Single-Ion Conductors

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Fluorenyllithium Salt Containing Polymers as Single-Ion Conductors

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Fluorenyl group substituted polysiloxane and poly(ethylene oxide) (PEO), respectively, have been synthesized. Their lithium salt conductivity behavior is discussed in relation to the solvent separated ion pair, ionic association with polymer chain, as well as the morphology of the media. As long as the metal ions are well separated from their counterions, as in the case of separated fluorenyl lithium ion pair by formation of Li^+-THF complex, high dielectric constant medium such as PEO may not be necessary to achieve higher ionic conductivities. As an example, a relatively high single-ion conductivity, $\sim 5 \times 10^{-6}$ s cm^{-1} at 25°C, is observed in fluorenyl-lithium salt containing polysiloxane.

INTRODUCTION

In order to optimize alkali ionic conductivities of poly(ethylene oxide) (PEO) based polymer electrolytes, considerable efforts have been expended in searching for alkali salts with lower lattice energy or lower dissociation energy to separate the ion pairs. Various salts with either inorganic anions such as I, BF_4, CF_3SO_3, ClO_4, SCN, AsF_6,[1] or organic anion such as acrylate, phenolate, naphtholate, tetracyanoquinodimethanide (TCNQ) and chloranilide,[1-3] have been extensively investigated. We have studied a number of sterically hindered phenolates for single-ion conducting polymers.[4-6] In this paper, we wish to report the initial results of fluorenyl-lithium salt containing polymers as a new group of single-ion conductors.

9-Fluorenyl and substituted 9-fluorenyl alkali metal salts have been used as model compounds to study the contact and solvent-separated ion pairs of carbanions in solution.[7] It is well recognized that the lithium ions can be solvent-separated from fluorenyl carbanions by ethereal solvents like tetrahydrofuran (THF), dimethoxyethylene, diethylether,[8] or by amino group containing solvents such as quinuclidine[9] and ethylenediamine.[10] The lithium ions can form stable complexes with those solvents and therefore can be dissociated from the fluorenyl carbanions. Results from proton NMR studies[8] indicated that the lithium cation, with the coordinating solvent molecules, is located directly above the plane of the aromatic carbanion, possibly in the π-cloud. The crystal structure examinations[11] displayed, in the case of the solvent being THF, that each lithium ion is surrounded tetrahedrally by four THF molecules and no contacts smaller than the van der Waals distances are found between lithium ions and carbon centers of the fluorenyl moieties.

Thus, we synthesized the fluorenyl group substituted polysiloxane and fluorenyl group terminated polyethylene oxide, and studied the conductivity behaviors of their lithium salts.

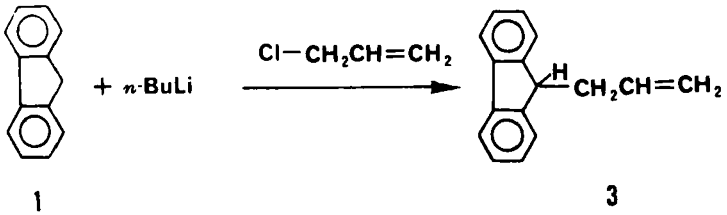
EXPERIMENTAL

Materials and Instruments

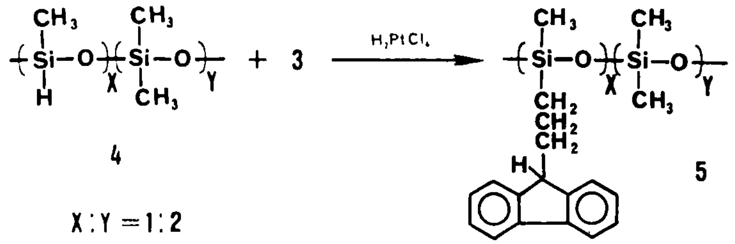
Polyethylene glycol (M.W. = 1000) was obtained from Polyscience, Inc.; the siloxane copolymer (M.W. = 2000) was provided by Petrach Silicones, Inc.; and fluorene and allyl chloride were purchased from Aldrich Chemical Company. Proton NMR and IR were used to identify the product in each step. The transition temperatures were determined by a DuPont 2100 Thermal Analyst equipped with 910 DSC and the AC conductivities were measured by a Hewlett Packard 4192A Impedance Analyzer.

Preparation of fluorenyl substituted polysiloxane

The fluorenyl substituted polysiloxane was synthesized by the following procedures:



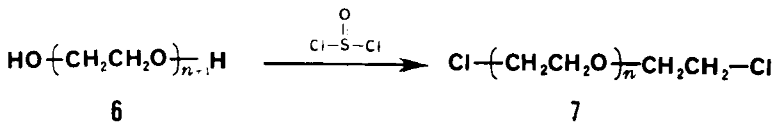
After 0.1 mole (16.6 g) fluorene was dissolved into 100 ml dried toluene in a 500 ml 3-neck flask which was equipped with a condenser and flushed with nitrogen, 40 ml n-BuLi/hexane (2.5 M) solution was injected into the fluorene solution with stirring. The color of the solution was turned to red and some particles appeared probably due to the precipitation of fluorene upon adding non-solvent hexane. The solution became cloudy and orange color when warmed up to refluxing point. After refluxed for 30 minutes, the solution was cooled to room temperature. Allyl chloride 9.1 g (0.12 mole) in 100 ml toluene was dropwise added into the above solution, the solution gradually became light red color and clear. The solution was refluxed overnight and the solution was filtered to remove LiCl salt. The filtrate was concentrated to remove solvent and 38% product (7.8 g) was obtained after distillation at 90°C/0.01 mmHg. IR and NMR spectra were measured and identified for the purified compound 3.



Siloxane copolymer, 3 g in 10 ml dried toluene, was bubbled with nitrogen and 0.1 ml of H_2PtCl_6 fresh catalyst[12] was injected into the solution. After stirring for a few minutes, 9-allyl fluorene 10 g was added, followed by heating in an oil bath to 70°C overnight. IR spectroscopy showed that the peak at 2150 wavenumber corresponding to Si-H had completely disappeared. The viscous polymer solution was then concentrated, washed with water, and the unreacted 9-allyl fluorene was removed under reduced pressure. About 12 g of product was obtained, which was confirmed by IR and NMR spectra.

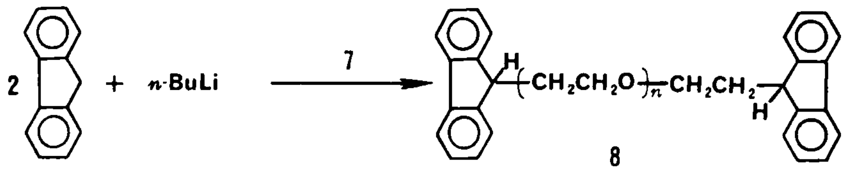
Preparation of fluorenyl terminated poly(ethylene oxide)

The fluorenyl terminated poly(ethylene oxide) was prepared by the following method:



$$HO\!-\!(CH_2CH_2O)_{n+1}\!-\!H \xrightarrow{Cl-\overset{O}{\overset{\|}{S}}-Cl} Cl\!-\!(CH_2CH_2O)_n\!-\!CH_2CH_2\!-\!Cl$$

The wax-like polyethylene glycol (50 g, 0.05 mole) was dissolved into 200 ml THF in a 500 ml 3-neck flask. Thionyl chloride 60 g (0.5 mole) was dropwise added into the solution, followed by refluxing overnight. The IR spectrum indicated that no more –OH groups remained in the system. The solution was evaporated on a rotatory evaporator to remove solvent and excess thionyl chloride. The crude product thus obtained was red in color. The crude product was dissolved into dried THF, activated carbon was added, and the solution was filtered. Upon evaporating the filtrate, a yellow viscous product was obtained. After drying in a vacuum oven at 60°C for 2 hours, 62.9 g of the product 7 was obtained. On cooling, the product became crystallized. IR and NMR were used to confirm the structure.

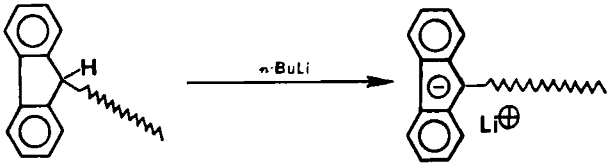


The reaction of fluorene with chloro-terminated PEO is basically the same as that of fluorene with allyl chloride which was described above. Fluorene 16.6 g (0.1 mole) and 40 ml n-BuLi/hexane (2.5 M) were used to prepared the lithium salt. The salt was then reacted with compound 7. The crude product obtained was acidified in aqueous solution with 1N HCl solution. The acidified solution was filtered, the yellow solid powder generated on acidification was found to be mostly excess fluorene.

A viscous orange liquid was obtained after concentrating the filtrate and IR and NMR spectra showed that fluorenyl groups were attached to PEO at the ends.

Preparation of fluorenyllithium salts

Typical lithium salt of polymers 5 and 8 were prepared by the following methods:



Sample 1: One gram (2.5×10^{-3} mole fluorenyl unit) of the fluorenyl substituted siloxane copolymer 5 was dissolved into 10 ml of toluene, bubbled with nitrogen for 10 minutes, and subsequently injected 1 ml 2.5 M n-BuLi/hexane (about 2.5×10^{-3} mole Li ion). The solution was stirred for 20 minutes at 50°C, and then evaporated, a yellowish product was obtained. The product was dried at 60°C in a vacuum oven overnight before conductivity measurements were performed.

Sample 2: The procedures were the same as above, except that instead of toluene, THF was used. As soon as the n-BuLi solution was injected, the polymer solution turned dark brown color. After evaporation, the gummy material remained was dried and used for conductivity measurements. The THF complex formation was determined by proton NMR spectrum.

Sample 3: The procedures were the same as in the preparation of sample 1. Instead of siloxane copolymer, the fluorenyl terminated polyethylene oxide was used to react with n-BuLi in toluene. The ratio of fluorenyl:Li was kept at 1:1.

RESULTS AND DISCUSSION

The glass transition temperature Tg of fluorenyllithium salt substituted polysiloxane was − 26°C as determined by DSC. The sample 1 prepared from toluene had a conductivity too low to be measured, while the one from THF (sample 2) had high conductivity (Figure 1). The conductivities are observed to be 3.3×10^{-6} s cm^{-1} at 22°C, 1.5×10^{-5} s cm^{-1} at 38°C, and 1.1×10^{-4} s cm^{-1} at 70°C, respectively.

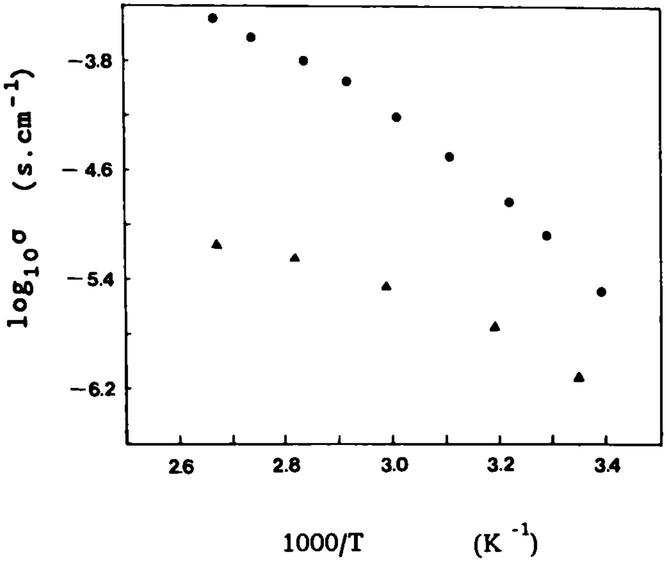


FIGURE 1 Conductivity as a function of temperature for fluorenyl-lithium substituted polysiloxane (●) and poly(ethylene oxide) (▲).

The dark color of this material indicated that the Li ions and the fluorenyl carbanions are well separated due to the solvation of the Li ion by THF molecules.

$$\mathrm{Li^+Fl^-} + \mathrm{4THF} \longrightarrow \mathrm{Li^+\ 4THF} \,\Big\|\, \mathrm{Fl^-}$$

It is well known fact that in the alkali salts of ketyl, fluorenyl, phenol, and other carbanions, red shifts in the absorption spectra were observed on increasing the radius of the cation.[7,13] These shifts can be rationalized by assuming that an enlargement of the cation size causes a greater destabilization of the ground state than of the excited state. A redistribution of charge occurs on excitation, and the cation, while close to the carbon of highest charge density in the ground state, is not allowed to readjust itself on account of the Frank-Condon rule. The transition energy, therefore, become smaller as the cation increases in size. Based on the same principle, increasing the distance between cation and carbanion by solvation is similar to the effect of increasing the size of cation; it will also result in a decreased frequency.

The strong coordination bonding of THF to Li ion makes the complex very stable; we cannot simply regard THF as a plasticizer in this case. Therefore, when the Li-THF complexes migrate in the polymer, they probably behave similar to Li-crown ether complexes. A relatively higher conductivity can thus be reached.

The temperature dependence of the conductivity as shown in Figure 2 follows the Vogel-Tammann-Fulcher (VTF) relationship which describes transport in an

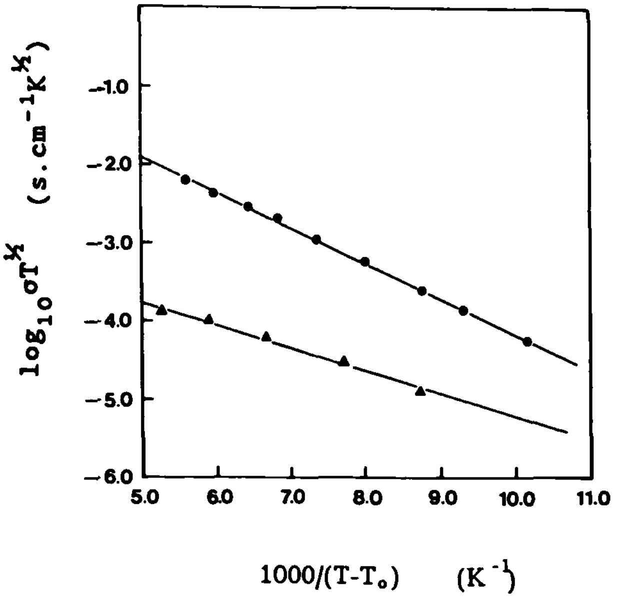


FIGURE 2 VTF plots of the conductivity of fluorenyl-lithium substituted polysiloxane (●) and poly(ethylene oxide) (▲).

amorphous matrix.[14] According to VTF equation, the temperature dependence of the conductivity is expressed as:

$$\sigma = \frac{A}{T^{1/2}} \exp\left[-E_a/R(T - T_o)\right]$$

where the constant A and the apparent activation energy E_a can be calculated from the conductivity vs. temperature data when the ideal glass transition temperature T_o is set to be $T_g - 50$ K. For fluorenyl-lithium-THF substituted polysiloxane, the values $A = 2.41$ s cm^{-1} K$^{1/2}$ and $E_a = 2.09$ Kcal/mole were obtained. The activation energy is low since all the measurements were conducted above the glass transition temperature with the polymer-salt complex in a fully amorphous state. It appears that in the fluorenyllithium substituted polysiloxane system, the absence of PEO segments enhances the ion movement possibly due to the ion transport not being directly coupled to the polymer chain motion as it is in PEO based electrolytes. Therefore, the dissociation of the alkali salts is the dominant factor in the enhanced conductivity in this polymer system.

With the Tg around −39°C, 13 degrees lower than the substituted polysiloxane, fluorenyllithium terminated poly(ethylene oxide) sample 3 showed lower activation energy ($A = 4.6 \times 10^{-3}$, $E_a = 1.30$ Kcal/mole) but the conductivity is about one order magnitude lower compared to that of fluorenyllithium substituted polysiloxane. This result is very similar to those of Li salts in the fully amorphous PEO systems[15–17] in which limited conductivities were recorded even with lower activation energy. The lower activation energy is due to the homogeneous amorphous nature of the polymer medium, while the lower conductivity can be ascribed to the strong ionic association between the cations and the ethylene oxide segments. Smid[18] studied, in detail, the complexation of polyethylene glycol dimethyl ethers $CH_3O(CH_2CH_2O)nCH_3$ with fluorenyl-alkali metal salts in solution. It was found that the cation solvation power for Li^+ ion increases with the number of oxygen atoms in the ethylene glycols, up to 3 ethylene oxide units; this may indicate that a maximum of four oxygen atoms coordinate with one lithium ion. Their ability to complex with alkali metals ions depends on the number of available coordination sites. Temperature studies[19] indicated that the effectiveness of the ethylene glycols is due to a smaller loss in entropy on complexation compared to a similar complexation of the cation by monodentate ligands such as THF. Based on the same explanation, although the lithium cations are freed from fluorenyl carbanions due to solvation with the ethylene oxide segments in the polymer, the complexation by the ethylene oxide will also limit their mobility and, hence, the conductivity. Therefore, although a highly amorphous state can be achieved with polymer electrolytes based on ethylene oxide, there appears to be fundamental upper limits to the conductivity which can be achieved.

CONCLUSIONS

By studying the conductivity behaviors of fluorenyllithium salt substituted polysiloxane prepared from toluene and THF, we have demonstrated that the separation of the cation from its counterion is the key element for achieving a high conductivity in single-ion conductors. The ion transport is only indirectly dependent on polymer chain motion, since there is an absence of ionic association with the polymer chain in this system. While fluorenyllithium terminated polyethylene oxide indicated that although effective separation of the ion pairs and a fully amorphous state can be achieved, the strong cation-polymer chain interaction inhibits the mobility of the cations. Therefore, in addition to controlling the morphology of polymer electrolytes, new salts with facile dissociation of cation and anion as well as novel polymers with less association of cation to polymer should be synthesized and investigated in order to bring the conductivities beyond the limited values in the PEO based systems.

Acknowledgments

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