Macromolecules **1986,** *19,* 606–611

Table I
Fluorescence Lifetime of Exciplex[a]

	decay component, ns			
	IV		II	
fitting range, %	τ_1	τ_2	τ_1	τ_2
0–70	3	114	3	36
0–90	3	117	8	65
15–100	5	116	20	96

[a] τ_1 is the minor component, <5% for IV and <20% for II. [II] = 2×10^{-5} M or [IV] = 1.5×10^{-5} M in 2-methyltetrahydrofuran (MTHF) at room temperature. Excitation: 345 nm. Monitor: ~440 nm.

state is either undetectably fast or unimportant. Also, these results support the presence of only one energy level for the excimer. If there are more than two excimers having different energy levels and different lifetimes, the shape of the excimer emission would change as a function of time after excitation.

Unlike excimer, the exciplex in a polymer shows a definite relaxation process, as shown in Figure 3. It is reasonable that relaxation should be slower in the polymer than in the monomer model. At the present time, however, we cannot decide whether the wavelength shift reveals gradual relaxation of an exciplex species or the presence of multiple exciplex species, each having a different energy level. Under these circumstances the conventional method of lifetime measurement results in a nonexponential decay curve. Within the framework of a two-component analysis, when the fast-rise component is neglected, the apparent lifetime components τ_1, τ_2 fluctuate depending on the range of channels analyzed (Table I). Although we do not understand the physical meaning of τ_1 and τ_2, these values are constant for IV but not for II. In particular, τ_2 of II becomes longer, approaching the value for IV upon shifting the analyzing channels toward the tail of the decay curve. When τ_2 of IV corresponds to the lifetime of the fully relaxed exciplex, the present results are very consistent. The exciplex lifetime is longer after relaxation, as expected.

The time-dependent shift of the fluorescence is a strong warning concerning fluorescence lifetime analysis in a polymer based on measurements at a fixed wavelength. If the fluorescence shift is indeed attributable to a gradual relaxation process, the lifetime analysis must be based on the integrated intensity of the corrected time-resolved spectra. This practice is extremely laborious and no such attempt in a polymer system has been reported to date.

Registry No. I (copolymer), 65289-73-8; I (SRU), 65289-38-5; II, 80683-28-9; III, 73535-83-8; IV, 80628-91-7.

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Preparation and Characterization of Polymeric Solid Electrolytes from Poly(alkylene sulfides) and Silver Salts

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ABSTRACT: Polymeric solid electrolytes have been prepared by complex formation between silver salts and various poly(alkylene sulfides). The polymer–salt complexes of poly(pentamethylene sulfide) (P5S) and $AgNO_3$ have total ionic conductivities comparable to poly(ethylene oxide). Infrared spectroscopy indicates ion pairing between Ag^+ and NO_3^- ions. The transference number for Ag^+ in P5S·$AgNO_3$, ca. 0.9, is much higher than that of most other polymeric solid electrolytes.

Introduction

Most of the recent research on solvent-free polymer electrolytes has concentrated on poly(ethylene oxide) (PEO, I) or poly(propylene oxide) (PPO II) complexes with alkali metal salts.[1-3] These complexes have been investigated extensively in attempts to understand the factors that govern ion transport, and they also are under evaluation as electrolytes in high-energy-density batteries.[4,5]

PEO, $(CH_2CH_2O)_n$
I

PPO, $(CH_2CH(CH_3)O)_n$
II

Polymer–salt complex formation appears to be enhanced by a high concentration of polar groups in the polymer, high polymer chain flexibility, which permits the polymer to more easily solvate the cation, low lattice energy of the salt, and low cohesive energy density of the polymer.[6] To test these ideas and to delineate the chemical variables that influence the formation and function of polymer electro-

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lytes, we have studied other polymer hosts such as poly(ethylene succinate),[7] poly(phosphazenes),[8] and plasticized polyelectrolytes.[9,10] The present research extends these studies to poly(alkylene sulfides).

Experimental Section

The poly(alkylene sulfides) were prepared by reaction of the disodium salt of the appropriate dimercaptan with a dibromoalkane. The disodium salt was prepared under a nitrogen atmosphere by the slow addition of sodium with ethanol or butanol to form a 0.2 M solution of the alkoxide. A half equivalent of the dimercaptan was then added all at once, and the reaction was stirred 15–20 min and then cooled to below 25 °C. An equivalent of dibromoalkane was slowly added over a period of 4–5 h. For example, poly(pentamethylene sulfide) was prepared by the interaction of the disodium salt of 1,5-pentanedithiol with 1,5-dibromopentane.[11] After allowing the components to react for 24 h, the solution was brought to reflux, cooled, and filtered in air. The solid contained predominantly high molecular weight polymers as well as NaBr and some low molecular weight polymers. The filtrate contained primarily low-MW polymers and cyclic thiaethers. The solid was suspended in water and stirred vigorously to dissolve the salt, filtered, and allowed to dry. After drying, the polymer was washed repeatedly with 500 mL of cyclohexane to remove residual low-MW and cyclic polymers. Dried 30-g portions were treated three times with 100 mL of water by mixing in a blender for 5 min and filtered after each mixing. All the fractions were blended in 100 mL of CH_3OH five times and then air-dried in a Buchner funnel for 24 h. Except for poly(ethylene sulfide), which is not soluble in $CHCl_3$, the polymers were recrystallized from $CHCl_3$ solution with the addition of CH_3OH. All of the poly(alkylene sulfides) were dried under medium vacuum (10^{-2} torr). The molecular weights determined by isopiestic methods were: PES, 7900; P3S, 6400; P4S, 8600; P5S, 10 000; P6S, 7000. No attempt was made to cap the end groups.

Silver nitrate (Gallard-Schlensinger, 99.999%) was dried under high vacuum (10^{-5} torr) and used without further purification. Silver trifluoromethanesulfonate was prepared by the reaction of Ag_2O and CF_3SO_3H, recrystallized from CH_3OH, and dried under high vacuum.

For the preparation of the polymer–salt complexes, reagent-grade methanol (Malinckrodt) was dried over I_2-activated magnesium for 1 day followed by distillation under a N_2 atmosphere. Dried materials were handled in a N_2 or Ar-filled drybox or by using standard Schlenk techniques. The complexes were prepared by combining polymer and salt in a desired ratio followed by the addition of anhydrous CH_3OH. The vessels were wrapped in aluminum foil to exclude light. The polymers, which are not soluble in CH_3OH, extract the salt from solution in the 3-h period, over which time the mixtures were stirred. The solvent was removed by evaporation under rough vacuum followed by high vacuum. Infrared spectra were obtained on 0.4-mm films with either a Perkin-Elmer 399 grating spectrometer or a Nicolet 7199 FT-IR. The absence of bands ca. 1650 and 3400 cm^{-1} in the infrared spectra indicates less than 100 ppm water present. The complexes were generally tan chunky powders at high salt concentrations (<2:1 S/Ag) and tan gums at lower salt concentrations (>2:1 S/Ag). Darkening occurred after prolonged exposure to light and was accelerated by heat and exposure to air. A solvent has not been found for any of the polymer–salt complexes.

Films for infrared spectroscopy were prepared by pressing by hand a small piece of sample between Teflon plates and metal blocks heated to about 80 °C. The resulting films, which showed no ill effects due to the brief heating, were sandwiched between KBr plates, and infrared spectra were quickly taken with the FT-IR. All of these manipulations were performed in a N_2-filled glovebag. Upon long standing there is visible evidence for reaction between the KBr plates and the electrolyte, but there was no apparent reaction in the time it took to obtain infrared spectra.

Differential scanning calorimetry measurements were performed on samples sealed in Perkin-Elmer aluminum sample pans with a Perkin-Elmer DSC-2 instrument equipped with a liquid nitrogen cooling system. A dry helium atmosphere was maintained over the sample chamber, and transition temperatures were obtained by extrapolation of observed transition temperatures vs. (heating rate)$^{1/2}$ to zero heating rate.

Table I
Nomenclature of Poly(alkylene sulfides)

formula of repeat unit	name	abbrev
$-((CH_2)_2S)-$	poly(ethylene sulfide)	PES
$-((CH_2)_3S)-$	poly(trimethylene sulfide)	P3S
$-((CH_2)_4S)-$	poly(tetramethylene sulfide)	P4S
$-((CH_2)_5S)-$	poly(pentamethylene sulfide)	P5S
$-((CH_2)_6S)-$	poly(hexamethylene sulfide)	P6S

X-ray diffraction measurements were performed with a Rigaku automated diffractometer and radiation analyzer with Ni-filtered Cu Kα radiation. A symmetrical reflection geometry was used on pressed pellets protected from the atmosphere by Scotch transparent tape.

Conductivity data were obtained with a Hewlett-Packard 4800A vector impedance meter. Complex impedance analysis was applied to the data obtained over the frequency range 5–500 000 Hz. Samples were pressed under an inert atmosphere in a $^1/_2$-in. diameter die to a thickness of 0.5–1.5 mm and loaded into a specially designed two-electrode Kel-F cell that permitted exclusion of the atmosphere.[12] Either ion blocking, Pt, or cation reversible, Ag, electrodes were used. Variable-temperature measurements were performed in a thermostated forced-air heating chamber that was controlled by a Bruker B-ST 100/700 temperature-control unit. Temperatures were measured to within ±0.1 °C by an iron–constantan thermocouple. All connecting leads were coaxial cable. Direct current polarization experiments were performed as described elsewhere.[13]

Results and Discussion

It has been shown that poly(ethylene sulfide), (PES, III) will extract $AgNO_3$ from aqueous solution[14] with the formation of a polymer–salt complex. Analogy with the

$$\underset{\text{III}}{\text{PES, }-(CH_2CH_2S)-}$$

poly(ethylene oxide) (PEO) electrolytes indicated that this PES–salt complex might be a good electrolyte. The investigation was extended to include the other polysulfides listed in Table I, and preliminary experiments showed the complexes formed between poly(pentamethylene sulfide)(P5S) and $AgNO_3$ had the best ionic conductivities. We chose to concentrate most of our investigations on materials derived from P5S. It is interesting to note that P5S has a relatively low concentration of polar groups when compared to PES, yet it forms a more highly conductive electrolyte than PES. This does not follow the expectation that a high density of polar groups is desirable in a polymer host for polymer electrolytes. Poly(pentamethylene sulfide) does have a low melting point, 65 °C, and low glass transition temperature, −25 °C, which are indicative of a flexible polymer backbone, and these factors may compensate for the lower sulfide concentration in P5S than PES.

Poly(pentamethylene sulfide)–Silver Nitrate Complexes. At room temperature the total ionic conductivities for the poly(pentamethylene sulfide) electrolytes are too low to measure on our equipment, which indicates an ionic conductivity of less than $10^{-9}\ \Omega^{-1}\ cm^{-1}$. Conductivities at elevated temperatures for some $P5S{\cdot}AgNO_3$ electrolytes are listed in Table II. The conductivities are comparable to those of other polymer–salt complexes listed in Table III. As shown in Figure 1 and Table II, the ac conductivities of $P5S{\cdot}AgNO_3$ complexes are not strongly dependent on the concentration of salt.

Examples of typical complex impedance plots obtained for $P5S{\cdot}AgNO_3$ complexes along with the corresponding equivalent circuits are shown in Figures 2 and 3. The complex plane plot shown for a $P5S{\cdot}AgNO_3$ 2:1 complex

Table II
Conductivities of P5S • $AgNO_3$ Electrolytes at 45 and 63 °C

	σ, Ω^{-1} cm^{-1}	
S/Ag[a]	45 °C	63 °C
1:1	1×10^{-8}	1×10^{-6}
2:1	6×10^{-8}	2×10^{-6}
3:1	8×10^{-8}	3×10^{-6}
4:1	9×10^{-8}	7.5×10^{-6}
6:1	7×10^{-8}	6×10^{-6}

[a] Polymer repeat unit to cation ratio.

Table III
Conductivities of Other Polymer Electrolytes

polymer electrolyte	R/M[a]	temp, °C	σ, Ω^{-1} cm^{-1}	ref
PESc·$LiBF_4$	1:1	65	2×10^{-7}	6
PESc·$LiBF_4$	2:1	65	5×10^{-7}	6
PESc·$LiBF_4$	3:1	65	2×10^{-6}	6
PESc·$LiBF_4$	4:1	65	3×10^{-7}	6
PEO·$NaBF_4$	4.5:1	60	3×10^{-5}	12
PEO·$LiSO_3CF_3$	4.5:1	65	5×10^{-7}	19
PEO·LiSCN	4:1	69	2×10^{-6}	11

[a] Polymer repeat unit to cation ratio.

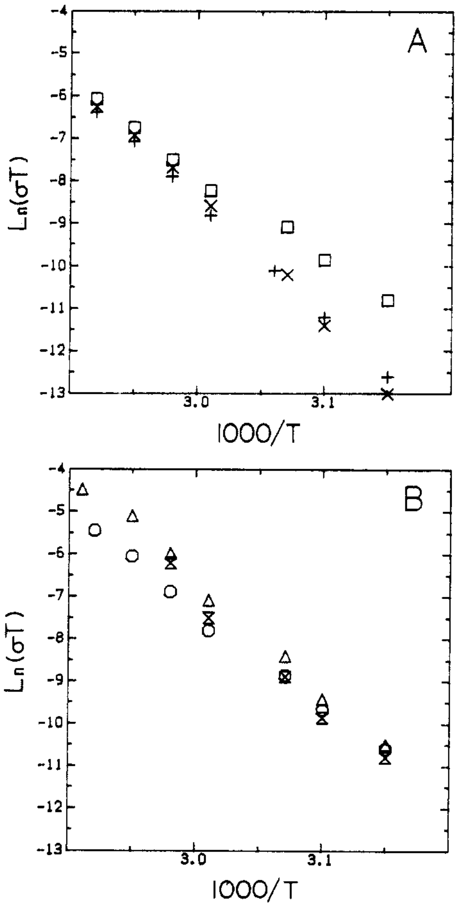

Figure 1. Variable-temperature conductivity plots for P5S·$AgNO_3$ electrolytes: (A) plus symbol for 1:1 ratio, cross for 1.4:1 ratio, and box for 2:1 ratio; (B) circle for 4:1 ratio, triangle for 6:1 ratio, and double triangle for 8:1 ratio.

at 70 °C sandwiched between ion-blocking Pt electrodes (Figure 2) contains a low-frequency spur that is indicative of double-layer charging at the ion-blocking electrode–electrolyte interface. The complex plane plot for the 2:1 sample at 96 °C between silver metal electrodes contains part of an arc but no spur or second arc. This indicates that silver metal electrodes are highly reversible to silver ion.[15-17]

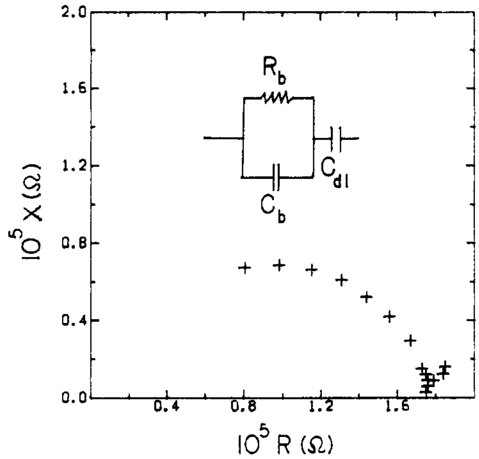

Figure 2. Complex impedance plot and equivalent circuit for a 2:1 P5S·$AgNO_3$ electrolyte at 70 °C with Pt electrodes. The point at the far right was determined at 8 Hz, and the minimum is at 1000 Hz.

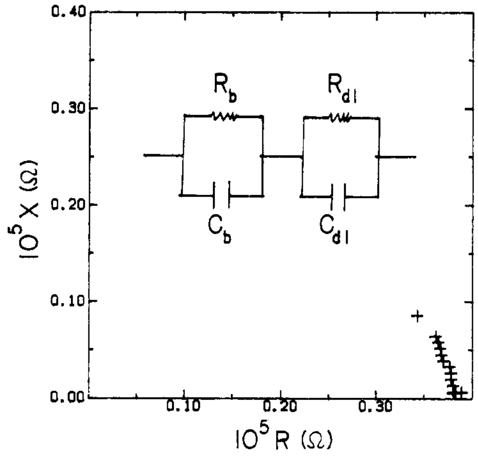

Figure 3. Complex impedance plot and equivalent circuit for a 2:1 P5S·$AgNO_3$ 2:1 electrolyte at 96 °C with Ag electrodes. The minimum ranges from 50 Hz to 110 kHz.

Table IV
Assignments for Important Poly(pentamethylene sulfide) Bands

sample	frequency, cm^{-1}	assignt[a]
P5S	1040	$\rho(CH_2)$
P5S·$AgNO_3$	1027	$\nu(NO)$
	1048	$\nu(NO)$ and $\rho(CH_2)$

[a] ν = stretch; ρ = rock.

The curved plot of ln (σT) vs. $1000/T$ for various P5S·$AgNO_3$ complexes (Figure 1) indicates liquidlike migration of the ions. This curvature is typical of conductivity data for amorphous polymer–salt complexes.[18,19]

Contact-ion pairing reduces the ionic conductivity of poly(ethylene oxide)–salt complexes.[18] Therefore, an infrared spectroscopic study of the nitrate ion bands in the poly(alkyl sulfide) electrolytes was undertaken detect whether ion pairing occurs in these materials. The 1050-cm^{-1} (ν_1) band is formally only Raman active but is seen in the solid-state infrared spectra of some nitrate salts[20,21] and also in the $AgNO_3$ complex of 1,3,5-trithiane.[22] The appearance of ν_1 may be attributed to distortion of the ion from D_{3h} symmetry, and a shift or split of this band is an indicator for contact-ion pairing.[23] Table IV lists the positions of the important bands, and Figure 4 illustrates the splitting of the 1050-cm^{-1} band in the P5S·$AgNO_3$ complex, which indicates contact-ion pairing between Ag^+ and NO_3^-. Apparently contact-ion pairing is more prev-

Figure 4. N–O stretch region for P5S (A) and P5S·$AgNO_3$ 1.8:1 (B).

alent in P5S·$AgNO_3$ electrolytes than it is in PEO electrolytes.

Uncomplexed P5S exhibits diffraction peaks suggestive of a semicrystalline polymer, and $AgNO_3$ displays peaks characteristic of a crystalline solid. Over the concentration range of 1.5:1 S/Ag to 10:1 S/Ag diffraction peaks were no longer apparent. This implies the formation of amorphous complexes. At salt concentrations higher than 1.4:1 S/Ag, very weak diffraction peaks appear at d = 2.91 and 2.05 Å that are not assignable to P5S or $AgNO_3$, indicating the formation of a semicrystalline complex in this concentration range. When the sulfur to silver ratio is 1:1, diffraction peaks are present at d = 4.04, 2.97, 2.70, 2.50, 2.28, 2.07, 1.70, and 1.63 Å, all of which are assignable to crystalline $AgNO_3$. These data indicate the limit for polymer–salt complex formation occurs somewhat below 1.5 P5S repeat units per formula unit of $AgNO_3$, and over most of the concentration range the polymer–salt complex is amorphous. The amorphous nature of these complexes may be beneficial to ion transport.[24]

A comparison between the structures of polyethers and polythiaethers (polysulfides) provided useful insights into the conformational preferences of the polymer backbone. Structural information is available for PEO, PES, and P5S but is not available for poly(pentamethylene oxide). Poly(ethylene oxide) forms a 7/2 helix consisting of a trans (anti) conformation around the C–O bonds and gauche conformation around the C–C bonds, resulting in the conformational sequence T_2G.[25,26] Upon complexation of Li, Na, or K cations, it has been proposed that the helix tightens and the conformation of the backbone becomes $T_2GT_2\bar{G}$.[3,6] Poly(ethylene sulfide), the sulfur analogue of PEO, is a glide-type polymer and consists of gauche conformations around C–S bonds and trans (anti) conformations around C–C bonds, resulting in the overall conformational sequence, $G_2T\bar{G}_2T$.[27] Conformations in the PES backbone upon complexation are unknown. The conformational differences in the two isoelectronic polymers have been attributed to differences in the bond lengths of C–O (1.43 Å) and C–S (1.82 Å), differences in the van der Waals radii of oxygen (1.52 Å) and sulfur (1.85 Å), and the presence of unfavorable 1,4-nonbonding interactions between methylene hydrogens in the polyethers around the C–O bonds. These differences have been noted both in the structures of the two polymers[28] and also in the corresponding macrocycles, 18-crown-6 and hexathia-18-crown-6.[29] The preference for the gauche conformation decreases in the order C–S ≫ C–C > C–O of the macrocycles.[29] This preference is so strong that in 18-crown-6, where all the oxygens are endo, 10 of the 12 C–O bonds are trans but in hexathia-18-crown-6, where there are only two endo sulfurs, there are no trans C–S bonds. This has a large influence on the coordination chemistry of the macrocycles. The conformational differences that occur in the macrocycles also occur in PEO and PES; there are no trans arrangements around C–S bonds in PES and only trans arrays around the C–O bonds in PEO. Space-filling models (CPK) of PES confirm that trans C–S bonds are sterically not allowed. Space-filling models also show that PEO can form a helix with the conformation $T_2GT_2\bar{G}$, where the oxygens are oriented toward the interior of the helix.[19] The oxygens in this case may be referred to as "endo". It is possible to construct a CPK model of PES for which the sulfur atoms are all "endo" and the overall conformation is G_3, but this model indicates severe strain owing to the presence of gauche conformations around C–C bonds. It appears that the sulfur atoms cannot be entirely endo in PES and, therefore, cannot wrap around cations in the same way as proposed for PEO. The presence of contact-ion pairing in the PES polymer–salt complexes may be attributed to the inaccessibility of a helical polymer conformation which encases the cation and thereby shields it from the anion.

Poly(pentamethylene sulfide) is a zigzag polymer, which implies trans conformations around all of the bonds. It is believed that this conformation would not be favored as a single chain, because of the unfavorability of trans C–S bonds, but is stabilized by chain packing.[11] Space-filling models indicate that conformations for P5S are unfavorable that would allow coordination of a cation by two or more adjacent sulfur atoms on the same chain. The observation that the limit of solvation of $AgNO_3$ by P5S occurs for a sulfur to silver ratio around 1:1 lends support to the postulate that the polymer does not form chelates. As in the example of PES, it appears P5S cannot shield the cation from its anion, thus contact-ion pairing is observed. Upon complexation of Ag^+ by P5S, the polymer conformation may change, particularly if the presence of the ions disrupts the chain-packing forces that stabilized the otherwise unfavorable trans C–S conformations. This disruption of the packing of P5S without a compensating new periodic structure may account for the lack of crystallinity of P5S complexes of $AgNO_3$.

It is not possible to determine directly the environment of the silver ion in these polymer–salt complexes but X-ray single-crystal data on silver nitrate complexes of 1,3,5-trithiane provide some clues. Studies of 1:1[30] and 2:1[31] complexes of 1,3,5-trithiane with $AgNO_3$ show either a tetrahedral or irregular trigonal bipyramidal coordination of the Ag^+ ion. In the example of the 1:1 complex some of the silver ions were coordinated by two sulfur atoms and others by three. None of the 1,3,5-trithianes form chelates with Ag^+, and the coordination sphere is completed by oxygen atoms of the nitrate anion. From these models it is not unreasonable to predict that the silver ions in the polysulfide electrolytes may be tetrahedrally coordinated with a combination of sulfurs from one or more chains and oxygens from the nitrate counterions.

Transference Number Measurements. The potentiostatic polarization cell method provides a simple way of estimating the relative contribution of charge carried by cations and anions.[13]

Complexes were formed between P5S and $AgNO_3$, and also P5S and $AgSO_3CF_3$, in the sulfur to silver ratio of 4:1. A potential of 0.01 V was applied to a symmetrical cell composed of an electrolyte sandwiched between silver

Table V
Conductivities of Various Poly(alkylene sulfide)-$AgNO_3$ Electrolytes

polymer host	S/Ag	temp, °C	σ, Ω^{-1} cm^{-1}
PES	3:1	70	1.5×10^{-8}
P3S	1:1	66	1×10^{-7}
P4S	2:1	62	1×10^{-6}
P6S	4:1	66	5×10^{-5}

ion-reversible Ag electrodes and the change in current carried by the electrolyte monitored with time. The small applied potential was used to decrease the chance of reducing the anion. The fraction of the current carried by silver ions is about 0.83 for 4:1 P5S·$AgNO_3$ and greater than 0.95 for 4:1 P5S·$AgSO_3CF_3$ at 50 °C.[13] These values are much higher than most other polymer–salt complexes.[10,13,32] Poly(ethylene oxide)-based electrolytes of alkali metal salts have cationic transference numbers of about 0.6,[13,15,16] poly(ethylene succinate) electrolytes range from 0.05[7,13] to 0.5,[13] and poly(phosphazene) electrolytes have cationic transference numbers that range from 0.03 to 0.32.[8] It is unclear why transference numbers vary so widely from one polymer electrolyte to the next.

The influence of applied potential on t_+ was investigated for P5S·$AgNO_3$ in an attempt to detect redox processes other than those associated with the Ag/Ag^+ couple. Potentials of 0.01, 0.30, and 1.00 V resulted in transference numbers of about 0.83 (3), 0.91 (3) and 0.98 (2),[33] respectively, for a 4:1 polymer–salt complex at 50 °C. This may indicate a redox process occurring with the nitrate anion. The triflate anion is known to have a reduction potential of about +2.9 V vs. Ag/Ag^+,[34] and, therefore, it should be much more resistant to reduction than NO_3^-. A 4:1 complex of P5S and $AgSO_3CF_3$ was polarized under the same conditions, and the transference number of the silver ion was found to be 0.98 (2)[32] over the potential range 0.01–1.00 V. These data indicate that a redox reaction associated with NO_3^- occurs in the P5S·$AgNO_3$ electrolyte applied potential of 0.30 and 1.0 V. A similar process appears to be absent in P5S·$AgSO_3CF_3$, but the inherently high value of t_+ in this complex makes the variation of t_+ rather insensitive for this material.

The transference number for silver ion is higher than most other reported cation transference numbers in a polymer–salt complex. The high cationic transference number of 0.83 for the $AgNO_3$ polymer–salt complex and 0.98 for the $AgSO_3CF_3$ polymer–salt complex implies the anion is practically immobile in these materials. The immobility of the anion is especially surprising in view of the strong ion pairing. We are inclined to believe that this high apparent transference number is an artifact of the experiment.

Complexes of Other Poly(alkylene sulfides). Ionic conductivity measurements were performed on $AgNO_3$ complexes of poly(alkylene sulfides) other than P5S. Except for the poly(hexamethylene sulfide) complex, the conductivities of these materials are lower than those of P5S complexes (Table V). The P6S complexes were difficult to handle owing to their soft sticky nature. Because of these problems the P6S electrolytes were not pursued further.

A measurable conductivity was observed for poly(ethylene sulfide) complexes of $AgNO_3$ above 70 °C. Poly(ethylene sulfide) melts at 210 °C, which implies a fairly inflexible polymer chain, so it is not surprising that the complex is a poor conductor. Poly(ethylene sulfide) also appears to complex less salt (the maximum S/Ag ratio is 3:1) than the other polysulfides. The other polysulfides, P3S and P4S, have much lower melting points, both near 60 °C.[11] Each complexes more salt, and these complexes have improved conductivities over PES complexes, although the conductivity is not quite as high as that of P5S electrolytes.

Conclusions

Poly(alkylene sulfides) form complexes with silver salts and the ionic conductivities increase with increasing length of the alkylene chain in the concentration range studied. The ionic conductivities of poly(pentamethylene sulfide)·$AgNO_3$ electrolytes are comparable to those of PEO–alkali metal salt complexes.

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Registry No. P5S (SRU), 57514-73-5; PES (SRU), 24936-67-2; P3S (SRU), 28758-48-7; P4S (SRU), 24937-37-9; P6S (SRU), 57514-74-6; (1,5-pentanedithiol disodium salt)·(1,5-dibromopentane) (copolymer), 37325-04-5; (1,2-ethanedithiol disodium salt)·(1,2-dibromoethane) (copolymer), 99809-26-4; (1,3-propanedithiol disodium salt)·(1,3-dibromopropane) (copolymer), 99809-27-5; (1,4-butanedithiol disodium salt)·(1,4-dibromobutane) (copolymer), 64773-31-5; (1,6-hexanedithiol disodium salt)·(1,6-dibromohexane) (copolymer), 64773-32-6.

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Studies of Chain Conformational Kinetics in Poly(di-*n*-alkylsilanes) by Spectroscopic Methods. 1. Poly(di-*n*-hexylsilane), Poly(di-*n*-heptylsilane), and Poly(di-*n*-octylsilane)

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ABSTRACT: A series of poly(di-*n*-alkylsilanes) having hexyl, heptyl, and octyl side chains have been investigated by spectroscopic methods. Whereas the UV spectrum provided information about the electronic structure of the polymer backbone, IR and Raman methods have been used to characterize the molecular conformation of both the main and side chains. These structural studies were correlated with results from thermal analyses and X-ray diffraction measurements. A mechanism involving the melting of the *n*-alkyl side chains with a subsequent disordering of the polymer backbone is proposed.

Introduction

Crystallization has been observed[1–7] in a number of polymers containing long unbranched side chains that can pack together in an ordered array. In many cases[1–6] this side-chain crystallization occurs without a corresponding crystallization of the main chain. X-ray evidence[5,6] suggests that the side chains of poly(*n*-alkyl acrylates) and poly(*n*-alkyl methacrylates) are extended at right angles to the main chain, thus enhancing the crystallization process but leaving the main chain amorphous even in materials that exhibit considerable tacticity. On the other hand, there have been studies on isotactic poly(1-alkenes)[7] that have found that both the main chain and the side chain crystallize, presumably due to the structural simplicity of the polymer backbone. Hence, in the absence of a bulky main chain, side-chain crystallization can cause changes in the main-chain conformation, which in turn makes it compatible with the crystal lattice.[5] It is this latter point that became important in understanding the thermally reversible behavior of the poly(di-*n*-alkylsilanes).

Although polysilanes have existed[8] for more than 60 years, there has been very little scientific interest because early materials were intractable and insoluble in all common solvents. Recently, however, there have been a number of reports[9–12] on the synthesis of soluble substituted polysilane derivatives that are processable and can thus be studied by conventional analytical techniques. Most of these polysilanes were unsymmetrically substituted in an atactic configuration, thus giving rise to an amorphous polymeric material. On the other hand, the alkyl derivatives exhibited an intense UV absorption in the range 305–320 nm attributable[13–15] to either a $\sigma\sigma^*$ or a $\sigma 3d\pi_{\mathrm{Si-Si}}$ electronic transition, and it was the electronic properties of the unsymmetrically substituted polysilanes that attracted the most attention and eventually led to the development of new applications.[16–19]

A change in the electronic structure with backbone conformation was recently reported[20] for poly(di-*n*-hexylsilane) (PDHexS) in the solid state. The as-polymerized material exhibited an anomalously long wavelength absorption at 374 nm, some 60 nm red-shifted from that of any simple, alkyl-substituted polysilane previously investigated. Subsequent spectroscopic studies revealed that the *n*-hexyl side chains had crystallized, locking the silane backbone into a more ordered conformation, which consequently altered its electronic structure. Although, as mentioned previously, the crystallization of polymers with long unbranched side chains has been known for many years, to date none of those contained a main chain that exhibited such a dramatic change in electronic structure with change in conformation. Thus, the di-*n*-alkyl-substituted polysilanes with side chains of intermediate length represent a novel class of materials that seem to exhibit a unique electronic structure due to conformational rigidity induced by side-chain crystallization.

The present work was undertaken to expand previous studies[20] of the anomalous long-wavelength electronic transition in PDHexS to include poly(di-*n*-heptylsilane) (PDHepS) and poly(di-*n*-octylsilane) (PDOctS), which together seem to form a class of structurally similar materials. The structure of these polysilanes has been further investigated by IR and Raman spectroscopy and correlated with the electronic structure previously described. In addition, wide-angle X-ray diffraction (WAXD) and thermal analysis have been used to better characterize the kinetics of side-chain crystallization.

Experimental Section

Synthesis of Poly(di-*n*-hexylsilane) (PDHexS). The procedure described here is specifically for PDHexS, but it is general, and the same technique has been used for the preparation

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