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New Polymer Electrolyte Hosts and Their Tetrabutylammonium Chloride
Complexes. Relationships Among Concentration of Polar Groups, ESR
Spin Probe Response, and Ionic Conductivity

by

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19 ABSTRACT (Continue on reverse if necessary and identify by block number) A new polymer electrolyte host was synthesized by hydrosilation of a poly(hydromethylsiloxane) with terminal olefin bearing a silyl ketene acetal. The derivatized siloxane was subsequently reacted with 4-nitrobenzenesulfonyl chloride, affording polymers having highly polar pendants. Complexes of these polymers with tetrabutylammonium chloride were prepared. The ionic conductivities of these materials are a function of concentration of polar pendant groups and, as a result, the glass transition temperature. The weak dependence of polymer host T _g on tetrabutylammonium chloride concentration makes these ideal model systems to explore the factors which ultimately limit ionic conductivity. We find that the temperature dependencies of the ionic conductivities and ESR spin probe (4-hydroxy-TEMPO) correlation times are similar and indicate that ion transport is dominated by (cont'd)					
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19. segmental motions, and the dependence becomes quite pronounced as T_g is approached.

New Polymer Electrolyte Hosts and Their Tetrabutylammonium Chloride Complexes. Relationships Among Concentration of Polar Groups, ESR Spin Probe Response, and Ionic Conductivity.

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Abstract

Polysiloxanes having various amounts of p-nitrothiophenoxy pendants have been prepared and their complexes with tetrabutylammonium chloride (TBAC) studied. The polymers have glass transition temperatures ranging from ca. -60 to -10°C which are essentially invariant with TBAC loading, making these useful candidates to probe the dependence of ionic conductivity on T_g . ESR spin probe correlation times of the nitroxide 4-hydroxy-1,1,3,3-tetramethylpiperidinoxyl (TEMPO) dissolved in these materials were also measured as a function of temperature. Ionic conductivities at room temperature vary by two orders of magnitude at constant TBAC loading, with the lowest T_g material having the highest conductivity as expected. The temperature dependencies of the conductivities parallel those of the spin probe correlation times, suggesting that in these systems ion transport is dependent on microscopic viscosity.

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Introduction.

Much work has been devoted to the study of polymer electrolytes which are polymer complexes of (typically alkali metal) salts. Such materials are of interest for the development of high-performance batteries and sensors ⁽¹⁻⁴⁾. It has been suggested that there are two principle characteristics for successful polymer electrolyte. The first is a low glass transition temperature to permit facile ion movement within the liquid-like regions of the material. Second, the polymer must contain polar groups to promote salt dissociation.

The low glass transition temperatures of polysiloxanes has encouraged studies to investigate their use as polymer electrolytes. ⁽⁵⁻⁷⁾ However, the nonpolar nature of polysiloxanes precludes dissolution of salts, and thus they must be suitably modified in order to be useful electrolytes. The most common approach is to carry out a hydrosilation of polymethylhydrosiloxane with an olefin-terminated polymer or oligomer which can complex alkali metal cations. However, the range of materials which can be synthesized is often limited by the range of terminal olefins which can be purchased or easily prepared.

We recently reported a new, apparently versatile method of functionalizing polysiloxanes with polar groups. ^(8,9) Our approach involves hydrosilation of polymethylhydrosiloxanes with olefin bearing silyl ketene acetals which can be subsequently reacted with numerous highly polar electrophiles. The latter reaction, like hydrosilation, affords high yields with appropriate chosen substrates and is thus attractive. The resulting materials have large dielectric constants over a broad frequency range and temperature and may serve as new electrolyte hosts, which are able to increase ion pair dissociation.

In this paper, we discuss a series of new polysiloxanes which serves as an interesting model system to explore factors which dominate ion transport in amorphous polymers. The polymers were prepared by hydrosilation of poly(methylhydrosiloxane) with mixtures of ethyl 2-methyl-4-pentenoate and ethyl trimethylsilyl-2-methyl-2-allylketene acetal, and then reacted with

p-nitrophenyl sulfenyl chloride. The resulting copolymers contain various amounts of p-nitrothiophenoxy-derivatized pendants (Chart 1).

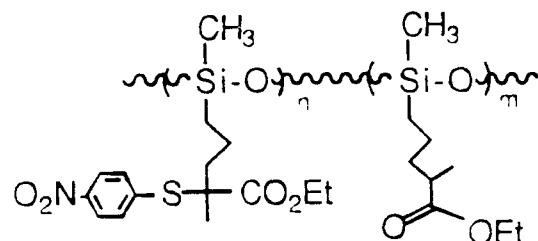


Chart 1

The series is interesting because (1) the polymers are liquids at room temperature, and their T_g 's vary over a 50°C range, (2) the polymers are capable of dissolving organic electrolytes such as tetrabutylammonium chloride (TBAC), and (3) the T_g 's do not change significantly upon addition of TBAC, allowing an exploration of salt concentration on conductivity without concern about T_g increases. We report ionic conductivities of TBAC complexes as a function of salt concentration and temperature. In addition, we discuss ESR spin probe correlation time results for these materials which suggest that ionic conductivity, at least in these systems, is dominated by microscopic viscosity at constant salt concentration.

Experimental.

Detailed procedures for the synthesis of the copolymers in Scheme I, as well as the results of their characterization (NMR, DSC) are presented elsewhere.⁹ Table 1 summarizes copolymer

composition derived from proton NMR and elemental analysis data, and T_g 's from DSC traces.

Salt complexes were prepared by weighing a stoichiometric quantity of dried salt and polymer in dry box. Methylene chloride was added, and the solution was stirred overnight. Upon removal of the solvent, a homogenous viscous liquid was formed, which was transferred to an ionic conductivity cell (ca. 1 cc capacity, 5 mm spacing between Pt electrodes), and then dried at 60 °C under vacuum for 1 day. The frequency dependent impedance of the samples was measured on a Solartron 1260 Impedance/gain-Phase Analyzer coupled with a 1286 Electrochemical Interface. Samples for ESR studies were prepared similarly except that a small amount (ca. 10^{-5} M) of TEMPO was added. Samples were placed in NMR tubes and ESR spectra were recorded on a home-built, X-band spectrometer equipped with a variable-temperature probe in the laboratory of Prof. R. K. MacCrone. Correlation times were extracted from the three-line nitroxide spectra as described earlier.⁽¹⁰⁾

Results and Discussion.

Table 1 gives the percentages of repeat units bearing p-nitrothiophenoxy groups from both elemental analyses and ^1H NMR. Also listed are the DSC-derived T_g 's using a heating of 10°C/min. Samples will be referred to as A1 through A4. The percentages of pendants which were originally silyl ketene acetals are shown in parentheses in column 1 of the Table (from NMR integration). The elemental analyses and NMR data for all samples are in reasonably good agreement.

The ionic conductivities of molten TBAC and the copolymer/TBAC complexes were determined from complex impedance measurements employing ion-blocking platinum electrodes. An example of typical complex impedance plot for A1- Bu_4NCl electrolyte at 30 °C shows the expected semicircle and low frequency spur (Figure 1). The temperature dependence of the ionic

conductivity of molten TBAC is shown in Figure 2.

Figure 3 shows x-ray diffraction patterns of A3-Bu₄NCl, A3, and TBAC. Tetra-butylammonium chloride, a crystalline solid, shows sharp diffraction peaks at $2\theta = 19^\circ$ and around $22-27^\circ$. The A3-Bu₄NCl complex and A3 exhibited no diffraction peaks. We conclude that TBAC dissolves completely in the amorphous host polymer A3. The profiles of DSC curves of A4-Bu₄NCl complexes with different concentration of TBAC show no melting peak (50°C) of TBAC in the dry complexes.

The variable-temperature ionic conductivity data for A2 and A4 with different ratios of $[\text{Cl}^-]/[\text{NO}_2]$ units yield curved plots of $\log\sigma$ vs. $1000/T$ (Figures 4 and 5). All plots show a downward curvature at low temperatures, as is usually found for amorphous polymer electrolytes. Also apparent is the higher conductivities for samples with higher TBAC concentrations. As shown more clearly in Figure 6 for sample A2, an increase in the ratio of $[\text{Cl}^-]/[\text{NO}_2]$ units affords a continuous rise in conductivity. This behavior is quite distinct compared with PEO/salt systems. It has been demonstrated that, when salts are dissolved in PEO and related polyethers, the T_g increases nearly linearly with salt concentration⁽¹¹⁾ and reaches a maximum. Since ion conduction appears to proceed via a free volume mechanism, increased stiffening of chains via ion complexation which hinder segmental chain motion and raise T_g will eventually cause the conductivity to decrease. On the other hand, an increase in the ratio of $[\text{Li}^+]/[\text{EO}]$ units raises the number of charge carriers, and is expected to increase conductivity. Thus, a maximum in the plot of conductivity as a function of the ratio of $[\text{Li}^+]/[\text{EO}]$ appears to be typical for predominantly amorphous polymer electrolyte complexes.⁽¹²⁾

We note that the glass transition temperature is essentially invariant for TBAC/A4 (Figure 7)

and increases only about 8°C with an increase in $[\text{Cl}^-]/[\text{NO}_2]$ units for TBAC/A2 (Figure 8).

Therefore, the conductivity will be dominated by the number of charge carriers, rather than an increase in chain stiffening, as TBAC is added.

It is expected that the ionic conductivities of samples A1 through A4 *with the same TBAC concentration* will reflect the differences in ion mobility, which in turn will be determined by the magnitude of T_g . Displayed in Figure 9 are plots of ionic conductivity with same salt molarity for A1, A2, A3, and A4 as a function of temperature. At room temperature, the conductivities vary by about two orders of magnitude. Sample A1 has the highest conductivity and the lowest T_g ; the opposite is true for sample A4. As the temperature increases, the variation in conductivity decreases, and suggests that ion mobility is becoming comparable as the samples move farther from T_g .

ESR correlation times from dissolved TEMPO are expected to *reflect changes in microscopic viscosity* in the sample with temperature and, if salt concentrations are comparable, may scale with ionic conductivity if ion motion is coupled with backbone motion. Figure 10 shows the temperature dependence of the TEMPO correlation time for the samples whose ionic conductivities were plotted in Figure 9. Sample A4 has the longest correlation time and highest T_g . Note that the correlation times for the samples decrease as T_g increases. Particularly interesting is that the correlation time differences among the samples become smaller with increasing temperature, as did the conductivities (Figure 9). Activation energies calculated from ESR and ionic conductivity measurements are collected in Table 2. In both cases, the activation energies increase with an increase in the concentration of polar pendant group or glass transition temperature.

Finally, we report the temperature-dependent conductivities of samples A1-A4 with different salt molarities, specifically where $[\text{Cl}^-]/[\text{NO}_2] = 1$. The data are shown in Figure 11. Note that the concentration of salt is lowest in sample A1 (lowest T_g matrix) and highest in A4 (highest T_g

matrix). As the temperature is increased, the conductivity of A4/TBAC increases quickly and at about 60°C surpasses that of A1, even though A1 has the lowest glass transition temperature. At room temperature, ion mobility is apparently more important than salt concentration. As the temperature is raised, differences between mobilities decrease (note ESR data), and hence carrier concentration now becomes important.

Conclusions.

A series of silicone copolymer fluids has been prepared and characterized. The copolymers have T_g 's which depend upon composition but are essentially invariant with added TBAC, making the copolymer series a useful model system to study the effect of T_g on ionic conductivity. At room temperature, conductivities at constant TBAC loading span two orders of magnitude, with the lowest T_g matrix affording the highest conductivity. As the temperature increases, the conductivity differences become smaller (within a factor of five at 100°C), suggesting that ionic mobilities become similar at temperatures well above T_g . The temperature dependencies of ESR spin probe correlation times also converge at elevated temperatures, suggesting that the ionic conductivity is dominated by microscopic viscosity at constant electrolyte loading.

Acknowledgements.

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Table 1. Compositions and Tg's of Copolymer Samples

Sample	NMR	EA ^a	Tg (°C)
A1 (32)	27.27	26.73	-60
A2 (48)	46.43	46.98	-42
A3 (69)	63.33	61.70	-27
A4 (100)	95.56	92.73	-10

a. Elemental Analyses

Table 2. Data of activation energy for samples A1 through A4 with same salt molarity calculated from the data in Figures 9 and 10.

Sample	Ea (kJ/mole) (ESR) ^a	Ea (kJ/mole) (IC) ^b
A1	17.78	55.84
A2	26.19	64.69
A3	25.50	76.16
A4	28.41	94.65

a. Electron Spin Resonance

b. Ionic Conductivity

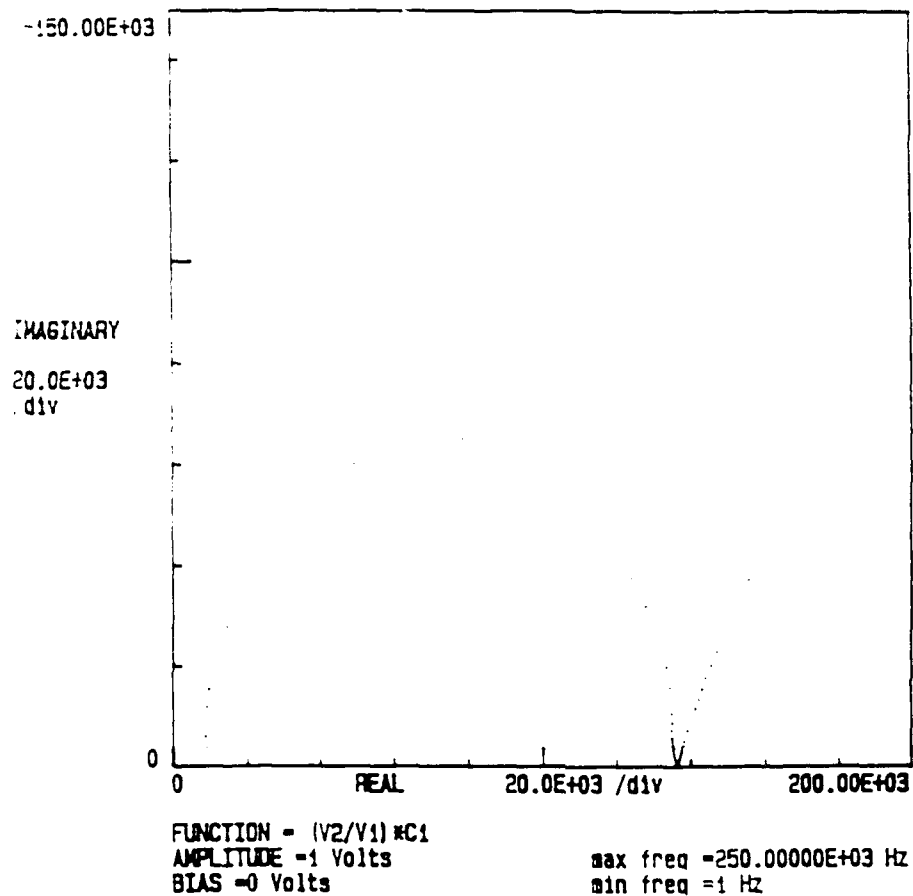


Figure 1. Complex impedance plot for Al-Bu₄NCl electrolyte at 30° C with Pt electrode.

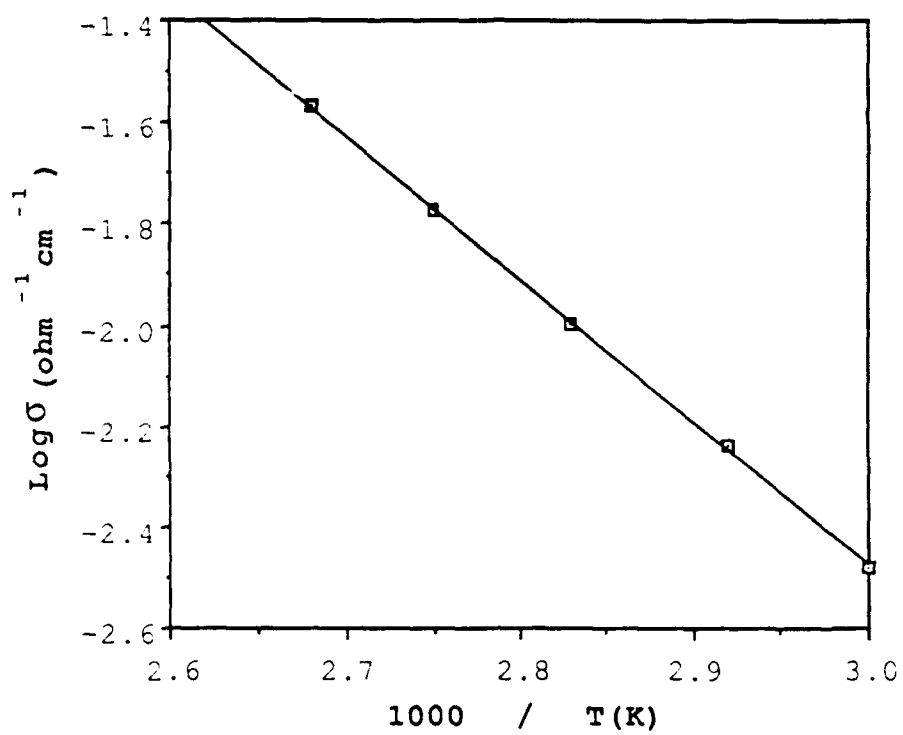


Figure 2. Plot of conductivity for tetrabutylammonium chloride as a function of temperature.

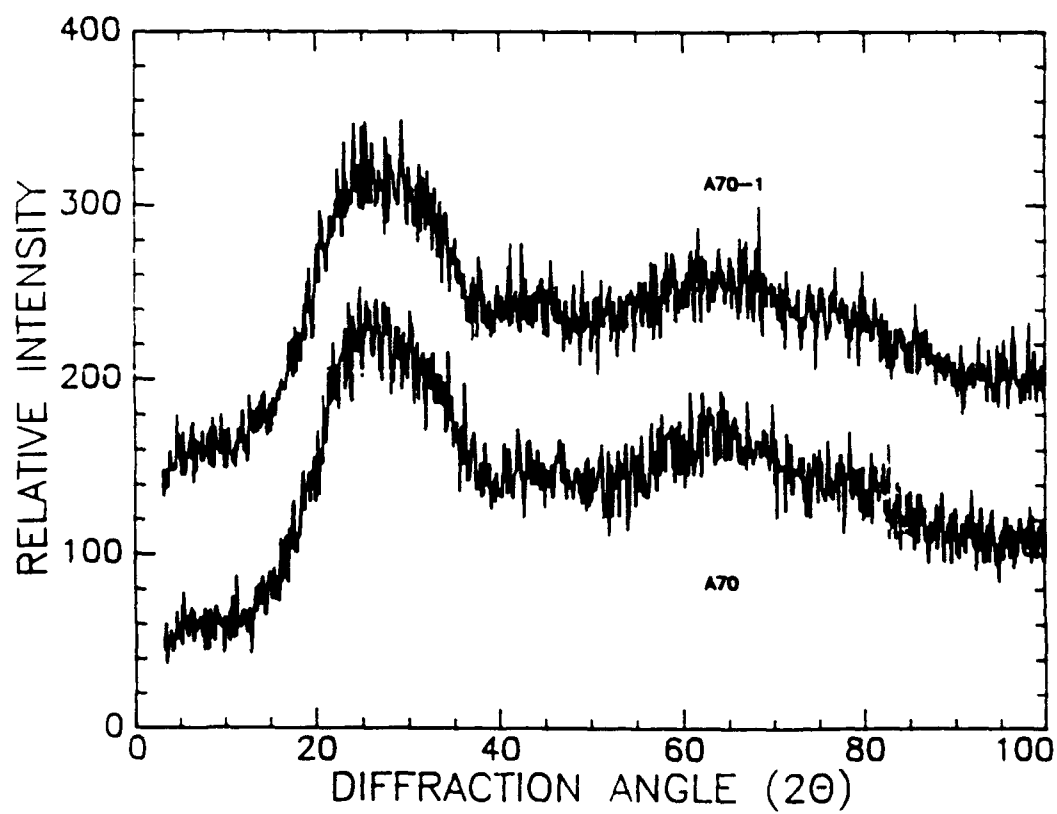
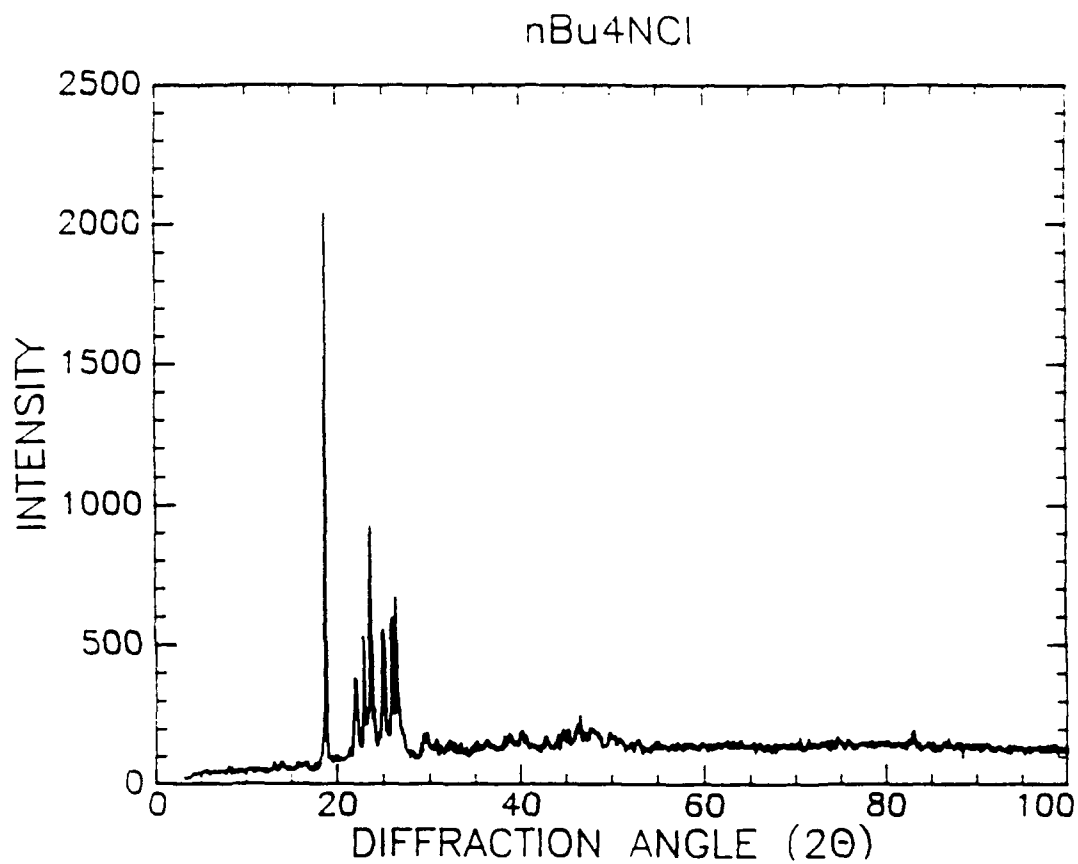


Figure 3. (a)x-ray spectrum of Bu_4NCl salt. (b)x-ray spectra of A3 and A3- Bu_4NCl complex.

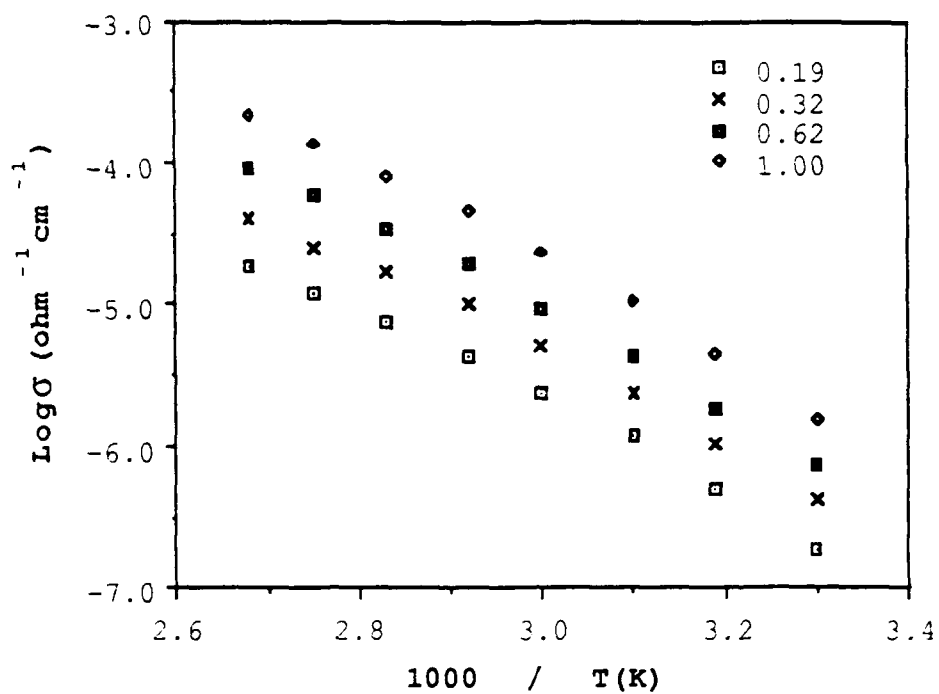


Figure 4. Plot of conductivity for A2 with different ratio of $[\text{Cl}^-] / [\text{NO}_2]$ units as a function of temperature.

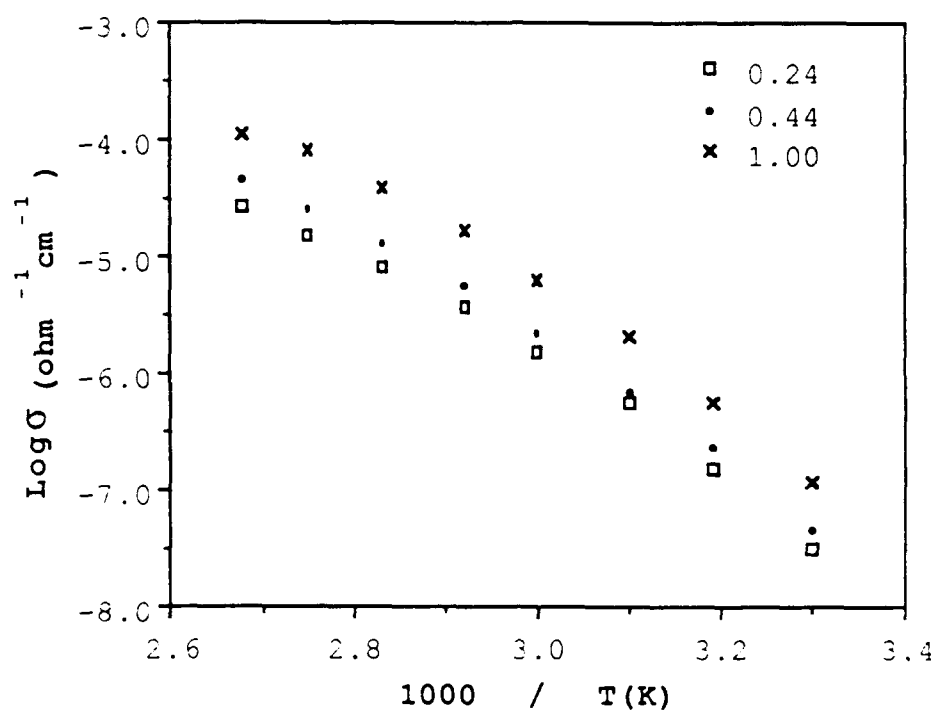


Figure 5. Plot of conductivity for A4 with different ratio of $[\text{Cl}^-] / [\text{NO}_2]$ units as a function of temperature.

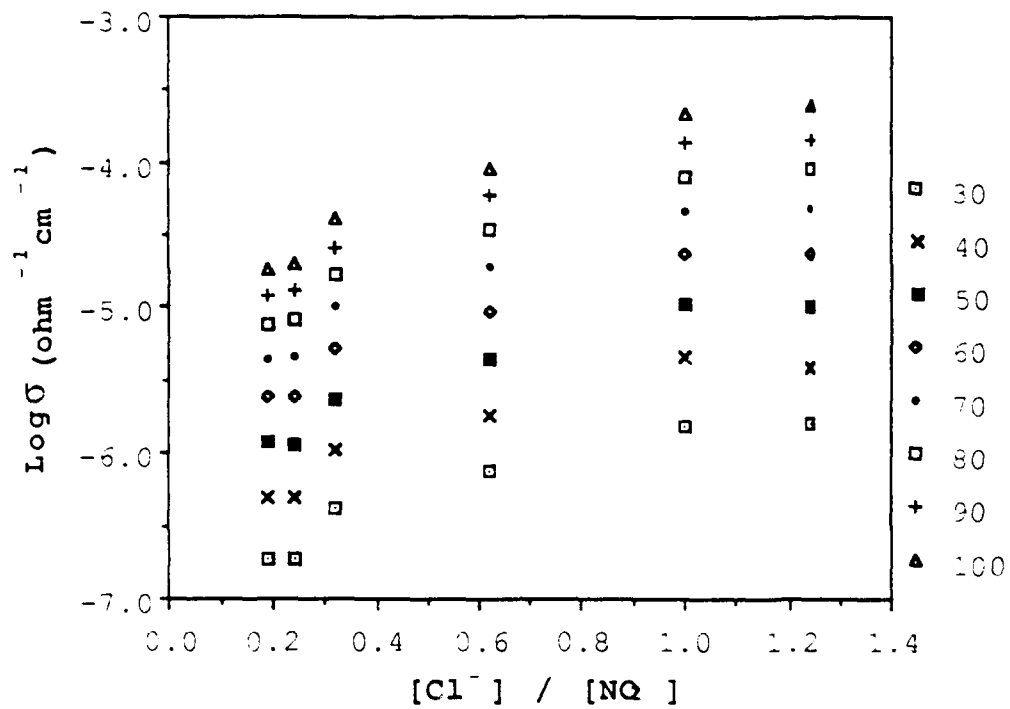


Figure 6. Plot of conductivity for A2 with different temperature as a function of the ratio of $[\text{Cl}^-] / [\text{NO}_2]$ units.

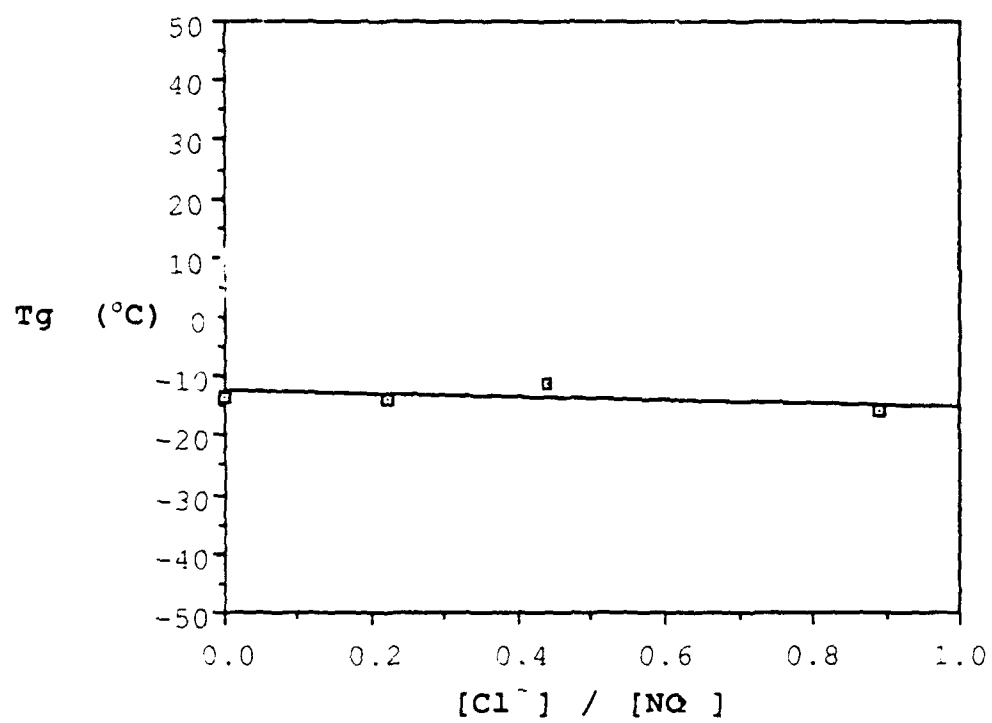


Figure 7. Change of the glass transition temperature of A4 with different ratio of $[Cl^-] / [NO_2]$ units.

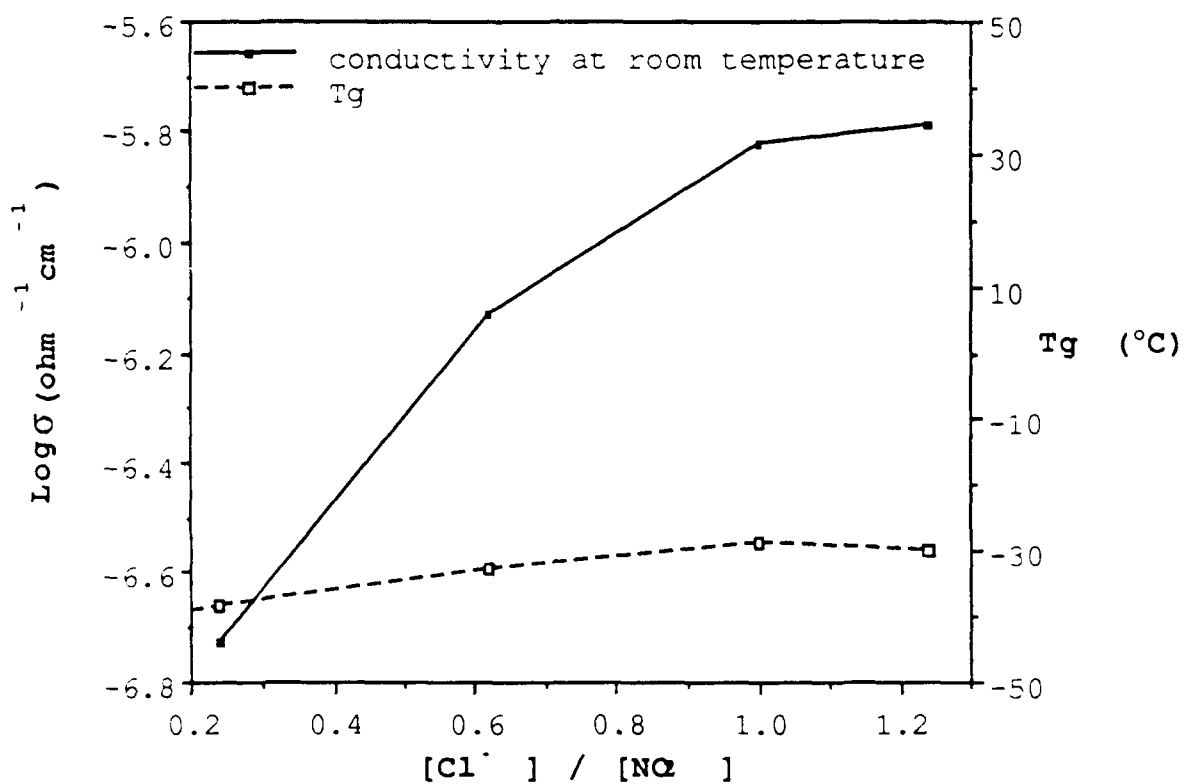


Figure 8. Plot of conductivity and glass transition temperature for A2 as a function of $[Cl^-] / [NO_2]$ units.

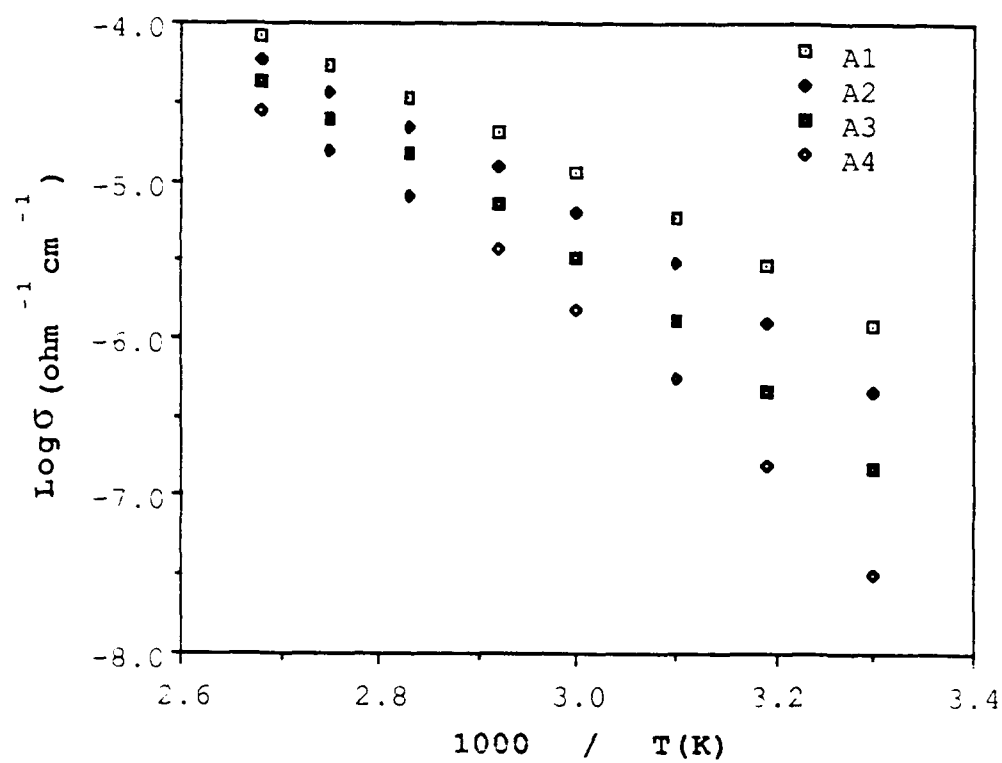


Figure 9. Plot of conductivity with same salt molarity for siloxanes with different concentration of polar pendant groups.

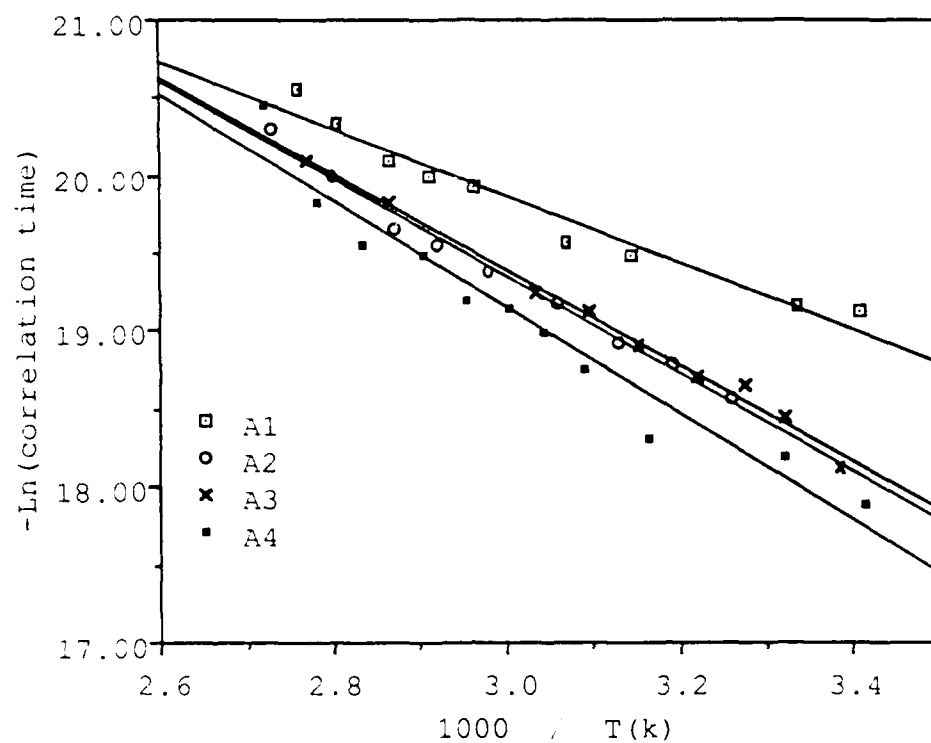


Figure 10. Temperature dependence of correlation time for samples A1 through A4 with same salt molarity.

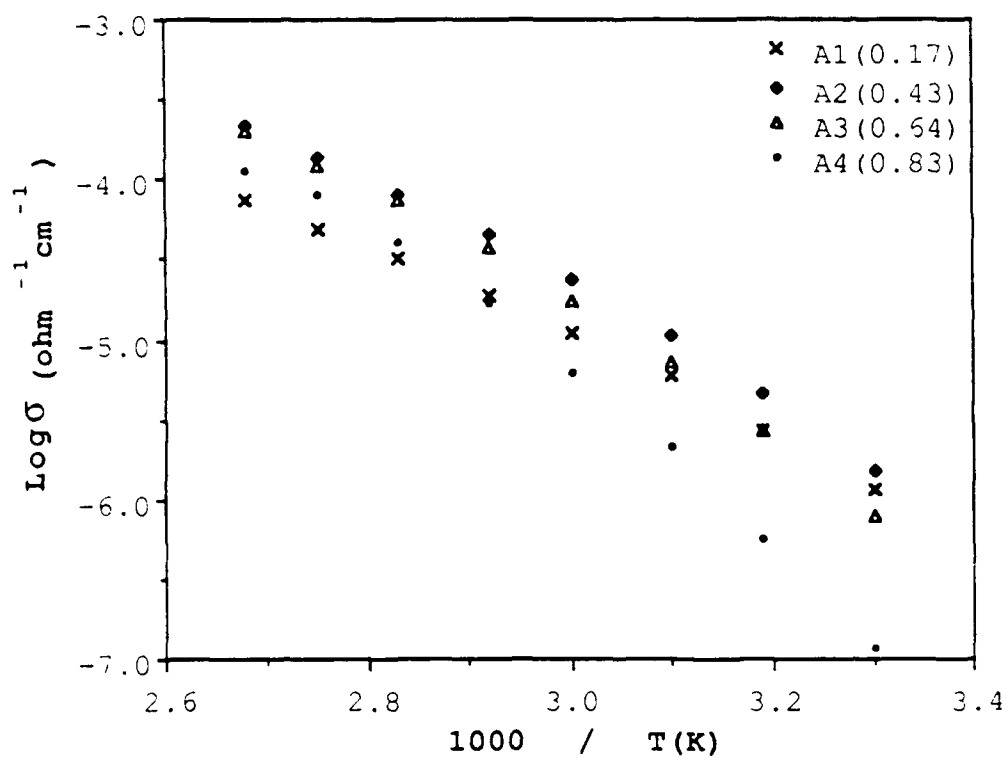


Figure 11. Plot of conductivity with a ratio of $[\text{Cl}^-] / [\text{NO}_2] = 1$ for different concentration of polar pendant group siloxanes.