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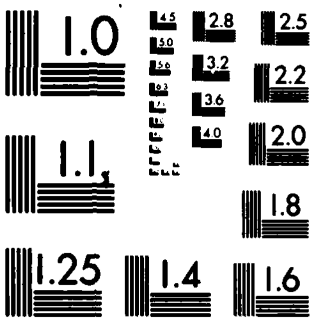

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Solid electrolyte complexes of poly(ethylene succinate), PESc, and $LiBF_4$ were proposed from the melt and found to be the compound amorphous over the polymer repeat unit to salt formula unit range of 1:1 to 3:1. Preparations with larger amounts of salt contained a pure salt phase, and at salt concentrations below the 3:1 ratio, free crystalline polymer was observed. Within the 1:1 to 3:1 concentration range, increasing salt concentration was accompanied by decreasing conductivity, and increasing glass transition temperatures.

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Ion Transport in the Polymer Electrolytes Formed Between Poly(ethylene succinate) and Lithium Tetrafluoroborate

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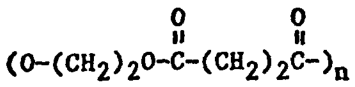
ABSTRACT

Solid electrolyte complexes of poly(ethylene succinate), PESc, and $LiBF_4$ were prepared by heating the salt with the molten polymer. The complexes were completely amorphous over the concentration range 1:1 to 3:1 polymer repeat units:metal cation. At salt concentrations above the 1:1 composition, a salt phase was present, and at salt concentrations less than 3:1, free crystalline polymer was observed. Within the 1:1 to 3:1 concentration range, increasing salt concentration was accompanied by decreasing conductivity, and increasing glass transition temperatures. This behavior is discussed in terms of a Gibbs-Adams-like excess entropy model.

Recent studies reveal an interesting and potentially useful class of solid polymer electrolytes formed by the interaction of polyethers with alkali metal salts (1-3). The formation of these polymer salt complexes appears to be facilitated by a high concentration of polar groups in the polymer, high polymer chain flexibility which permits polymer reorientation for the effective solvation of a salt, and low cohesive energy density of the polymer (4). With these ideas in mind we have studied the interaction of poly(ethylene succinate), I, with alkali metal salts. This host polymer has



$$(\mathrm{O{-}(CH_2)_2O{-}\overset{\overset{O}{\|}}{C}{-}(CH_2)_2\overset{\overset{O}{\|}}{C}{-}})_n$$

(I)

the requisite high concentration of polar groups and judging from the relatively low glass transition temperature, T_g (-1°C), the polymer chain is fairly flexible. Also the value of T_g and mechanical properties suggest that the cohesive energy density is low.

We report here the first preparation and characterization of the polymer salt complexes formed between PESc and alkali metal salts; along with information on the electrical properties of these materials. A very brief preliminary description of this system has appeared (3).

EXPERIMENTAL

Poly(ethylene succinate) (Aldrich) was dissolved in chloroform, filtered, precipitated with hexane, air dried, and then dried under high vacuum. Reagent grade $LiBF_4$ (Pfaltz and Bauer) was dried by heating under vacuum at 125°C for 12 h. Infrared spectra were used to check for the presence of water in the purified salt, polymer, and polymer electrolytes. Only anhydrous materials were used for electrical measurements. Starting materials and complexes were manipulated in a nitrogen-filled glove box or in air-free apparatus. Poly(ethylene succinate)·$LiBF_4$ complexes were prepared by heating above the polymer melting point on intimately-ground stoichiometric mixtures of anhydrous polymer and salt contained in a Teflon dish. The samples were then cooled slowly over a period of 2 h.

Infrared spectra were recorded using a Perkin-Elmer 399 grating infrared spectrophotometer for samples in the following form: $LiBF_4$ as a Nujol mull and PESc as a cast film from chloroform solution. The IR spectra of pure PESc were obtained using the cast sample contained in an evacuable cell and PESc·$LiBF_4$ complexes as heat pressed films between KBr plates.

The pure polymer and the respective complexes between sealed glass plates were examined at 12.5 power magnification using a Leitz Wetzlar polarizing microscope equipped with a Mettler FP52 hot stage. The heating rate was typically 10°/min.

Differential scanning calorimetry measurements were performed on samples sealed in Perkin-Elmer aluminum volatile sample pans using 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 a plot of observed transition temperatures vs $(\text{heating rate})^{1/2}$ to zero heating rate.

X-ray diffraction patterns were determined using CuK_α radiation on pressed samples protected from the atmosphere. Scattering and receiving slits were adjusted to optimize sample illumination. Slit widths were changed at the same 2θ locations for all samples and the scans at different slit widths were overlapped in order to estimate relative peak intensities.

Conductivities were measured using complex admittance/impedance techniques over the frequency range 5 Hz to 500 kHz. Samples were pressed (under an inert atmosphere) at 10,000 psi into 1/2" diameter pellets. Samples which were relatively non-compliant were pressed at 50°C. Electrical measurements were made in a specially designed two-electrode Kel-F cell, which permitted exclusion of the atmosphere. Ion blocking platinum discs, 1/2" in diameter, 0.005" thick, were used as electrodes. Variable temperature measurements were performed in a thermostatted forced-air heating chamber which was controlled by a Bruker B-ST 100/700 temperature control unit. Temperatures were monitored to within ±0.1 °C by an iron-constantan thermocouple. All connecting leads were coaxial cable. The data were collected using a Hewlett Packard 4800A vector impedance meter, which is accurate to ±5% under our conditions.

RESULTS

The average molecular weight of the PESc was determined to be 1700 from the sharp melting endotherm of this polymer using the empirical melting point (Tm) - molecular weight relationship, eq. 1 (5).

$$1/T_m = 2.59 \times 10^{-3} + 0.179/\bar{M} \qquad (1)$$

The limiting stoichiometry of the poly(ethylene succinate)-$LiBF_4$ complex formation was determined by physical measurements on materials prepared with various polymer to metal salt ratios. The X-ray diffraction patterns of pure polymer, salt, and unreacted mixtures agreed well with the published data

(6,7). In contrast to the highly crystalline parent PESc, all of the PESc-$LiBF_4$ complexes were found to be amorphous. Crystalline phases which were observed in the PESc-$LiBF_4$ materials always matched with the pure polymer or pure salt. The maximum salt concentration in the complex was thus established as one polymer repeat unit per salt formula unit, ±10%. As judged by X-ray diffraction and optical microscopy, the PESc•$LiBF_4$ complexes remain completely amorphous as the salt concentration is progressively decreased to a value of 3:1 polymer repeat units per $LiBF_4$. These amorphous materials range from a hard, plastic-like material at 1:1 concentration to compliant, rubbery species at 3:1 stoichiometry.

Below salt concentrations corresponding to the ratio 3:1 PESc:$LiBF_4$, crystalline regions of uncomplexed PESc appeared. These were observed as spherulites when viewed through the polarizing microscope, and their identity was confirmed by the presence of X-ray diffraction peaks at d = 3.80 Å and 4.39 Å. The infrared spectra of the pure polymer (Figure 1) showed sharp, well-defined bands over the spectral range 700-4000 cm^{-1}, whereas the spectra of the complexes are broad and diffuse, especially in the 1500-1000 cm^{-1} region, which is characteristic of amorphous polyester systems (8). Comparison of the spectra before and after complex formation revealed no detectable shifts for any of the polymer band positions. Spectra obtained for amorphous samples cooled to 77°K displayed no significant improvement in resolution. Judging from the published kinetics of crytallization of poly(ethylene succinate) (7, 9-11) and various annealing experiments which we performed on the complexes, the amporphous phases do not arise from supercooled glassy PESc.

The observed change in mechanical rigidity and in electrical conductivity (see below) over the 1:1 to 3:1 range prompted an investigation of the glass transition temperatures. The values of T_g were found to increase with increasing salt concentration, Table 1. The trend in glass transition temperatures thus parallels qualitative changes in mechanical properties.

Complex admittance plots of the conductivity response in these systems, using ion-blocking electrodes, were consistent with a model equivalent circuit containing a capacitance (geometric) in parallel with both a resistance (bulk) and a second capacitance (double layer). Such a combination should result in a single arc followed by a spur when plotted in the complex plane. A representative plot is shown in Figure 2 for a $PESc \cdot LiBF_4$ sample at 70°C. Within the 1:1 to 3:1 stoichiometry range, the conductivity decreases dramatically as the salt concentration increases, Fig. 3. In addition, a gentle curve is obtained when the conductivity data are plotted in Arrhenius coordinates, Fig. 4, which agree with expectations for amorphous conductors. It should be noted that samples of pure PESc exhibited a conductivity response outside of the measuring capability of the vector impedance meter over the temperature range 25-90°C. The uncomplexed polymer thus has a conductivity less than $10^{-9}(\text{ohm-cm})^{-1}$ over this temperature range.

As stated above, at salt concentrations lower than the 3:1 stoichiometry, uncomplexed crystalline polymer appeared in the X-ray diffraction patterns. In the 3:1 to 4:1 stoichiometry range a large decrease in conductivity is observed as a second phase of crystalline PESc appears. Between 4:1 and 5:1 stoichiometry the amount of crystalline PESc continues to increase but the conductivity remains nearly constant and low, Fig. 3.

DISCUSSION

The identity of the charge carrier in PESc•alkali metal salt complexes has not been determined unambiguously, however several lines of evidence suggest that both cation and anion mobility are important. The absence of an obvious electronic conduction mechanism in pure PESc and the observed low conductivity of this material suggest that the conductivity of the complex is ionic in nature. The similarity in the observed magnitudes of the conductivity for a variety of Li^+ salts ($LiCF_3SO_3$, $LiCF_3COO$, $LiBF_4$) implicates the Li^+ ion as a charge carrier (3).

To further clarify the nature of the mobile species, the conductivity responses of PESc•$NaCF_3SO_3$ complexes were investigated using both ion-blocking Pt electrodes and sodium ion-reversible amalgam electrodes. The complex admittance spectrum of PESc•$NaCF_3SO_3$ using ion-blocking Pt electrodes consists of an arc followed by a spur. This behavior may be effectively modeled with an equivalent circuit containing a capacitance (apparently geometric) in parallel with both a resistance (apparently bulk electrolyte) and a second capacitance (apparently electrical double layer). The admittance plots obtained using sodium ion-reversible Na-Hg electrodes consisted of a single vertical line, a result which may be modeled by an equivalent circuit containing a capacitance (geometric) in parallel with a resistance (bulk). Since the magnitude of the double-layer capacitance was greatly reduced by the use of sodium ion-reversible electrodes, the cation is implicated as a charge carrier. However it appears from preliminary measurements, performed with a polarization cell, that the transference number for Na^+ is on the order of 0.1 at 60°C; therefore the bulk of the current is carried by the anion (15).

The conductivity behavior observed in the PESc·LiBF$_4$ stoichiometry range 1:1 to 3:1 demonstrates that effects other than than of charge carrier concentration dominate the ion mobility. The temperature dependent conductivity, whether of Arrhenius form or in a form related to amorphous behavior contain a pre-factor which predicts increasing conductivity with increasing carrier concentration. The observation of the opposite behavior indicates that changes in the physical characteristics of the PESc·LiBF$_4$ complexes dominate the conductivity response.

Decrease of conductivity with increasing carrier concentration is well-known in framework solid electrolytes, where it is associated with strong correlation of the charge carriers (16). It has also been observed previously for polymeric solid electrolytes such as poly(ethylene oxide) (13) and poly(propylene oxide) (17).

Large amplitude polymer segmental motion is thought to be important in the ion transport process in polymer electrolytes (3, 12-14). The variation in ionic conductivity with carrier concentration in the PESc·LiBF$_4$ complexes may be attributed to the relative freedom of mobility of polymer chain segments. The 3:1 PESc·LiBF$_4$ stoichiometry represents the lowest salt concentration for which complex formation is complete, i.e., no crystalline regions of uncomplexed polymer remain. As salt concentration is increased above the 3:1 ratio the rigidity is observed to increase, and higher glass transition temperatures and diminished conductivity result, apparently due to the progressive immobilization of polymer chains. It is, however, noteworthy that in the present case the variations in conductivity (and in apparent fluidity) are so sizeable, given the very small change in glass transition temperatures. Table 1 shows only small changes in glass transition temperature over the same stoichiometry range for which Figure 3 shows large conductivity variation, and over which the apparent viscosity rises sharply. The inverse viscosity, or the fluidity, is given, using simple free-volume type arguments, by eq. 2 (13,17).

$$\eta^{-1} = C \exp \{- \frac{E_a}{kT} - \frac{\gamma V^*}{V_{Fg} + \alpha(T-T_g)} \} \qquad (2)$$

Here C is a constant, E_a an activation energy for polymer rearrangement, γ a geometric factor accounting for free-volume overlap; V^* and V_{Fg} are respectively the minimum hole size to accommodate the moving chain segment and the free volume at T_g; α is the derivative of free volume with temperature. Now upon changing from 1:1 to 3:1 salt concentration, only α and T_g in eq. 2 will change very much. But the very small T_g change (17° out of 300) substituted into eq. 2 will not lead to substantive changes in η^{-1} unless α is very large.

Again using free-volume theory, the ionic conductivity can be written (13)

$$\sigma T = \sigma_0 \exp \{ - \frac{\gamma V_2^*}{V_{Fg} + \alpha(T-T_g)} - \frac{E_a + E_b + W/2e}{kT} \}, \qquad (3)$$

where σ_0 is temperature-independent, V_2^* is the minimum hole size for an ionic hopper, and the second, activation-energy term in the exponent characterizes the ion-pair dissociation and activated jumping. The simple point to be made, then, is that the observed sharp peak in Figure 3 appears to go beyond the free-volume result, eq. 3: the essential behavior of the σT product should, from comparison of eq. 3 with eq. 2, follow the sample fluidity, if free-volume ideas hold. This is reasonable in a free-volume context: as T is increased above T_g, the volume available for motion, either of polymer chains or of solvent, should increase proportionally to $T-T_g$. As T_g increases, with increased salt concentration, the free volume should drop, decreasing both σT and η^{-1}. What is not expected is the very sharp drop of Figure 3, given the small change in T_g. A possible explanation for this lies in the kinetic behavior of the free volume: if the polymer motions occur slowly (high viscosity), the ions may not be able to take advantage of the free volume for transport. This possibility was alluded to by Cohen and Grest (18), and forms the basis of a dynamic percolation theory being developed in this laboratory (19).

ACKNOWLEDGMENT

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Table 1. Comparison of glass transition temperatures and conductivities for PESc·$LiBF_4$ complexes at various stoichiometries

Ratio of PESc to $LiBF_4$	T_g, °K	Conductivity at 65°C, $(\Omega\ cm)^{-1}$
(pure PESc)	272.1	-
3:1	288.2	3.4×10^{-6}
2:1	288.4	1.8×10^{-6}
1.5:1	295.8	4.9×10^{-7}
1:1	299.7	2.0×10^{-7}

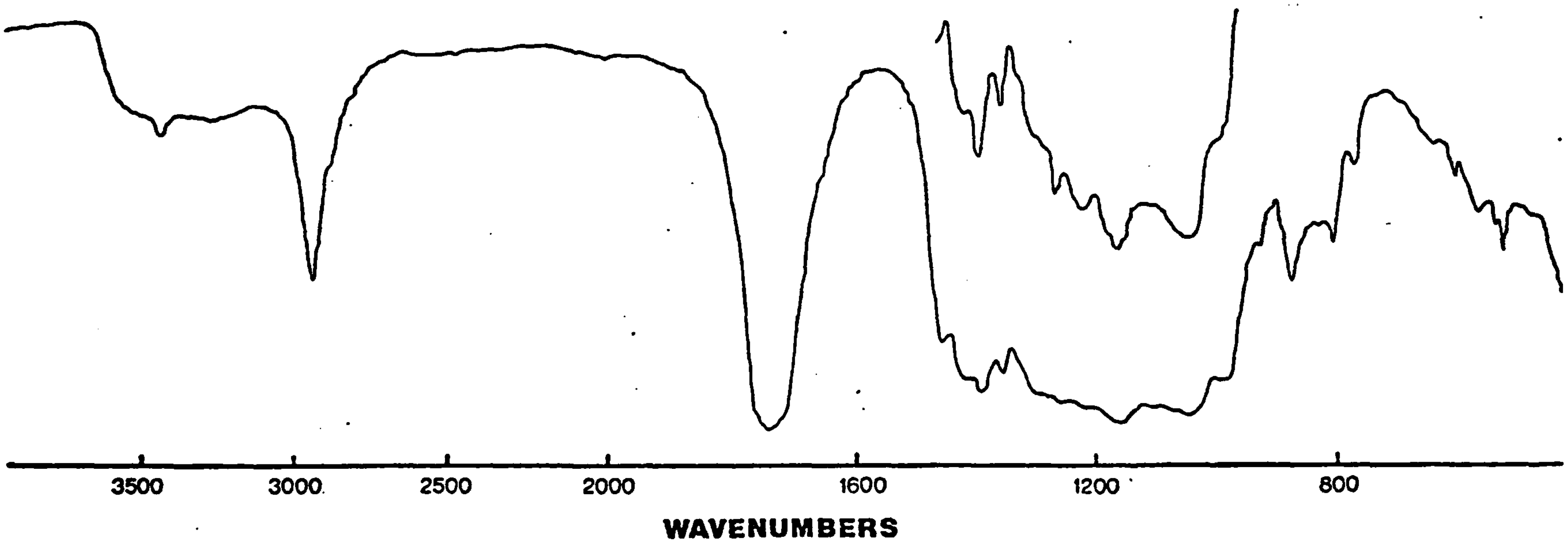
Figure Captions

Figure 1. Infrared spectrum of PESc·$LiBF_4$, 2:1.

Figure 2. Representative complex admittance plot for PESc·$LiBF_4$, 3:1, complex at 70° using ion-blocking electrodes.

Figure 3. Conductivity vs. composition for PESc·$LiBF_4$.

Figure 4. Variable temperature conductivity for PESc·$LiBF_4$: 1:1 (●); 2:1 (▲); 3:1 (■); 6:1 (+).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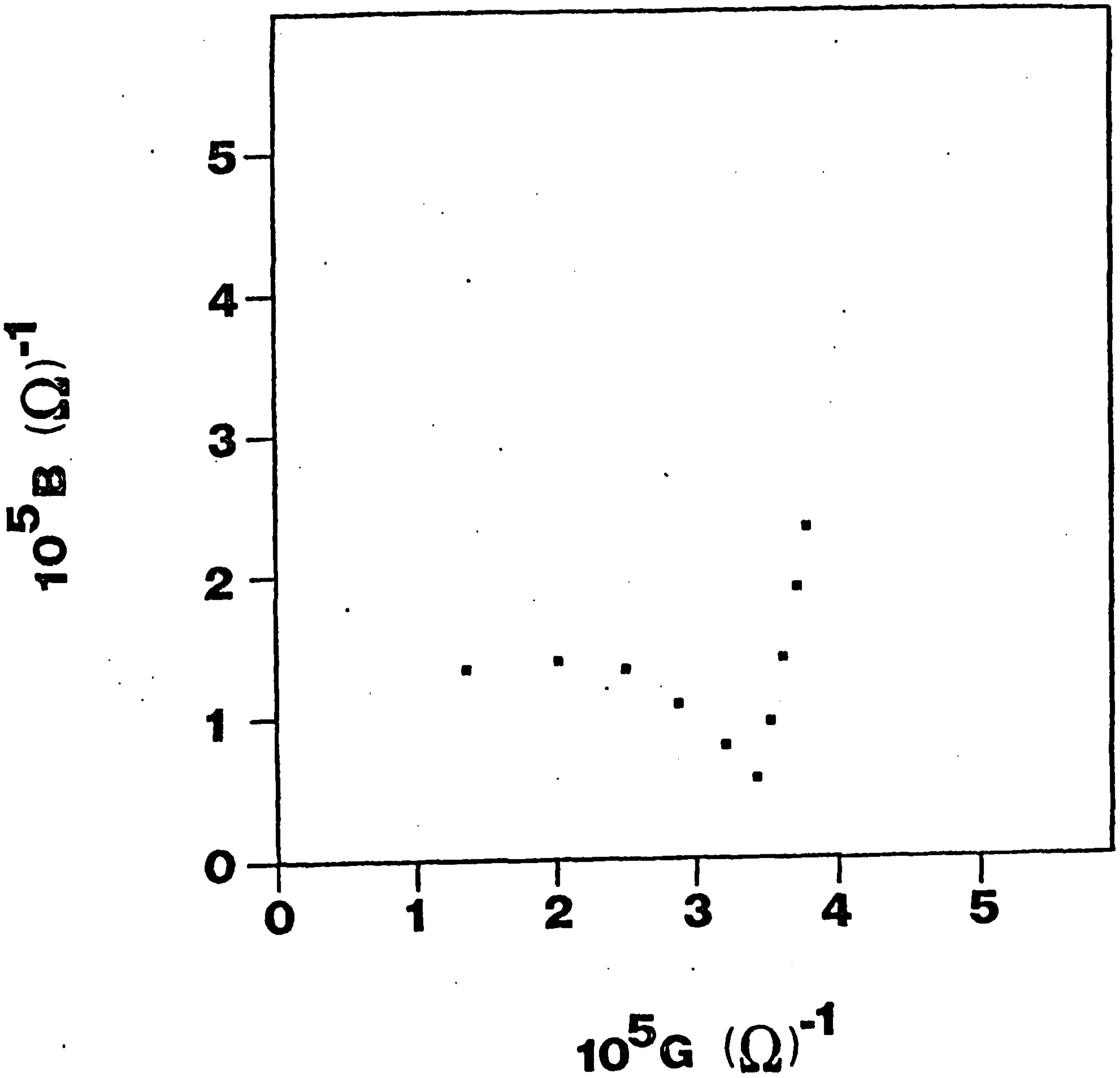

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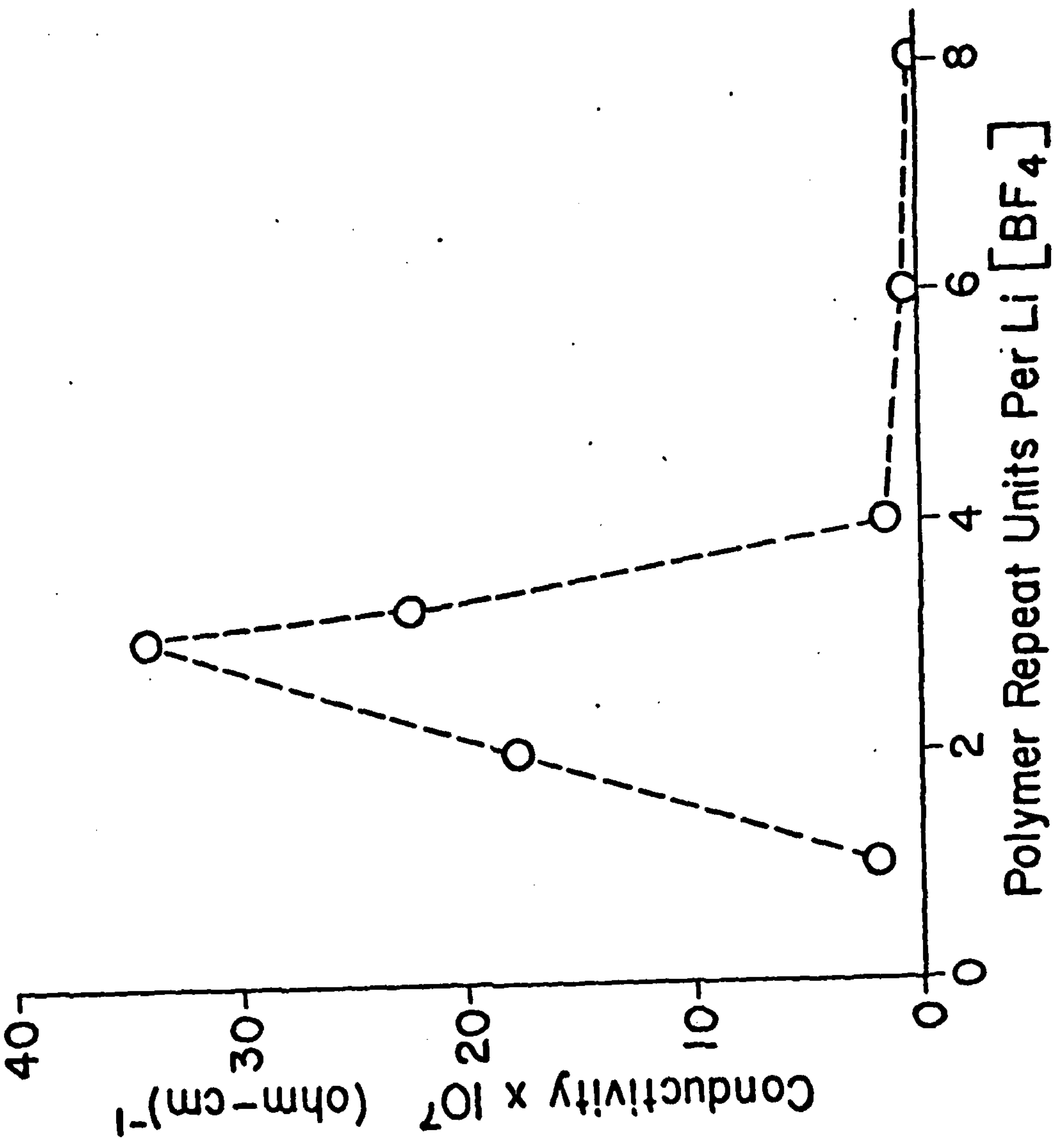
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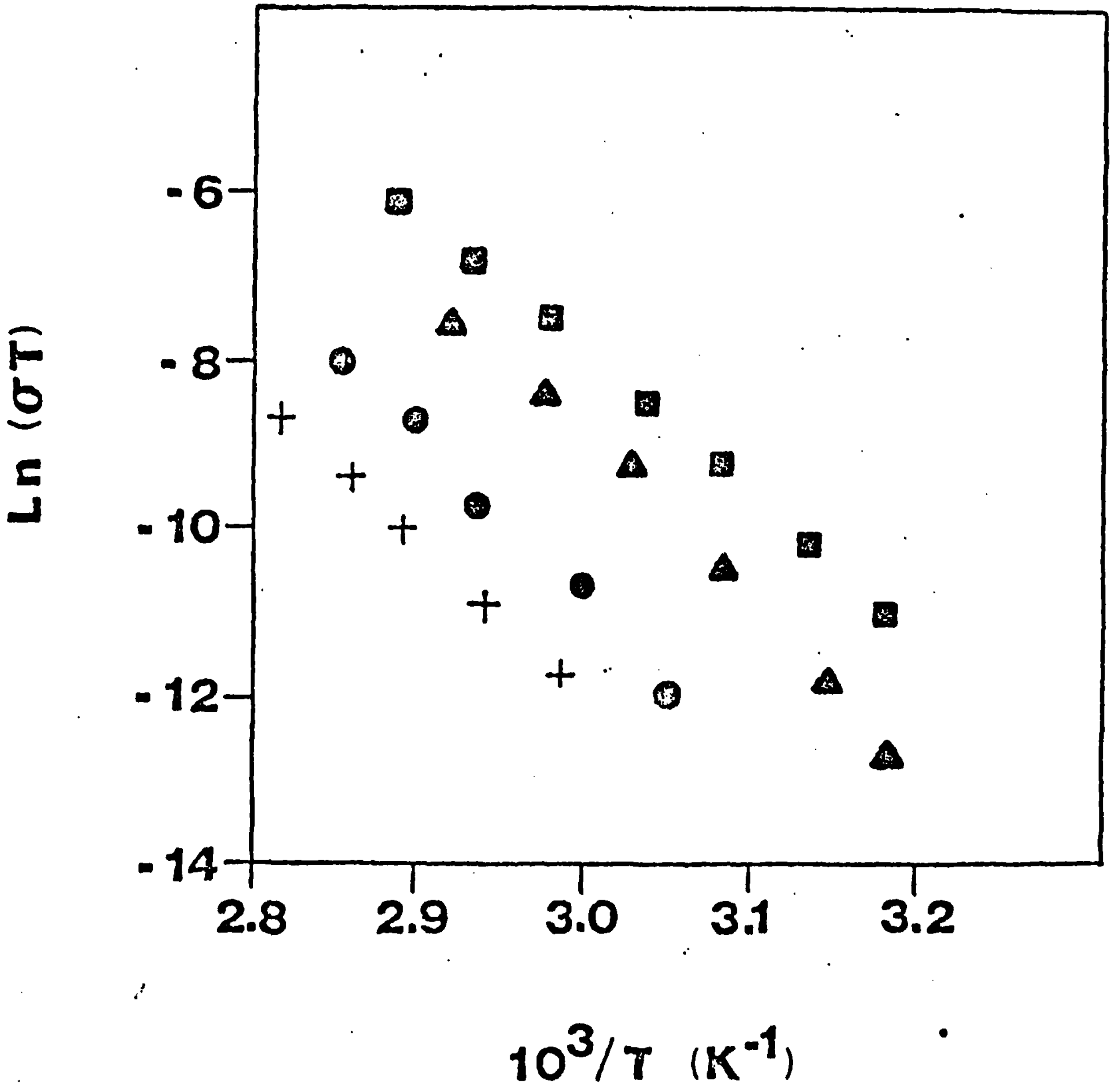
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