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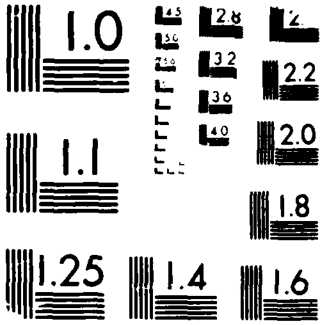

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CONTRACT N00014-80-C-0532

Task No. NR359-746

Technical Report No. 019

Polymeric Electrolytes

by

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Accepted for publication in ChemTech

ABSTRACT

Complexes between polar polymers and alkali metal salts often exhibit electrical conductivity by ion transport. The principles governing polymer-salt complex formation and ion transport in these polymers are reviewed. A variety of polymer electrolytes is described including the best room temperature conductors, which are based on polyphosphazenes.

Introduction

Research on solvent-free polymer electrolytes is currently very active, because of their potential applications in high energy density batteries, specific ion sensors, electrochromic displays, and other electrochemical devices. Pure ionic and mixed ionic-electronic conducting polymer-salt complexes will be discussed in this report.

P. V. Wright first reported the ionic conductivity of solvent-free polymer-salt complexes formed from poly(ethylene oxide), PEO.(1,2) Alkali metal salts and PEO form complexes according to Equation 1. Armand and co-workers, after more extensive studies on PEO and poly(propylene oxide), PPO, polymer-salt complexes, first proposed the use of these complexes in solid state devices.(3,4)

$$(m)MX + (C_2H_4O) \dashrightarrow [(MX)_m(C_2H_4O)] \qquad (1)$$

M = alkali metal, X = large anion.

Vibrational spectroscopy,(5) X-ray diffraction(6) and EXAFS(7) spectroscopy studies have provided structural information on PEO-salt complexes. For the sodium and lithium complexes, the cations are coordinated to the polyether oxygen atoms, and these cations reside within the helical tunnel of the PEO which is in a $(T_2GT_2\bar{G})$ conformation.(5) This proposed structure is comparable to the complexes formed between alkali metal salts and crown ethers.(8,9) The formation of PEO-salt complexes, as in Equation 1, can be understood in terms of a balance between the lattice energy of the salt and the coordination energy of the cation by the polymer. In general, salts with large mononegative anions favor complex formation because of their low lattice energies.

The free volume and configurational entropy models have been used to describe the temperature and concentration dependent behavior of the

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Per Dr. Robt. Nowak, ONR/Code 1113ES

conductivity.(3,10) The cations and anions may both be mobile in the polymer-salt complexes, and NMR spectroscopy has given insight into the ion transport mechanisms. Several methods have been employed to elucidate the various contributions to the conductivity, these include a coulometric method,(12) pulsed field gradient NMR,(13) radiotracer diffusion(14) and potentiostatic polarization.(15) In addition to ionic conductivity, an electronic component is possible, either through the polymer chain or by inter-ionic electron transfer. Knowledge of the fraction of charge carried by the various mobile species is fundamental to understanding the charge transport in these materials.

Applications

Currently most of the work on solvent-free polymer salt complexes is focused on the development of batteries, in which these complexes serve as the electrolyte sandwiched between a lithium anode and a cathode material.(16) The polymers are sufficiently compliant to maintain electrical contact through many charging and discharging cycles. The relatively low conductivity, in comparison to other electrolytes, is overcome by using thin sheets of the polymer. Cell testing programs are underway in several countries using cells such as $Li/LiSO_3CF_3.PEO/TiS_2$.(17,18)

Complex Formation and Conductivity

Polymer properties which are conducive to polymer-salt complex formation include:(5,19,20)

1. A high concentration of polar groups to solvate the cations.
2. A highly flexible backbone to permit polymer reorganization and ion solvation.
3. A low cohesive energy to produce a favorable free energy change upon polymer-salt interaction.

Factors 2 and 3 are associated with the physical properties of the polymer host, such as low glass transition temperature, T_g, and/or a low melting point, T_m. These properties can be inherent to the polymer or induced by adding plasticiziers.(21,22,42) The importance of the amorphous phase to ionic transport is indicated by the significant enhancement of the conductivity seen on the transition from a crystalline complex to a metastable amorphous phase, see Figure 1.(23)

The polymer-salt complexes are generally formed by dissolving the desired amount of salt and polymer in an appropriate solvent(s), from which thin films are cast. The concentration of the dissolved salt changes the physical properties of the electrolyte. The glass transition temperature increases with increasing salt concentration making the polymer less flexible, see Figure 2.(24)

The conductivity, σ, of a polymer electrolyte varies with the concentration of dissolved salt. In several systems a maximum has been observed in the conductivity at an intermediate salt concentration. The observed maximum is qualitatively understandable in terms of Equation 2, which is emperically observed for the transport of small molecules(25) and ions in polymers,(17) and which may be derived from either the free volume or excess entropy models.(26,27)

$$\sigma = AT^{-1/2} \exp[-B/(T-T_0)] \qquad (2)$$

In this equation, the preexponential term, A, is proportional to the charge carrier concentration, the B term is the apparent activation energy and T_0 is a parameter closely related to the T_g of the sample. In the absence of any other effects, an increase in the salt concentration should increase A and hence the conductivity. However, the associated increase in T_g will decrease the conductivity, thus the maximum conductivity occurs at intermediate salt concentrations, see Figure 3.(24,28) Equation 2 is generally applied to ionic conductivity in amorphous polymers, but the simpler Arrhenius equation (see Equation 3) is an adequate representation of the temperature variation of the conductivity for crystalline polymer electrolytes. In our studies, variable

$$\sigma = AT^{-1}\exp(-E_a/RT) \qquad (3)$$

temperature conductivity measurements were typically determined between 25 and 100 °C on polymer-salt complexes sandwiched between ion-blocking (Pt), cation reversible (Li, Na, Ag, Na/Hg) or anion reversible (Hg_2Cl_2) electrodes. The data was analyzed by complex impedance/admittance techniques over a frequency range of 5 to 500,000 Hz. The conductivity, σ, is calculated from Equation 4 using the bulk resistance value R_b(ohms) and the geometric factor: g(cm^{-1}), of the cell.

$$\sigma = g/R_b \qquad (4)$$

Ion Transport

Early work in the field of polymer electrolytes was performed on PEO and PPO systems. The initial belief was that the cations traversed the polymer by moving through a tunnel created by the helical PEO backbone. Based on spectroscopic and X-ray diffration studies, the conformation appears to be trans (CC-OC), trans (CO- CC), and alternating ± gauche (OC-CO), which is represented by ($T_2GT_2\bar{G}$).(5,29) Ion pairing studies on complexes of PEO and $NaBF_4$/$NaBH_4$ mixtures indicate that cation transport is not limited to ion motion through the helical channel of the polymer, but conduction between chains is the dominant process.(30) Berthier and co-workers have concluded from NMR studies that the amorphous phase is responsible for the ionic conductivity.(11) Similarly, it was recently shown that the amorphous form of a PEO-salt complex has a significantly higher conductivity than the corresponding crystalline form.(23)

The current theory of ionic motion in polymers is that large amplitude polymer motions are responsible for ion transport. This explains why polymers with highly flexible backbones, low glass transition temperatures and large free volumes exhibit the highest ionic conductivities.

Survey of Polymer Electrolytes

A discussion of investigations carried out in this laboratory follows. Included is a brief description of the polymers studied, their physical properties and the reasons they were chosen for study.

Polyphosphazenes(32) The phosphazenes were studied as electroyte hosts because of their low T_g and relative ease of sidegroup substitution. They consist of a backbone of alternating nitrogen and phosphorus atoms with each phosphorus having two sidegroups, ie. $[N=PR_1R_2]_n$.(33) The sidegroups can vary from simple halides to a variety of organic, inorganic and organometallic moieties. The physical and chemical characteristics of these polymers are modified by the selective incorporation of sidegroups to give low T_g,(33) low T_m values and ionic conduction.

The polymer, poly(bis(methoxyethoxyethoxy)phosphazene), MEEP(1),(24) is produced by the reaction of sodium 2-(2-methoxy ethoxy)ethoxide with poly(dichlorophosphazene). MEEP (T_g = -83.5 °C) is amorphous and soluble both in water and THF. It forms solvent-free, single phase, amorphous complexes with a wide variety of mono-, di- and trivalent salts.(34) The room temperature conductivity, of MEEP-lithium salt complexes, is 2 to 3 orders of magnitude higher than any lithium ion conductor of PEO. At 25 °C the conductivity of $[(LiSO_3CF_3)_{0.167}$ MEEP$]$ is 2.2 x 10^{-5} $(ohm^{-1}\ cm^{-1})$ compared to 1.8 x $10^{-8}(ohm^{-1}cm^{-1})$ for $[(LiSO_3CF_3)_{0.125}PEO)]_n$. Figure 4 shows the electrical conductivity of $[\{M(SO_3CF_3)\}_{0}.25\ MEEP]_n$ complexes for M = Sr, Li, Na and Ag.(24)

Poly(ethylene oxide).(35) PEO has a polymer repeat unit of CH_2CH_2O (abbreviated to EO) and is the most widely studied and characterized polymer-salt host. We are now investigating this material, as a host for ions which will give mixed ionic-electronic conductors. PEO will take up high concentrations of salts, and in most complexes the anions and cations appear to be separated by the polymer. If the anions are large and in contact or capable of inter-ionic electron transfer then electronic conduction may occur. This behavior is observed when iodine is added to a $[(NaI)_{0.25}EO]_n$ complex, where the formation of the polyiodides is indicated by Raman spectroscopy. The new materials have a metallic luster and appear blue/black in reflected light. Preliminary photo-response measurements have been obtained using thin films sandwiched between platinum and tin oxide coated glass electrodes. Significant photo-voltage and current were observed over the range 700 to 350 nm, see Figure 5.

Poly(alkyene sulfides)(36) The poly(alkylene sulfides), $[(CH_2)_xS]_n$ where $x=2-6$, used have molecule weights in excess of 5000. It was first thought that these analogues of PEO would provide information on the influence of different polar groups on complex formation and ionic conductivity. However, the poly(alkylene sulfides) form no lithium salt complexes and only weakly conducting silver salt complexes. In a study of the $AgNO_3$ complexes with $[(CH_2)_xS]_n$, the highest conductivity value, on varying x, was obtained for $x=5$. On varying the polymer to salt ratio for the $x=5$ $AgNO_3$ complexes, conductivities in the range of 1 to 9 x 10^{-8} (ohm^{-1} cm^{-1}) at 45 °C were recorded a for a 4:1 polymer to salt ratio.

Poly(ethylenimine).(37) PEI is usually synthesized as a highly branched polymer, which makes characterization difficult.(38) Linear PEI was first reported in 1972;(39) the preparation of high molecular weight linear PEI

(10^5) followed in 1983.(40) Linear PEI $(CH_2CH_2NH)_n$ is an analogue of PEO where the polar oxygen atom is replaced by NH. The parent polymer melts at 60 °C, has a T_g of -20 °C and like PEO forms amorphous and semi-crystalline complexes with a variety of alkali metal salts. PEI and a salt were dissolved in MeOH to form the polymer-salt complexes upon solvent removal. The X-ray diffraction patterns for $[(NaSO_3CF_3)_x \, PEI]$ ($0 \leq x \leq 1$) and the pure polymer are shown in Figure 6. A semi-crystalline complex is formed with a salt to polymer ratio of 0.25:1. Both the $x = 0.20$ and $x = 0.167$ complexes are amorphous, and have a lower T_g, and a higher conductivity than the $x = 0.25$ complex. The chemical versatility of the polymer backbone allows chemical modification either by replacing the hydrogen atom on the nitrogen or by quaternizing of the nitrogen to produce a polyelectrolyte.(22,38,40,41)

Poly(vinyl pyrrolidone)(42) Poly(vinyl pyrrolidone), PVP (II), is known to complex a wide variety of metal salts in solution.43 The parent polymer has a very high T_g of 180 °C, which should rule this polymer out as a host material. However, the brittle PVP can be plasticized with poly(ethylene glycol), PEG (molecular weight 300), which reduces the T_g to -55 °C; the optimum ratio of PEG to PVP being 2:1. The plasticized polymer readily forms complexes with $LiSO_3CF_3$ that exhibit ionic conductivity. $[PVP_x.LiSO_3\,CF_3.PEG_{2x}]_n$ ($1 \leq x \leq 10$) forms amorphous homogenous systems as indicated by DSC (single T_g) and X-ray diffraction (no peaks). The ionic conductivities of the plasticized polymer-salt complexes are relatively constant over a wide range of polymer to salt ratios; conductivities of 5×10^{-5} ($ohms^{-1}\,cm^{-1}$) at 100 °C are typical, see Figure 7. One problem with plasticizing the polymer with PEG is that the hydroxyl groups react with lithium metal, and hence the PVP plasticized electrolyte could not be used in high energy density batteries.

Other Polymer Hosts Other polymer electrolyte systems which have been investigated include PPO (III) which forms complexes primarily with lithium and sodium salts, and poly(ethylene succinate), PESc (IV), which forms semi-crystalline complexes with sodium and lithium salts.(29,44) Poly(β-propiolactone), PPL (V), polymer salt complexes when quenched rapidly from the melt form amorphous materials which have significantly higher ionic conductivities than the corresponding crystalline complexes.(45) Poly(diallyldimethylammonium chloride), DDAC (VI),(22) and sodium poly(styrene sulfonate), NaPSS (VII),(23) plasticised with PEG contain only one mobile ionic species, thus their electrical properties may be attributed to a single charge carrier. Highly conducting and dimensionally stable crosslinked networks based on polysioloxanes (46) (VIII) and polyphosphazenes (47) have also been synthesized and characterized, see figure 8.

Conclusions

A wide variety of polymers can serve as hosts for ionic species to form polymer electrolytes. A strong correlation is observed between the physical properties of the polymer and the conductivity. Plasticizers provide a means of altering the T_g, one of the critical physical properties, and thereby improving ionic conductivity. Solvent-free polymers can also host anions or cations which are good electronic conductors the resulting polymer-salt complex becomes a mixed ionic-electronic conductor.

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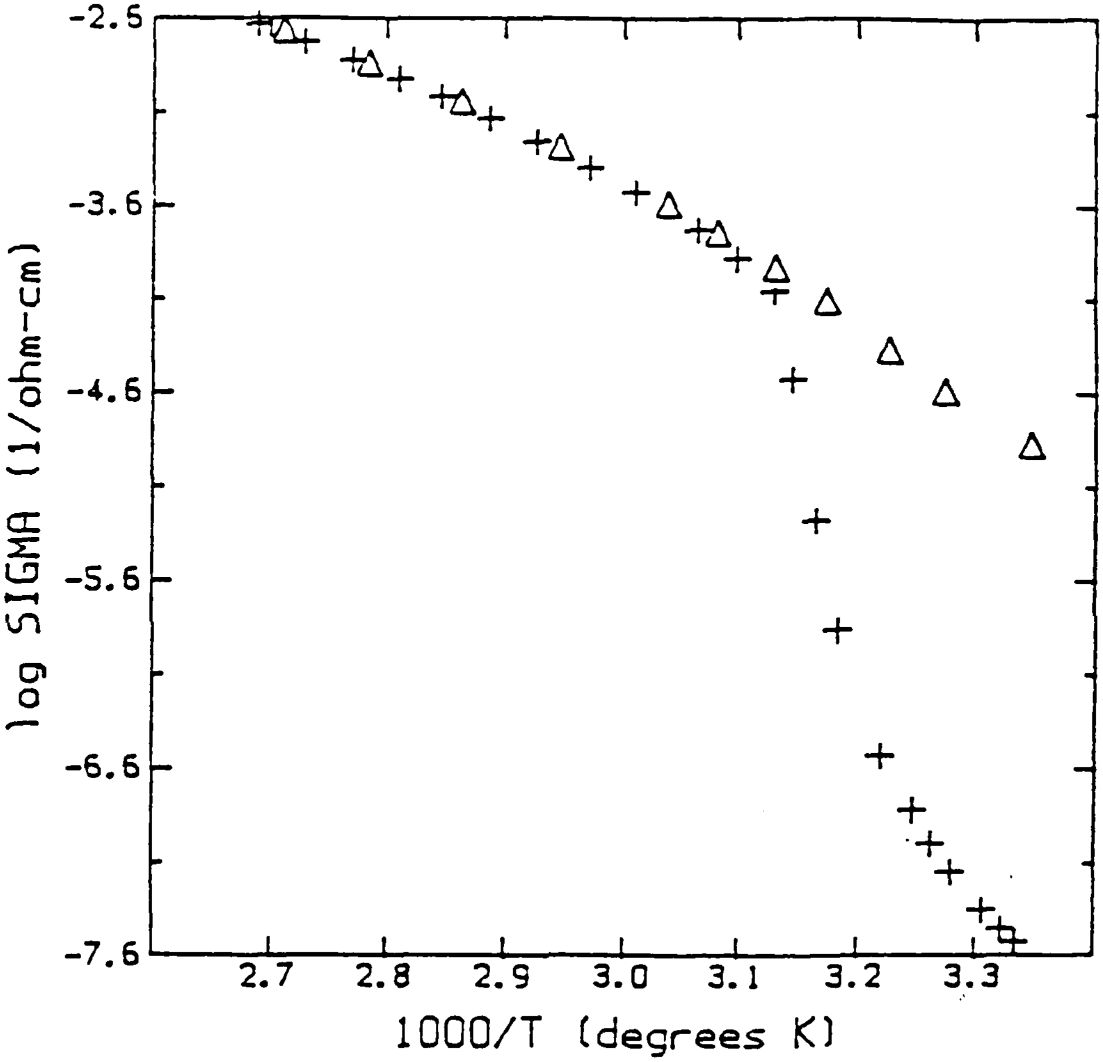
Figure Captions

1. Electrical conductivity, σ (1/ohm-cm), plotted as $\log(\sigma)$ vs 1/T for $[(NH_4SCN)_{0.125}PEO]_n$; +, heating; Δ, cooling.
2. Observed glass transition temperature (°K) of $[(A_gSO_3CF_3)_xMEEP]_n$ complexes ($0 \leq x \leq 0,5$).
3. Log sigma vs. cation per polymer repeat unit, at 70 °C for $[AgSO_3CF_3)_xMEEP]_n$ complexes ($0 \leq x \leq 1$).
4. Electrical conductivity for $\{[M(SO_3CF_3)_x]_{0.25}MEEP\}_n$ complexes; Δ, pure uncomplexed polymer; +, Sr; [ ], Li; Δ, Na; x, Ag.
5. Short circuit photocurrent vs. wavelength for $[(NaI_3)\ _{0.25}EO]_n$ between indium-tin oxide and platinum electrodes.
6. X-ray powder patterns for $[(NaSO_3CF_3)_xPEI,]_n$ complexes ($0 \leq x \leq 1$) and pure $NaSO_3CF_3$.
7. Electrical conductivity, at 80 °C, for $[PVP_x \cdot LiSO_3CF_3, PEG_{2x}]_n$ complexes ($1 \leq x \leq 5$).
8. Host polymers for solvent-free polymer electrolytes.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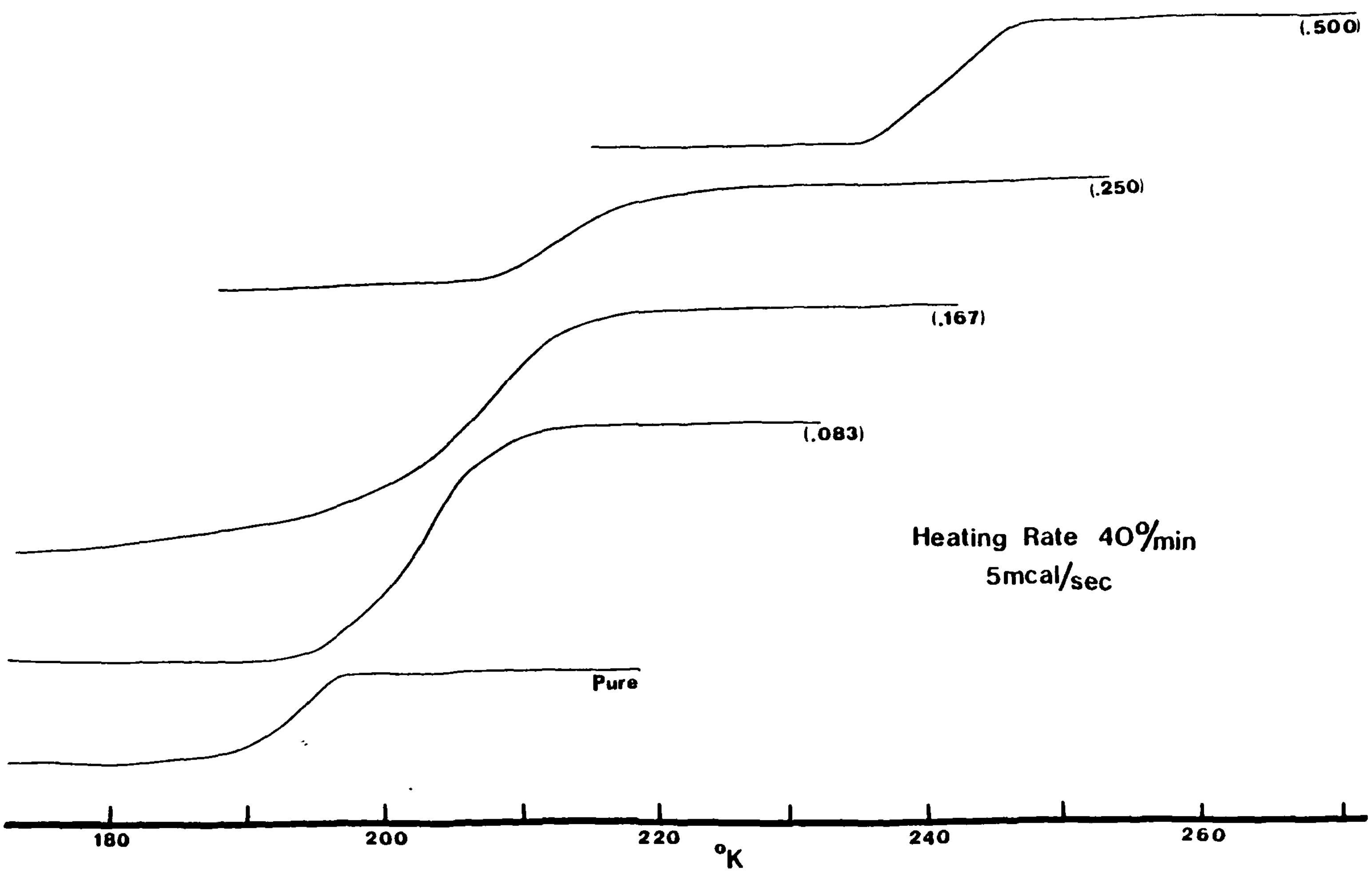
1000/T (degrees K)



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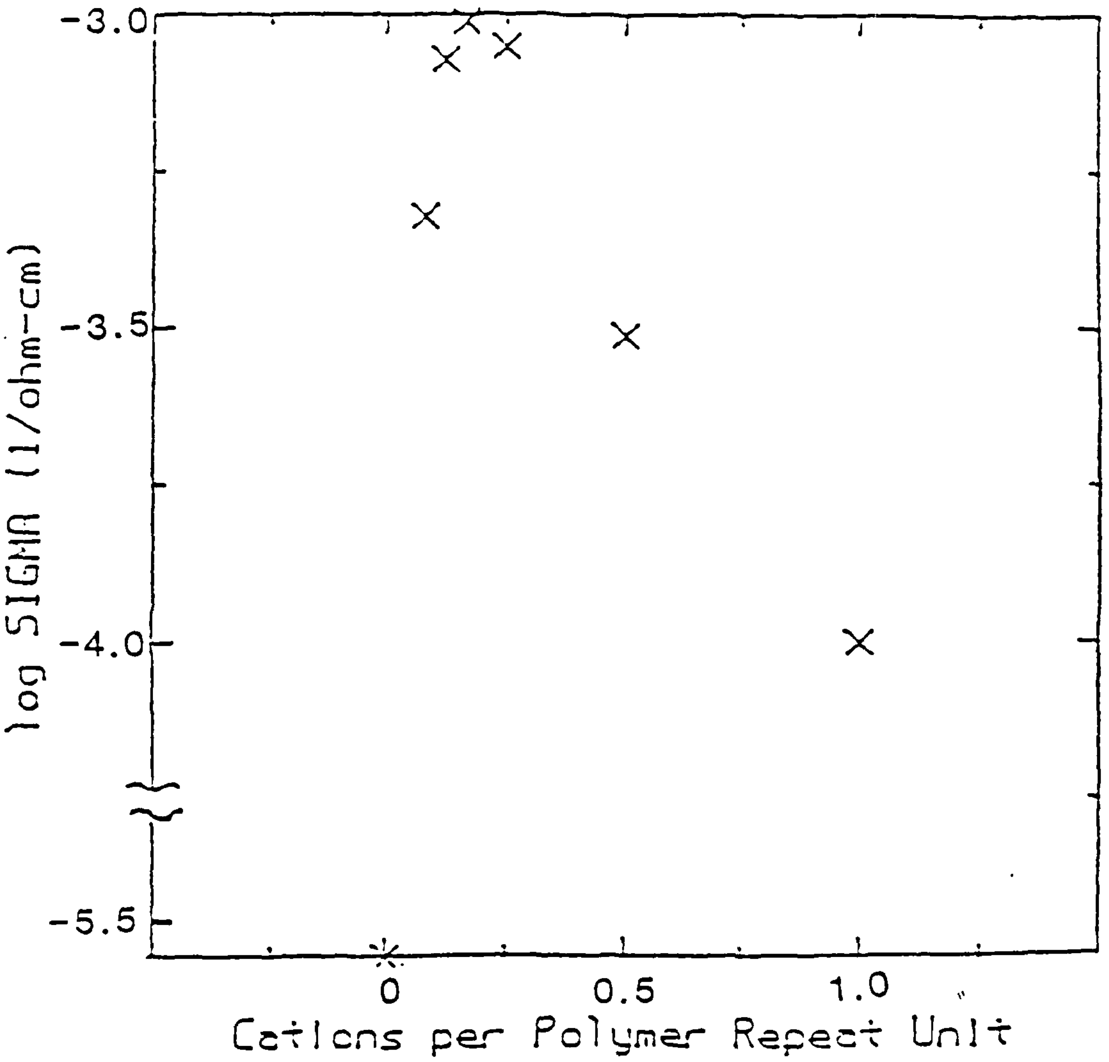
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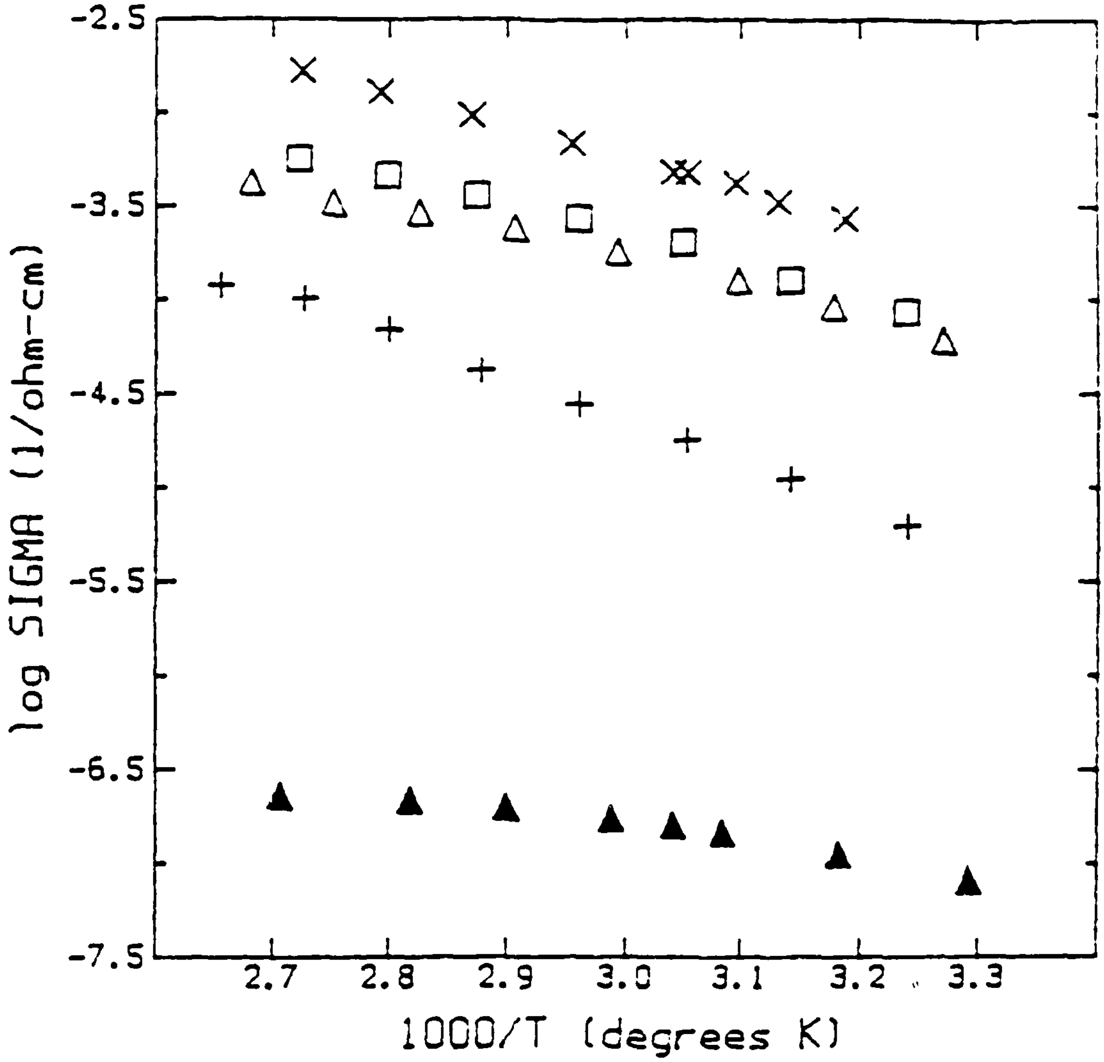
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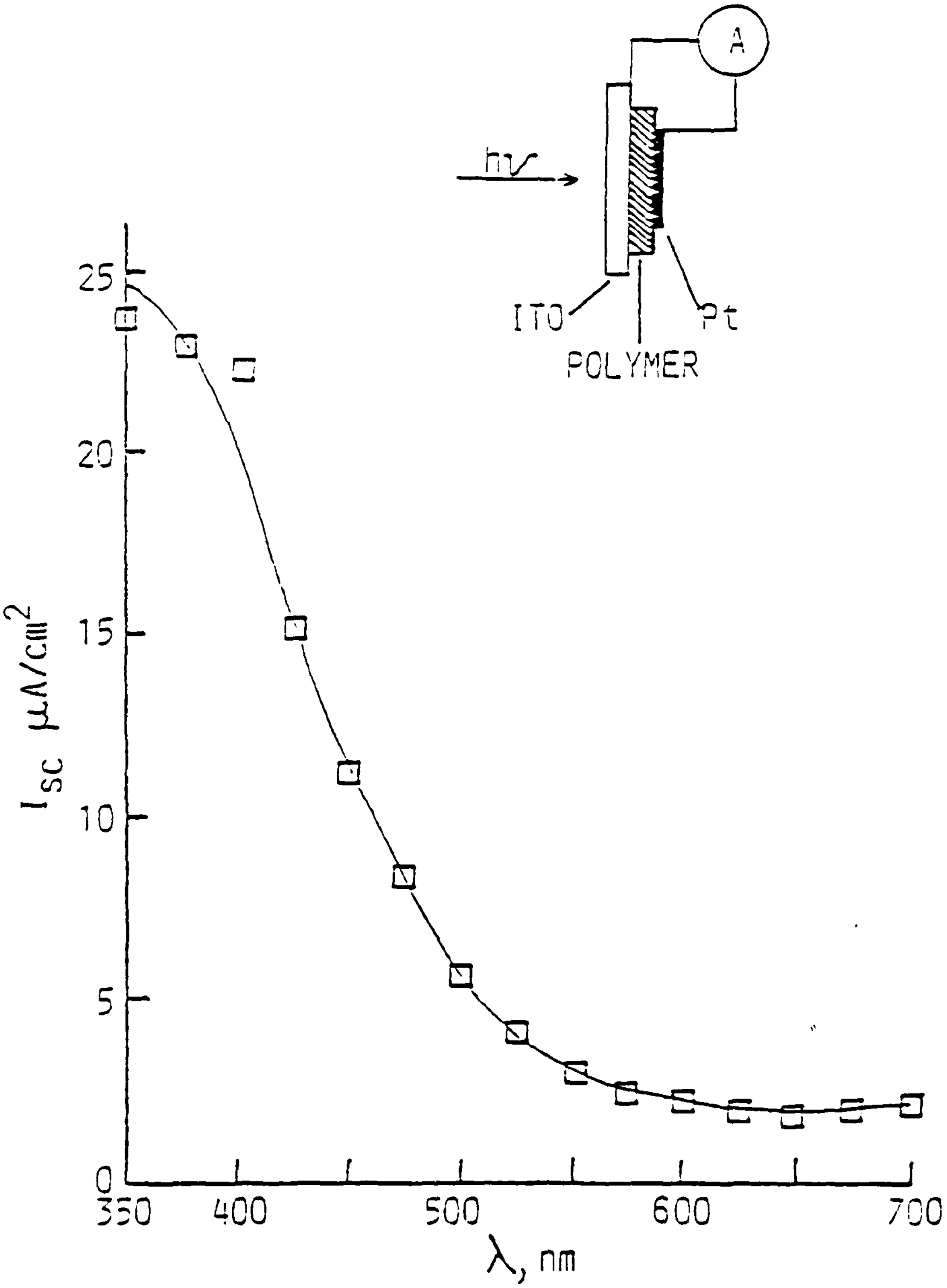

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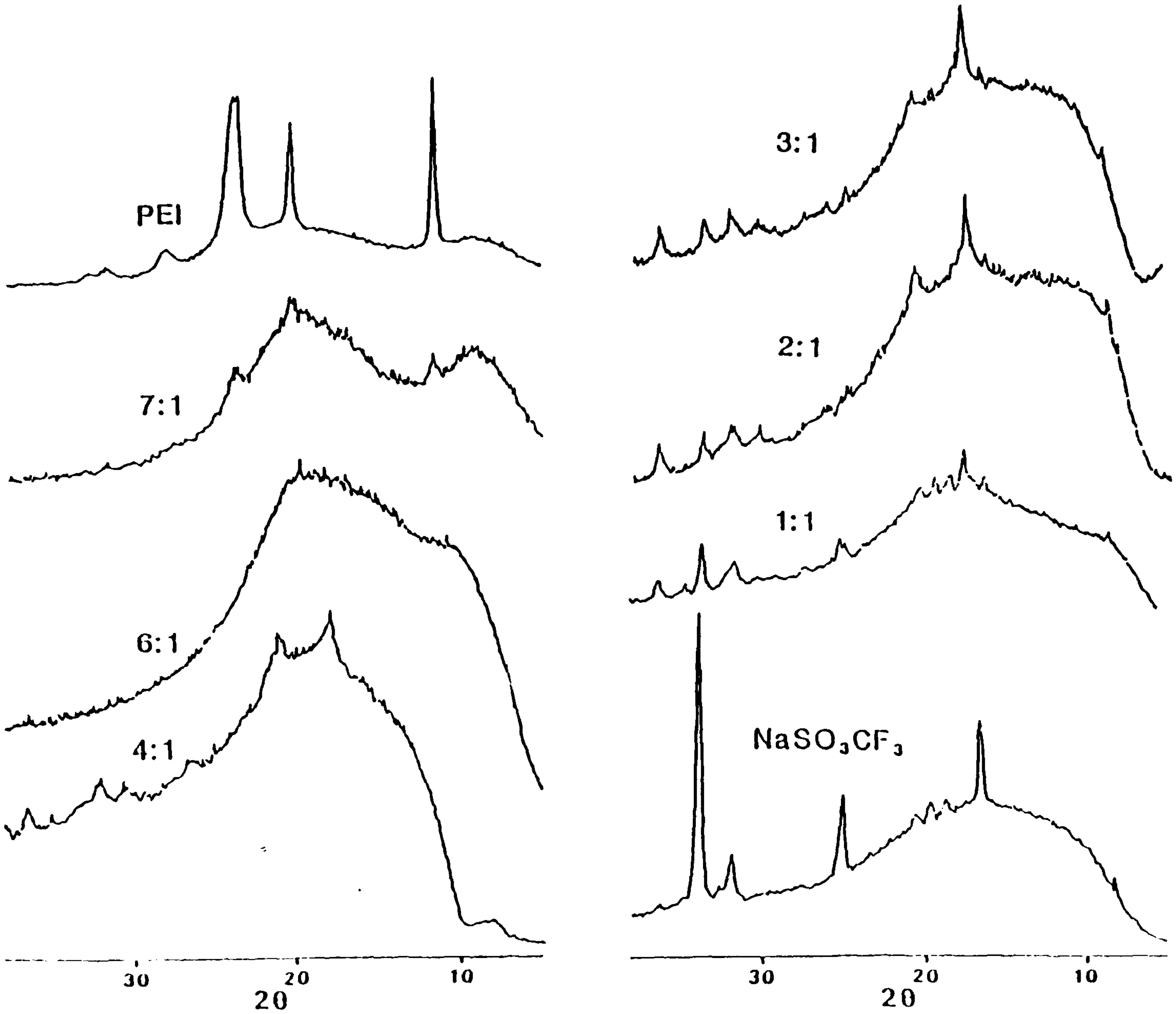
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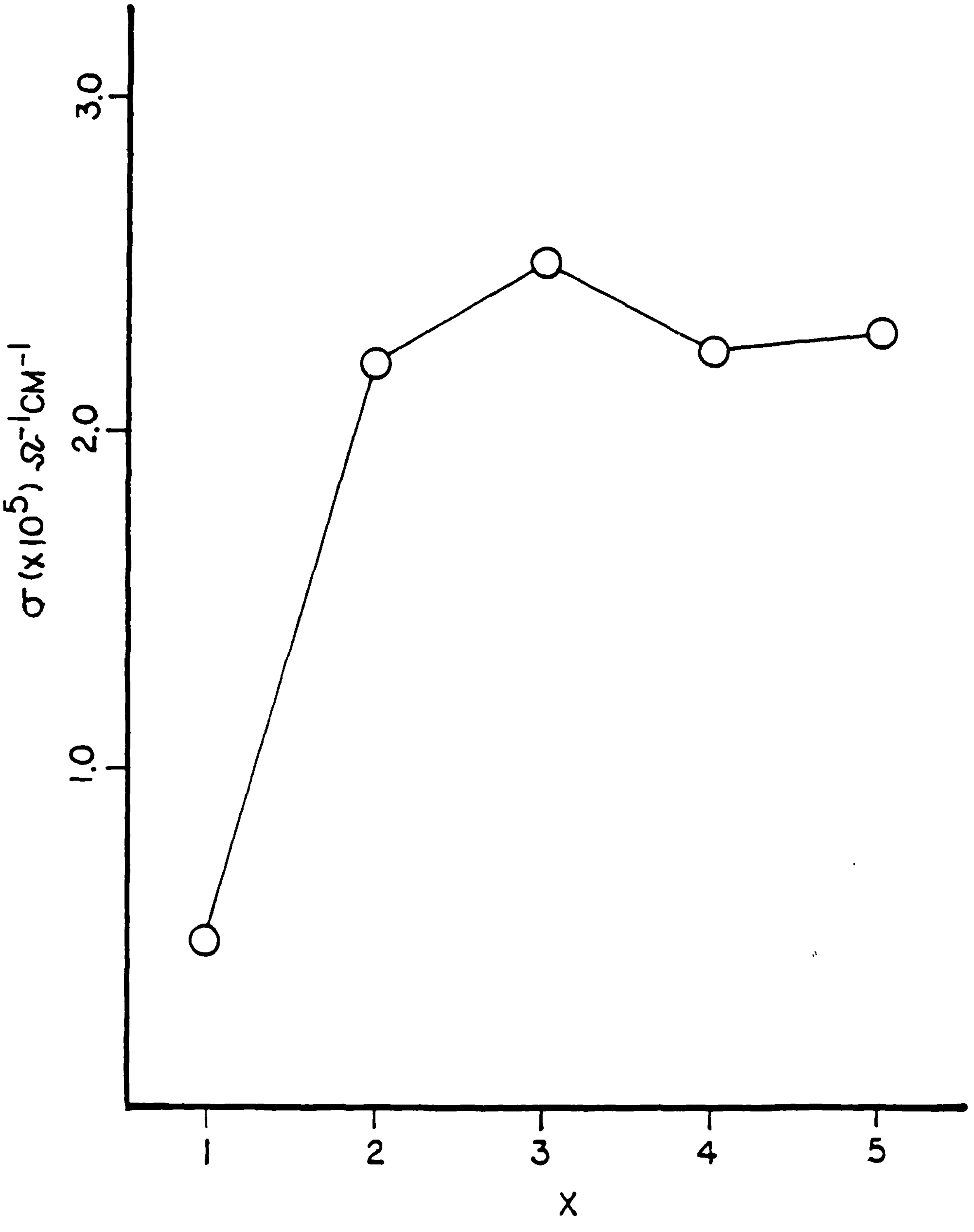

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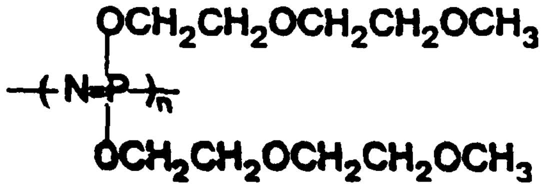

$\left(N{=}\overset{OCH_2CH_2OCH_2CH_2OCH_3}{\underset{OCH_2CH_2OCH_2CH_2OCH_3}{P}}\right)_n$

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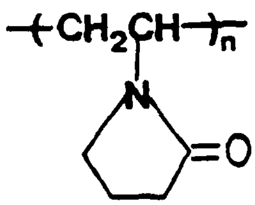

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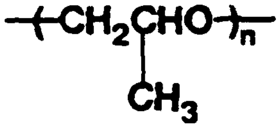

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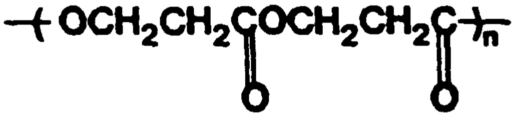
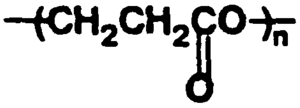


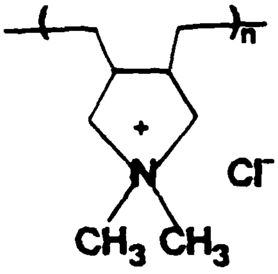
$\left(OCH_2CH_2\underset{\underset{O}{\|}}{C}OCH_2CH_2\underset{\underset{O}{\|}}{C}\right)_n$

V

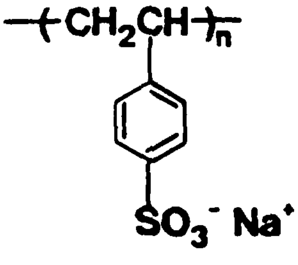


$\left(CH_2CH_2\underset{\underset{O}{\|}}{C}O\right)_n$

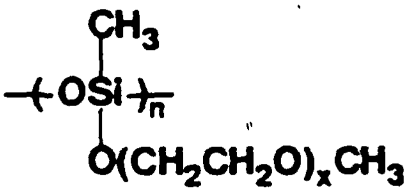
VI



VII



VIII



$\left(O\overset{CH_3}{\underset{O(CH_2CH_2O)_xCH_3}{Si}}\right)_n$

END
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