TECHNICAL REPORT NO. 8

"PIEZOELECTRICITY IN POLYACRYLONITRILE"

by

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The piezoelectricity and related properties in ion-doped ($NH_4 NO_3$, $NaNO_3$) and undoped films of polyacrylonitrile have been measured as a function of temperature. The piezoelectric constants of both ion-doped and undoped films show a maximum around $80°C$ and thereafter decrease markedly with temperature. A maximum of thermally stimulated discharge current (TSDC) around $90°C$ is observed in both ion-doped and undoped films. An abrupt decrease of piezo-electric constant around $90°C$ and TSDC maximum around $90°C$ are ascribed to randomization of nitrile dipoles in ordered regions. The piezoelectric

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Abstract

The piezoelectric and related properties in ion-doped (NH_4NO_3, $NaNO_3$) and undoped films of polyacrylonitrile have been measured as a function of temperature. The piezoelectric constants of both ion-doped and undoped films show a maximum around $80^{\circ}C$ and there- after decrease markedly with temperature. A maximum of thermally stimulated discharge current (TSDC) around $90^{\circ}C$ is observed in both ion-doped and undoped films. An abrupt decrease of piezo- electric constant around $90^{\circ}C$ and TSDC maximum around $90^{\circ}C$ are ascribed to randomization of nitrile dipol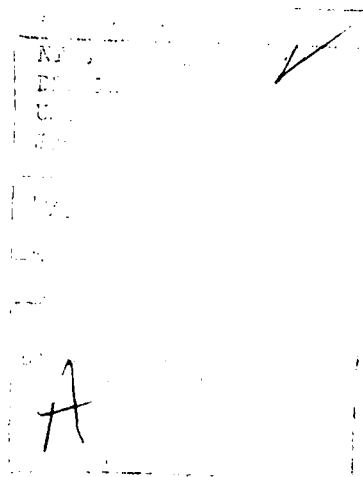es in ordered regions. The piezoelectric constant of stretched films has a tendency to increase with stretching. The piezoelectric constant, d_{31}, changes from positive to negative when temperature rises above $110^{\circ}C$.

INTRODUCTION

Piezoelectric properties have been investigated for a variety of polymers (1,2). Since the discovery of strong piezoelectric activity in stretched and poled polyvinylidene fluoride (PVDF) (3), PVDF has attracted special interest and has received a variety of practical applications. But a complete understanding of the piezoelectricity in polymers has not been achieved.

Space charges and/or preferred orientation of small parts of macromolecules having nonzero dipole moments are usually considered to be the origin of the residual polarization of electret polymers. If residual polarization arises from dipole orientation, a polymer which has large dipole moment may have high piezoelectric activity. The value of dipole moment per monomer unit of the form-I crystal of PVDF, which has high piezoelectric activity, is 2.1 Debye units. However, polyacrylonitrile (PAN) repeat units have dipole moments in excess of 3 Debye units, and its dipoles can be oriented by an applied electrical field (4,5). Thus, high piezoelectric activity of PAN is expected.

According to results of infrared internal reflection spectroscopic measurements by Stupp, et al., (5), randomization of oriented dipoles is thermally induced as the temperature is raised above $90^{\circ}C$. Around this temperature, both dielectric relaxation (11-14) and mechanical relaxation (8-10) have been observed. Therefore, one would expect the piezoelectric constant to decay irrecoverably in this temperature region.

Piezoelectricity arises from a combination of dielectric and elastic characteristics. Even though it is a rather complicated phenomenon, some information about chemical and/or physical structure of a polymer might be obtained from piezoelectric measurements, since piezoelectricity is strongly influenced by internal structure of the sample.

Many papers concerning the structure (16-21) and properties of PAN have been published, but the piezoelectricity of PAN has not been reported in any detail. In this paper, the results of the temperature dependence of the piezoelectric constant of PAN is reported.

EXPERIMENTAL

Polyacrylonitrile (PAN) was purified as follows: PAN powders were dissolved in dimethyl formamide (DMF) at a concentration of 5 wt%. The solution was then poured into distilled water to obtain purified PAN in a loose fibrous form. This PAN was again dissolved in DMF (2 wt%). PAN films were cast on a glass surface from the 2 wt% DMF solution under reduced pressure for 24 hours at room temperature. The cast films were then dried in an evacuated vacuum oven for 24 hours at 40°C. As-cast films were uniaxially stretched at 90°C and then annealed at 130°C for 30 min. Gold was evaporated onto each side of the sample to serve as electrodes. PAN films doped with $NaNO_3$ and NH_4NO_3 were prepared by first dissolving the salt in DMF and subsequently adding it dropwise to the PAN solution in DMF. The PAN powders were supplied from Standard Oil Company (Ohio), Cleveland, Ohio. The material is reported to have a weight average molecular weight in excess of 35,000. Thicknesses of samples ranged from 30 to 54 μm. Dimensions of film samples for piezoelectric measurements were 2 cm by 0.4 cm, and the area of electrode was 0.21 cm^2. Dimensions of film samples for thermally stimulated discharge (TSD) measurements were 2.5 cm by 2.5 cm, and the area of electrode was 3.14 cm^2.

A Rheovibron model DD-II (Toyo Kogyo Co., Japan) was used to measure the piezoelectric-strain constant, d_{31}, piezoelectric-stress constant, e_{31}, and elastic modulus, C. The 1-axis is taken along length (stretching direction) and 3-axis along thickness (poling direction). The dynamic stress and the piezoelectric polarization induced by applying a sinusoidal alternating strain of 11 Hz (with oscillating displacement strain of approximately 5×10^{-6}) were measured, and absolute values of d_{31}, e_{31}, and C were obtained. The piezoelectric polarization was detected using charge amplifier under short-circuit conditions. The measurement was made in the temperature region between room temperature and about 150°C, with a heating rate of about 1°C/min.

TSDC thermograms and direct current (d.c.) conductivity were recorded with an Electret Thermal Analyzer (Toyo-Seiki, Seisaku-Sho, Ltd.) (4). The heating rate was 2°C/min. All specimens that were polarized were held for 30 min. under the imposed electrical field at 130°C and then cooled at room temperature under the applied electrical field. The conditions of the specimens are listed in Table 1.

RESULTS

Figures 1 and 2 show the temperature-dependence of the piezoelectric-strain constant, d_{31}, and -stress constant, e_{31}, for stretched (2 times), designated PE, and unstretched, designated PN, PAN films. When tension is given to the specimen at room temperature, negative charge is induced on that surface to which the positive field was applied. In the case of stretched films, the piezo-exciting tension is applied in the direction of the orientation of molecular chains. In the temperature region below about $70^{\circ}C$, both d_{31} and e_{31} increase with temperature. However, above $80^{\circ}C$, d_{31} and e_{31} decrease remarkably. The piezoelectric constants of PE1 (first run of a plain, stretched specimen) show a second peak around $120^{\circ}C$. The piezoelectric constants for a second run, (PE2) at room temperature, are about 2.5×10^{-2} of those of the first run. The d_{31}- and e_{31}-constants of PN (a plain but not-stretched specimen) do not show the second peak, and these values at room temperature are about 0.2 of those of PE1.

Figure 3 shows the temperature-dependence of the dynamic elastic modulus, C, of unstretched film. The decrease of C around $50^{\circ}C$ and the remarkable decrease above $70^{\circ}C$ may be due to β-relaxation and α_a-relaxations, respectively, as observed by Okajima, et al. (7). Ishida, et al. (11) also confirmed the β-relaxation around $60^{\circ}C$ (160Hz) in dielectric measurement, and they attributed it to a local mode relaxation.

Figure 4 represents the temperature-dependence of both of NH_4NO_3- and $NaNO_3$-doped films. The e_{31}-constants decrease steeply above $80^{\circ}C$, in the same manner as those of undoped films. The d_{31}-constants for each of these samples are listed in Table 1. Since material AE (doped with ammonium nitrate and stretched) and SN (doped with sodium nitrate but not stretched) had been polarized under a field of 2×10^4 V/cm and 1×10^4 V/cm respectively, the

observed d_{31}-constants of AE and those of SN are multiplied by normalizing

factor 2.5 and 5, respectively. It is observed that the piezoelectric

constants of PAN have a tendency to increase with elongation. Polarization

by high intensity electrical field also induces high piezoelectric activity.

DISCUSSION

The piezoelectric constants of unpolarized film is negligible, and the piezoelectric constants of the second run of a polarized film are very small as compared to those of its first run, as shown in Figures 1 and 2. This indicates that the piezoelectricity of PAN arises from the residual polarization induced by applying an electric field to the specimen.

Such polarization arises in PAN from a partial preferred orientation of dipoles and from space charge effects. Ion-doped PANs are expected to exhibit greatly magnified space charge effects, as the ions deliberately added have mobilities suitable for their being displaced during poling treatments. Since space charges tend to be trapped at a boundary between two different phases, electrical polarization due to space charge should be stabilized in inhomogeneous system. This effect is expected to be important in the case of PAN, because it is inferred to have "structure" at the 10's of Angstroms size scale. Miyachi and Andrews (10) suggested a three-phase structure consisting of two different amorphous phases (one more ordered or strongly cohesively bonded than the other) and a crystalline phase. Hinrichsen and Orth (18) proposed a two-phase structure based on an observation of electron micrograph of the surface of drawn PAN. Recent work by Stupp and Carr (22) contributes further to clarifying this issue. It is thought that polarization due to space charge may be stable in PAN based on its homogeneity and its large nitrile dipole moment.

Figure 5 represents TSD thermograms of both ion-doped and undoped films. One notes the existence of a depolarization current peak around $90^\circ C$ in both ion-doped and undoped film. The maximum is not observed in the second run (P2). As expected, the depolarization current is increased by ion-doping. This result supports the notion that the apparent residual polarization is increased by ions. The total charge, Q, released around $90^\circ C$ for A (containing

ammonium nitrate) and P1 (plain) is about 2×10^{-6} Coul./cm^2 and 1.8×10^{-7} Coul./cm^2, respectively. One sees, therefore, that Q for NH_4NO_3-doped films is about ten times that of undoped PAN. It is obvious that the large apparent residual polarization of ion-doped film is due to the ions serving as space charges; the value of nitrile side group dipole moment should not be influenced by the presence of ions. One would ordinarily expect that ion-doped films might have high piezoelectric activity if the piezoelectricity arises from the residual polarization due to space charge. As shown in Table 1, the piezoelectric constants of ion-doped film at room temperature fail to reflect the enhanced persistent polarization that the dopant ions create.

In the temperature region where the TSDC shows maximum, loss of the preferred nitrile dipole orientation along the thickness direction has been confirmed from ATR analysis by Stupp and Carr (5). Piezoelectric constants also decrease remarkably in the same temperature region. Such a decrease in piezoelectric constants associated with an increase of D.C. conductivity has been observed for some polymers (23,24). If the decrease of both d_{31} and e_{31} (shown in Figures 1 and 2) is principally caused by the electrical conductivity, both d_{31} and e_{31} of ion-doped films should decrease at lower temperatures than those of undoped films, because of their relatively high electrical conductivity of ion-doped films, as shown in Figure 6. Figure 6 shows the second run of the temperature dependence of D.C. conductivity. According to Figure 4, the e_{31}-constants of ion-doped films decrease steeply in the same temperature region as that of undoped films. Depolarization current maximum around 90°C is also observed in both the doped film and the undoped film. The result suggests that the abrupt decrease in the piezo-electric constant of PAN around 90°C can be attributed to randomization of nitrile dipoles. It follows that the main origin of piezoelectricity below

$100^\circ C$ can probably be ascribed to the orientation of nitrile dipoles.

Piezoelectric constant is increased by stretching, as shown in Table 1. This can be explained as follows: the preferential orientation of the main chains induces an increase of the orientation of nitrile side groups into planes tending to be perpendicular to the stretching direction. This evidence is consistent with other experimental results. Comstock, et al. (4) noted that stretching PAN to its natural draw ratio (4x) permits a substantial increase in polarization from TSD measurements. The increase of the infrared dichroic ratio of nitrile stretching band (2700 cm^{-1}) due to drawing was also confirmed by Bohn, et al. (16). Similarly, it is well known that stretched and poled PVDF has very high piezoelectric activity (3,25).

The piezoelectric constant of PAN is smaller than that of PVDF in spite of the large dipole moment of nitrile groups. Such low piezoelectric activity of PAN may result from the following. The residual polarization due to dipoles is small and the degree of rotation of nitrile dipoles due to applied strain is also small. Since these factors are strongly dependent upon the micro-structure and crystallinity (order) of the specimen, the difference in piezo-electric activity between PAN and PVDF is probably caused by the difference in the inter- and intra-chain molecular organization between them. Chains in Form-I PVDF, the crystal polymorph having high piezoelectric activity, have a planar zig-zag conformation, and most of CF$_2$ dipoles orient in a common direction perpendicular to the chain backbones (26,27).

Bohn, et al. (16) proposed a single phase-laterally ordered model. They believed that the nitrile groups protrude through the cylinder wall of chain in random locations, owing to irregular kinking of the chain. Lindenmeyer (15) suggested, based on the average distance along the c-direction per monomer unit, that the chains are coiled in some sort of helical conformation. Calvin and Storr (20) also suggested a helical configuration for PAN. Hinrich-

sen, et al. (18) proposed a two-phase structure consisting of more and less ordered regions with planar zig-zag conformation in ordered regions. Recently, Warner, et al. (21) presented a rod-like model consisting of ordered and less ordered regions and a contorted helical conformation with the nitrile group oriented at various angles to the axis of the rod within each rod.

Although many details of structure of PAN are not clarified, it may be thought that the regularity in structure in PAN is less than that of PVDF. The arrangement of nitrile groups in ordered regions seems to be a crucial aspect of electrical polarization and piezoelectricity of PAN. The evidence of relative low piezoelectric activity suggests the random orientation of nitrile dipoles in ordered regions. This suggestion is consistent with the result obtained by Bohn, et al. (16) that the dichroic ratios are not very high, even at very high degrees of chain orientation in the fibers.

It is reasonable to think that the piezoelectricity arises principally from the residual polarization in ordered regions rather than that in un-ordered regions. According to the above supposition, the remarkable decrease in both d_{31} and e_{31} around $90^{\circ}C$ is due to the randomization of nitrile dipoles in ordered regions. The molecular motion around $90^{\circ}C$ and at high temperature region have been observed in various measurements. Nevertheless, the molecular characterizations of these relaxations or transitions are not clear. Minami, et al. (9) ascribed the mechanical relaxations around $110^{\circ}C$ (110 cps) and $160^{\circ}C$ to a molecular motion in paracrystalline regions and amorphous regions, respectively. Imai, et al. (8) demonstrated that completely amorphous PAN does not show mechanical relaxation around $95^{\circ}C$ (110 Hz) and solution grown crystals give a high intensity of relaxation about $95^{\circ}C$ but no relaxation around $140^{\circ}C$. Bohn, et al. (16) and Hinrichsen (18) observed a transitional change of interchain distance around $90^{\circ}C$.

Two mechanisms for piezoelectricity due to orientating dipoles are 1)

intrinsic piezoelectricity due to the rotation of dipoles, and 2) apparent piezoelectricity due to the combination of electrostriction constant and the residual polarization (2). According to the phenomenological theory of piezoelectricity of inhomogeneous system (28,29), the increase of both d_{31} and e_{31} in the temperature region below $80^\circ C$ may be due to one or more of the following factors: 1) the increase of dielectric constant in amorphous phases, (2) the decrease of elastic modulus in piezoelectric phases, and (3) the increase of electrostriction constant in amorphous phases. Although it is known that the temperature-dependence of piezoelectricity in electret polymers is affected by the change of electrostriction constant with temperature (2), it remains unknown at present which factor is the main reason for the increase of piezoelectric constants below $80^\circ C$ in PAN. A similar ambiguity likewise applies to our current understanding of piezoelectricity in PVDF (29).

The sign of piezoelectric constant of PAN changes above $110^\circ C$. When the specimen is stretched above $110^\circ C$, positive charge (negative charge below $110^\circ C$) is induced on the surface of specimen to which a positive electrical field is supplied. Some authors have observed the sign reversal of piezoelectric constant due to the reasons: 1) the sign reversal of the piezoelectric constant in piezoelectric phases (30) or (2) a phase angle exceeding 90 degrees of complex piezoelectric constant which arises from Maxwell-Wagner effect (31). The sign reversal of the electrostriction coefficient, and the coexistence of two origins of piezoelectricity (which are opposite in sign), are considered as other reasons for sign reversal of piezoelectric constant. The reason for the sign reversal of the piezoelectric constant of PAN is not clear at present. Somewhat complicated factors, one of them being thermal degradation, should be taken into account when the properties of PAN at high temperature are considered.

CONCLUSIONS

The piezoelectric constants of electrically polarized films of purified PAN decrease abruptly with temperature around $90^{\circ}C$. The decrease of piezoelectric constant around $90^{\circ}C$ is ascribed to the randomization of nitrile dipoles in ordered regions. The piezoelectric constants of ion-doped films $(NH_4NO_3, NaNO_3)$ also decrease with temperature around $90^{\circ}C$. In the same temperature range, a sharp decrease of elastic modulus and a maximum of depolarization current of both undoped and ion-doped films are observed. Even though the total charge released around $90^{\circ}C$ of NH_4NO_3-doped film $(2 \times 10^{-4}$ mole/gm PAN) is about ten times that of undoped films, the piezoelectric constants of ion-doped films are almost the same, or even less than, those of undoped films at room temperature. The sign of piezoelectric constant, d_{31}, changes from positive to negative above $110^{\circ}C$.

ACKNOWLEDGEMENTS

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Table 1

Code	Dopant Species	Dopant Concentration*	Poling Field (V/cm)	Elongation Ratio	$10^8 \times d_{31}$ (cgsesu)		
					room temp.	around 85^oC	around 120^oC
PE	none	--	5×10^4	2	1.7	4.3	3.6
PN	none	--	5×10^4	1	0.32	0.65	--
AE	NH_4NO_3	2×10^{-4}	2×10^4	2	0.26(0.65)**	0.80(2.0)**	1(2.5)**
SN	$NaNO_3$	2×10^{-4}	1×10^4	1	0.07(0.35)**	0.16(0.8)**	8(40)**
PE(10^5)	none	--	10×10^4	2	3.0	6.3	10.7

*Molar concentration units: moles salt per gram PAN. For example, 1×10^{-4} mol/gram PAN = 0.85 wt% salt = 5.3×10^{-3} mol/AN residue.

**Normalized to be equivalent to a poling field of 5×10^4 V/cm.

FIGURE CAPTIONS

Figure 1.   Temperature-dependence of d_{31}-constants for stretched (PE) and unstretched (PN) polyacrylonitrile poled at 130°C under 5×10^{4} V/cm for 30 min. PE 1 = the first run; PE 2 = the second run (cooled after the first run without an applied field).

Figure 2.   Temperature-dependence of the e_{31}-constants for stretched and unstretched polyacrylonitrile poled at 130°C under 5×10^{4} V/cm for 30 min. PE 1 = the first run; PE 2 = the second run (cooled after the first run without an applied field).

Figure 3.   Temperature-dependence of the elastic modulus, C, for unstretched polyacrylonitrile measured at 11 Hz.

Figure 4.   Temperature-dependence of the e_{31}-constants for NH_4NO_3-doped and stretched (AE) and $NaNO_3$-doped but unstretched (SN) polyacrylonitrile. Specimens were poled at 130°C under 2×10^{4} V/cm and 1×10^{4} V/cm respectively for 30 min.

Figure 5.   Thermally stimulated depolarization currents from undoped (P) and from ion-doped polyacrylonitrile (A = NH_4NO_3 doped film; S = $NaNO_3$ doped film) poled at 130°C for 30 min. P1 = the first measurement, P2 = the second measurement (cooled after the first run without an applied field). Heating rate was 2°C/min.

Figure 6. Temperature-dependence of the second run of d.c. conductivity

(cooled after the first measurement under an applied field)

for $NaNO_3$ doped and undoped polyacrylonitrile measured at

heating rate of $2^{\circ}C/min$. P = undoped film; S1 = 2×10^{-5}

[mole/gm PAN] $NaNO_3$ doped film; and S2 = 5×10^{-4} [mole/gm PAN]

$NaNO_3$ doped film. Doped specimens were poled under an electrical

field of 5×10^3 V/cm, and undoped films were poled using

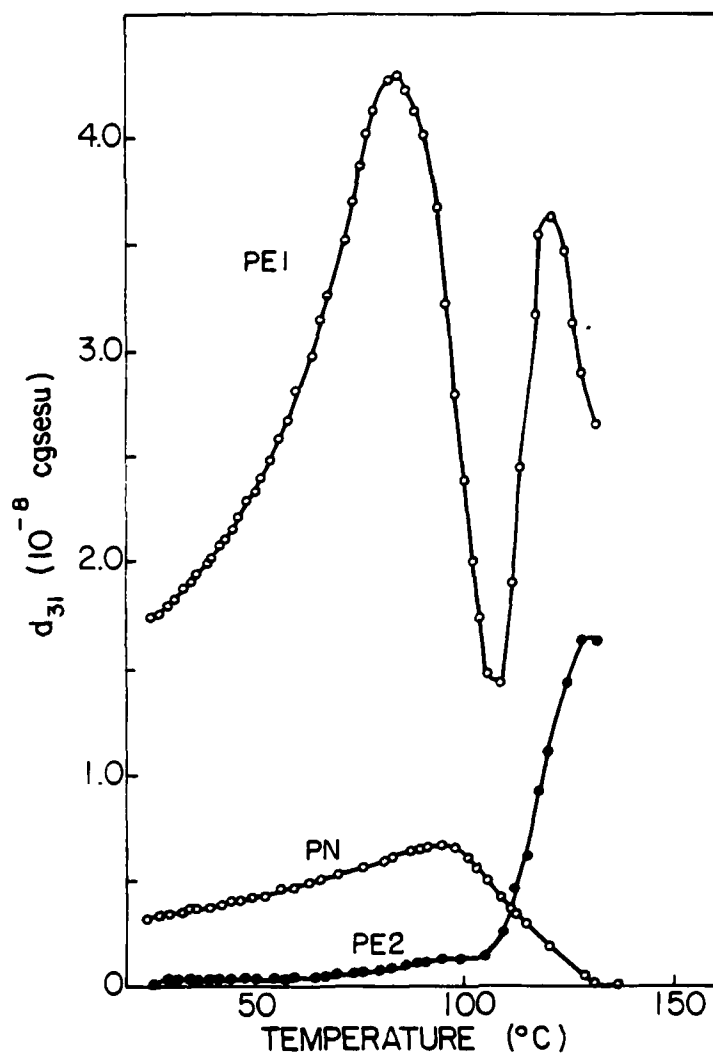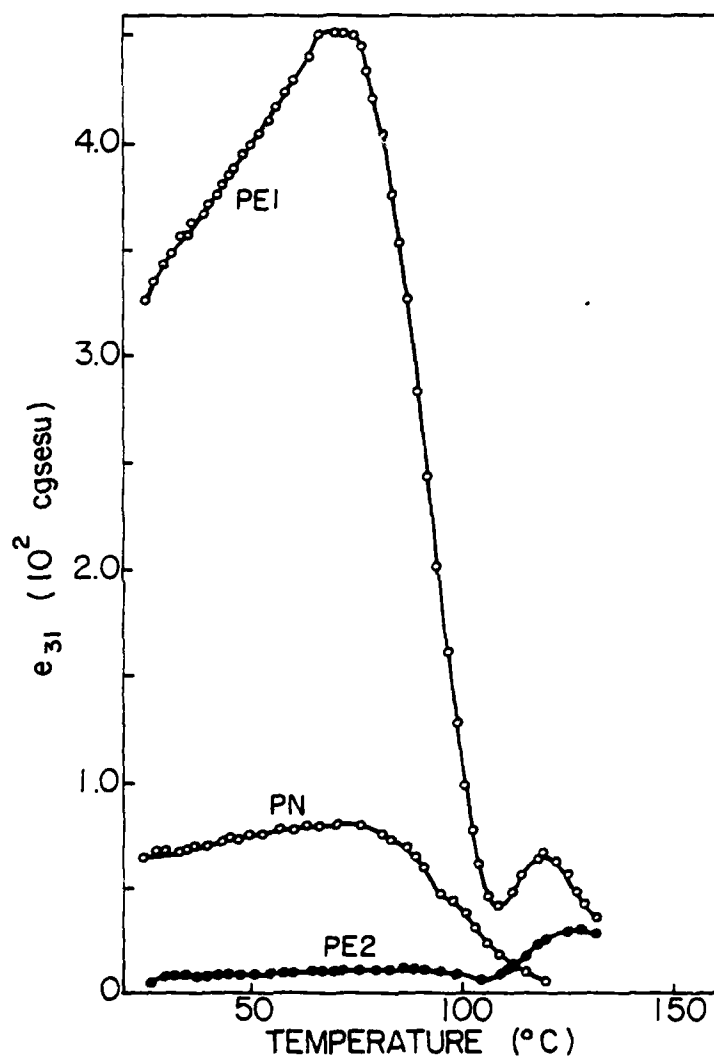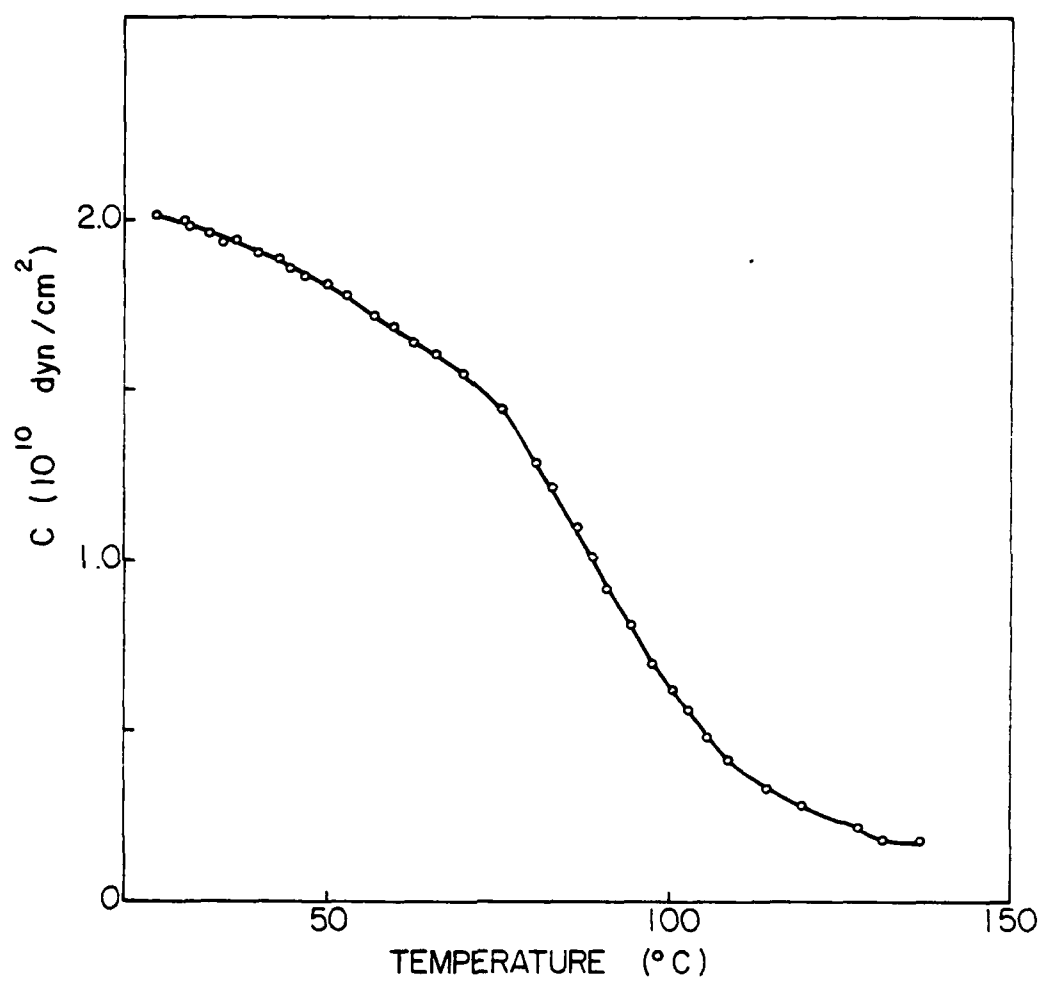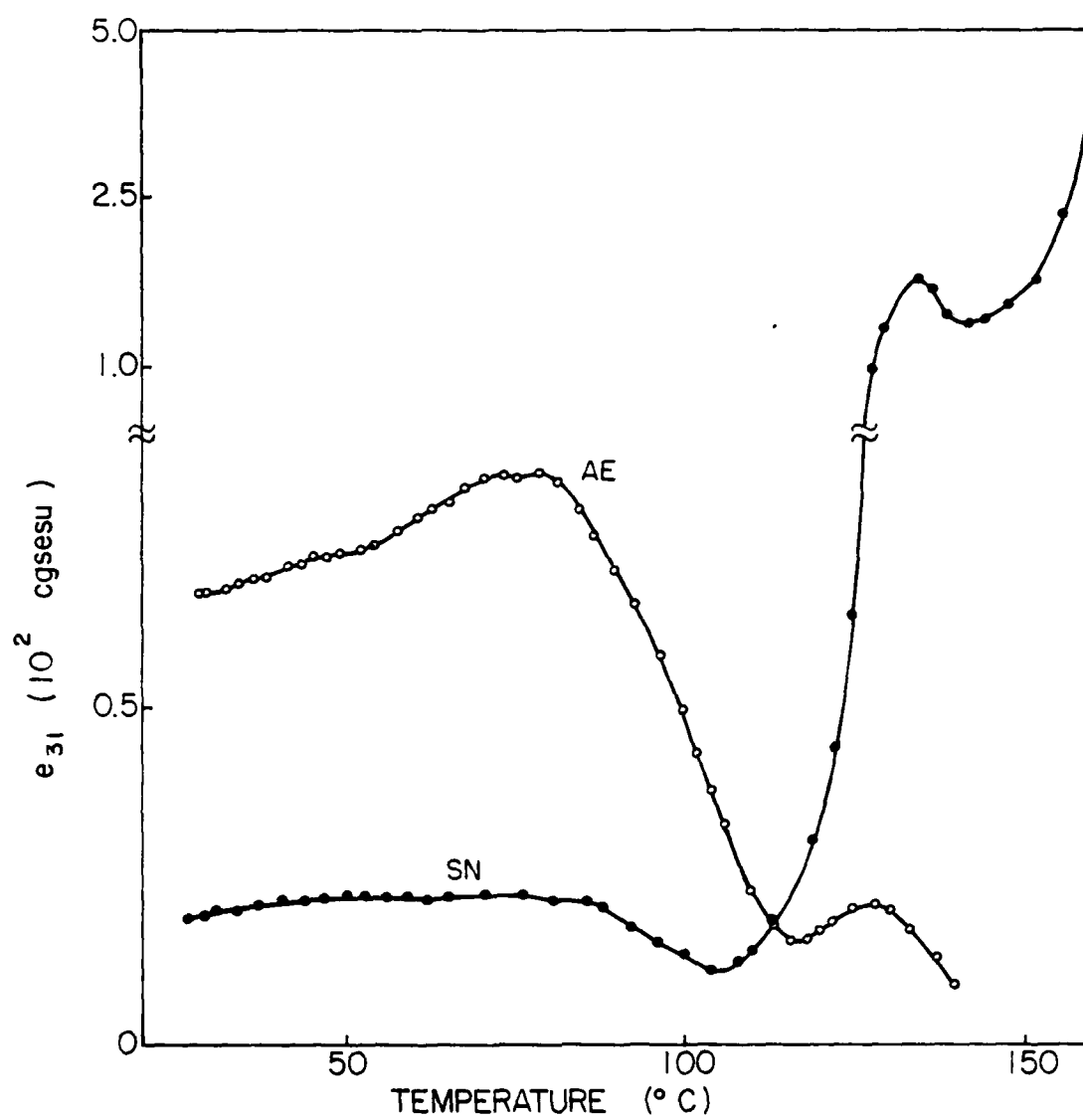1×10^4 V/cm.

Fig. 1

Fig. 5

Figure showing log σ (Ω^{-1} m^{-1}) versus TEMPERATURE (°C) for curves S2, S1, and P.
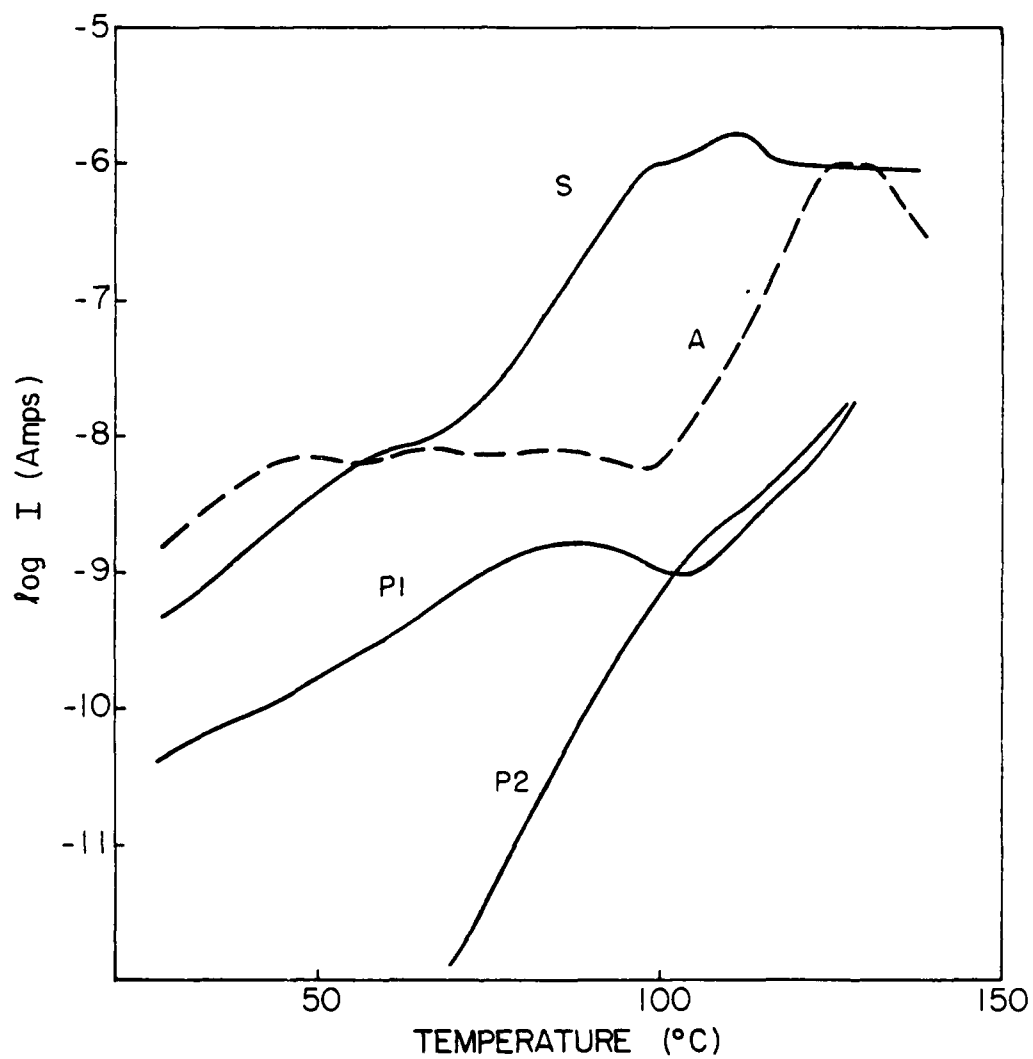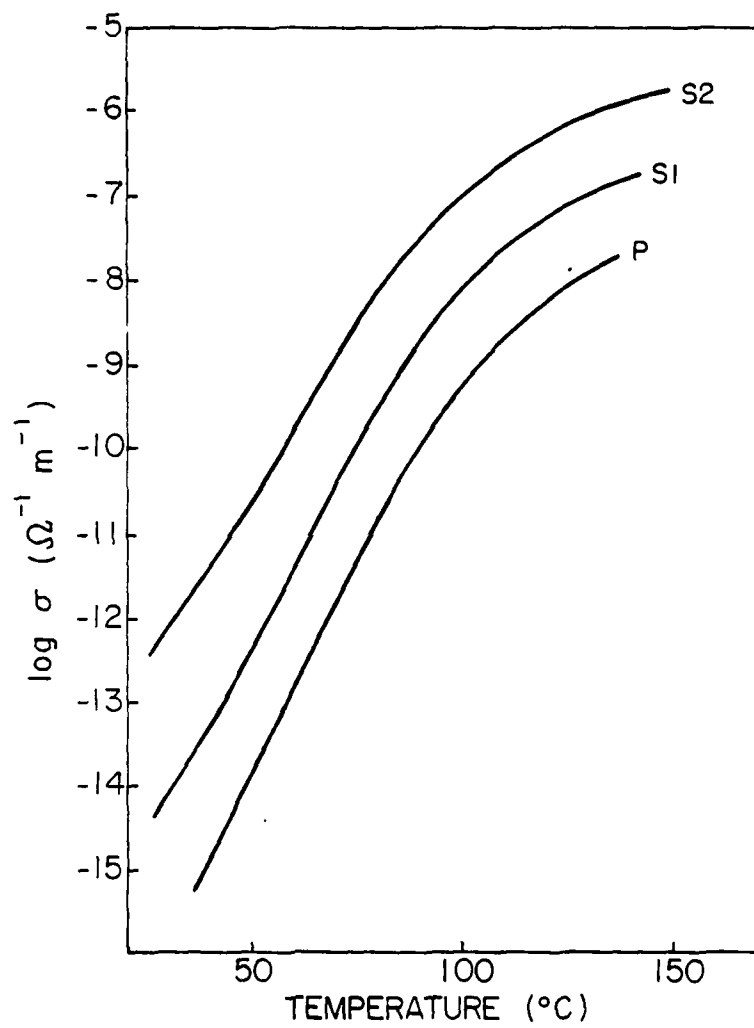
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