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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER # 4	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) Annealing Effects on Phase I Poly(vinylidene fluoride)		5. TYPE OF REPORT & PERIOD COVERED Technical Report April, 1988 - December, 1988
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Y. Takase, J.I. Scheinbeim and B.A. Newman		8. CONTRACT OR GRANT NUMBER(s) N00014-88-K-0122
PERFORMING ORGANIZATION NAME AND ADDRESS Rutgers, The State University of New Jersey College of Engineering, P.O. Box 909 Piscataway, NJ 08855-0909		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Arlington, VA 22217		12. REPORT DATE December 1988
		13. NUMBER OF PAGES 28
MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

DISTRIBUTION STATEMENT (of this Report)

Technical report distribution list DL/1113/87/2
for unlimited distribution and release

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

For unlimited distribution and release

18. SUPPLEMENTARY NOTES

Submitted, J. Poly. Sci., Poly. Phys. Ed.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The effects of annealing temperatures on stretched poly(vinylidene fluoride) films were systematically studied from the "as-received" condition up to the melting range (180°C). X-ray diffraction studies indicate that the annealing process brings about better chain packing and increased crystallite perfection. The elastic modulus and piezoelectric strain and stress constnats, d_{31} and e_{31}, decrease as the annealing temperature, T_a, increases up to 160°C, while the remnant polarization, P_r, remains almost constant. Some of these characteristics may be interpreted in terms of a morphological transformation of microfibrils. The values of P_r, d_{31} and e_{31} increase dramatically as T_a increases from 160 to

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180°C; P_r goes from 56 to 85 mC/m^2, d_{31} from 20.2 to 27.7 pC/N and e_{31} from 51.4 to 65.2 mC/m^2. As a result, P_r and d_{31} recorded the largest values obtained from any of the samples used in the present study. e_{31} showed a value close to the largest one; this usually occurs in unannealed samples. Samples annealed in the melting range also exhibit significantly improved aging characteristics. The large value of P_r and the small relaxation strength of both the dielectric constant and elastic modulus indicates that the largest crystallinity obtained is approximately 70%.

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Contract [redacted] N00014-88-K-0122

Technical Report # 4

Annealing Effects on Phase I Poly(vinylidene fluoride)

by

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Prepared for Publication in

J. Poly. Sci., Poly. Phys. Ed.

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Annealing Effects on Phase I Poly(Vinylidene Fluoride)

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Synopsis

The effects of annealing temperatures on stretched poly(vinylidene fluoride) film were systematically studied from the "as-received" condition up to the melting range (180°C). X-ray diffraction studies indicate that the annealing process brings about better chain packing and increased crystallite perfection. The elastic modulus and piezoelectric strain and stress constants, d_{31} and e_{31}, decrease as the annealing temperature, T_a, increases up to 160 °C, while the remnant polarization, P_r, remains almost constant. Some of these characteristics may be interpreted in terms of a morphological transformation of microfibrils. The values of P_r, d_{31} and e_{31} increase dramatically as T_a increases from 160 to 180°C; P_r goes from 56 to 85 mC/m^2, d_{31} from 20.2 to 27.7 pC/N and e_{31} from 51.4 to 65.2 mC/m^2. As a result, P_r and d_{31} recorded the largest values obtained from any of the samples used in the present study. e_{31} showed a value close to the largest one; this usually occurs in unannealed samples. Samples annealed in the melting range also exhibit significantly improved aging characteristics. The large value of P_r and the small relaxation strength of both the dielectric constant and elastic modulus indicates that the largest crystallinity obtained is approximately 70 %.

INTRODUCTION

It is well known that low temperature drawing (50 - 80°C, draw ratio ~4) of isotropic poly(vinylidene fluoride) (PVDF) films with the phase II crystal structure produces oriented PVDF films which have predominantly the phase I structure. It is also well known that crystals with the phase I structure in PVDF and its copolymers with trifluoroethylene [P(VDF-TrFE)] exhibit ferroelectricity. Both of these polymers also exhibit high piezoelectric and pyroelectric activity after they are subjected to a poling procedure.

These piezoelectic and pyroelectric characteristics have been explained by an idealized model in which the film consists of (infinitly) thin plates or spherical crystallites distributed in an amorphous matrix.[1,2] According to these models, the most fundamental factor determining the piezoelectric and pyroelectric activities is the bulk remnant polarization. To our knowledge, the highest remnant polarization among polymer ferroelectrics has been obtained from a P(VDF-TrFE) copolymer.[3] This is simply because the crystallinity of P(VDF-TrFE) is higher than that of PVDF, in spite of its lower dipole density.

Ideally, PVDF has some advantages over the P(VDF-TrFE) copolymers. PVDF has the highest dipole density among the vinylidene fluoride copolymers, which yields the highest spontaneous polarization. PVDF does not show a ferroelectric to paraelectric phase transition in a temperature region lower than the melting point. As a result, the piezoelectric and pyroelectric activities do not decay up to a high temperature near the melting point. Actually, however, it has been reported that the crystallinity of PVDF does not exceed around 50 %.[4-7] The reason of this rather low value of crystallinity has not been fully explained as yet.

Until now, many techniques have been employed to obtain improved piezoelectric and pyroelectric activity in PVDF film. These include; high drawing at high temperatures[8], high pressure crystallization,[9] pressure quenching,[10] forced-quench drawing,[11] plasticization,[12] high energy irradiation,[13] perdeuterization,[14] and annealing. Among these techniques, the highest piezoelectric constant is obtained by the forced-quench drawing method,[11] and the highest remnant polariztion has been obtained by the perdeuterization technique.[14]

Annealing is one of the most fundamental techniques employed during experiments in order to obtain enhanced thermal stability and improved crystal perfection. We usually observe, however, that the annealing of PVDF films before poling reduces the piezoelectric activity of the poled films. For this reason, the annealing effect has not been systematically investigated for the purpose of obtaining improved piezoelectric and pyroelectric activity in PVDF film.

The present study demonstrates an anomalous annealing effect that brings about striking increases in remnant polarization (~50 % increase from the usual value) by employing a special annealing technique near and in the melting range (175 - 180 °C) of the films. In addition to studies of this anomalous effect, systematical investigations of annealing effects are carried out by measuring X-ray diffraction profiles, remnant polarization, dielectric constant, dynamic mechanical modulus and piezoelectric strain and stress constants.

EXPERIMENTAL

Samples used in this study were 7-μm-thick uniaxially oriented PVDF films (KF1000) supplied by Kureha Chemical Industry, Co., Ltd. Annealed samples were prepared by heat treatment in nitrogen gas at several temperatures including 100, 120, 140, 160, and 175 - 180°C (in 1°C steps) for 2 hours. During the heat treatment, it was essential to mechanically fix the film to prevent shrinkage and maintain crystallite orientation.

Gold electrodes, each about 2.5 x 5 mm^2 in area, were deposited on opposite surfaces of the films by vaccum evaporation.

All measurements, except X-ray measurements, were carried out by placing the sample in an electrically shielded copper cell which was equiped with both heaters and temperature sensors.

X-ray diffraction profiles were obtained at room temperature with a Philips XRG 3100 X-ray generator. CuK_α reduction filtered with a Ni foil and a pulse height-analyzer were employed.

The D - E hysteresis characteristics were measured at 20°C by using a high voltage power supply and a picoammeter (Keithley 485) connected in series with the sample. The period of the triangular high voltage wave form was 640 s.

The dielectric constant, elastic modulus and piezoelectric constants were measured by using a Rheolograph (Toyoseiki). The frequency of the excitation signal was 10 Hz.

Operation of various functions in the system was consigned to a microcomputer (IBM-XT) which also performed the task of data processing.

RESULTS

X-ray Diffraction Profiles

The 2θ values and half widths for the composite (110)(200) phase I reflection of the films are plotted as a function of annealing temperature in Fig. 1. The 2θ -value increases monotonically as the annealing temperature, T_a, increases from 100 to 180°C, while the half width decreases monotonically as T_a increases from 100 to 180 °C. These annealing effects on the crystalline regions of the PVDF film indicate a decrease in interplaner separation caused by better chain packing and increased perfection of the crystallites.

Fiber diagrams of the as-stretched film and of the film annealed at 180°C are shown in Figs. 2 (a) and (b), respectively. Both of these samples exhibit fiber diagrams representative of the highly oriented phase I crystalline form. It is important to note that no significant loss of orientation in the crystalline regions was observed and that any transformation from the phase I to the phase II crystal structure in the PVDF film was neglegible, even if the films were annealed to a partially melted condition, provided that the films were mechanically fixed during annealing.

D - E Hysteresis Characteristics

Figures 3 and 4 show current density, J, and electric displacement, D, as a function of electric field when the sample is subjected to triangular shaped electric field pulses with a maximum field of $E_p = 200$ MV/m. An exceptionally high current peak around the coercive field and, consequently, a quite high value of remnant polarization, P_r, has been found for the sample annealed at 180°C. To our knowledge, this value of $P_r = 85$ mC/m^2 is significantly higher than what has been previously observed for this commercial PVDF film and close to the value found for perdeuteriated PVDF film ($P_r = 100$ mC/m^2).[14]

Dielectric, Mechanical and Piezoelectric Characteristics

Figure 5 shows the real part of the dielectric constant, ε', the elastic modulus, c', the piezoelectric strain constant, d'_{31}, the piezoelectric stress constant, e'_{31}, and the polarization, P_r, as a function of annealing temperature. Two different sets of data are presented by circles and triangles, which represent data measured 50 minutes after poling and 90 hours after poling, respectively.

The annealing temperature dependences of ε' and c' resemble each other. They decrease as the annealing temperature increases from 100 to 180°C. In the case of the 50-min-aged sample, for example, ε' decreases from 16.5 for the sample annealed at 100°C to 15.1 for $T_a = 180$°C, c' decreases from 3.4 GPa for $T_a = 100$°C to 2.3 GPa for $T_a = 180$°C. Although the values of ε' and c' of the unannealed samples are nearly the same as those for T_a = 100 °C, the aging characteristics of the unannealed samples are the poorest of all. They changes from ε' = 16.7 to 15.6 (6.6 % decrease) and from c' = 3.27 to 2.64 GPa (19.3 % decrease).

On the other hand, the annealing temperature dependence of d'_{31} and e'_{31} are qualitatively the same. Their values decrease as the annealing temperature increases from the unannealed condition to 160°C. For example, d'_{31} decreases from 25.7 to 20.2 pC/N and e'_{31} decreases from 84.2 to 51.4 mC/m^2 (50-min-aged sample). Annealing at temperatures from 175 to 180 °C reveals steep increases in these quantities. For example, d'_{31} increases from 20.2 to 27.7 pC/N (an increase of 37.1 %), and e'_{31} increases from 51.4 to 65.2 mc/m^2 (an increase of 26.8 %); d'_{31} = 27.7 pC/N is the largest value obtained from any of the samples, unannealed or annealed. In the case of e'_{31}, the unannealed sample shows the largest value of all. However, the aging characteristics of the annealed sample at T_a = 180°C are superior to that of the unannealed samples; comparison of samples aged for 50 min and 4 days, respectively, shows that the value of e'_{31} decreases from 65.2 to 64.2 mC/m^2 (only a 1.5 % decay) in the annealed sample, while it decreases from 84.2 to 67.4 mC/m^2 (a 20 % decay) in the unannealed sample. In fact, after 4 days aging, the value of e_{31} for the 180 °C annealed sample is close to that of the unannealed samples.

Studies of the annealing temperature dependence of the remnant polarization produced the most important results. The value of P_r remained almost constant ($\sim$56 mC/m^2) from T_a = 100 to 160 °C. However, it revealed an exceptionally steep increase from $P_r = 56$ to 85 mC/m^2 (an increase of 52 %) over a narrow range of T_a from about 170 °C to 180 °C. This increase in P_r is quite remarkable and suggests some anomalous annealing mechanism.

Figures 6 - 10 show ε vs T, c vs T, d_{31} vs T, e_{31} vs T, and k vs T characteristics, respectively, for two samples heat treated at annealing temperature of 160 °C and 180 °C; where k is the electromechnical coupling constant calculated from the equation

$$k = (\varepsilon c)^{-1/2} e_{31}. \tag{1}$$

The dielectric and mechanical relaxation strength of the sample annealed at 180 °C is much less than that of the sample annealed at 160 °C (see Figs. 6 and 7). This represents additional evidence other than the X-ray diffraction measurements, which shows that the crystallinity significantly increases under the partially melted annealing condition. The piezoelectric constants, d'_{31} and e'_{31}, and the electromechanical coupling constant, k, for the sample annealed at 180 °C exhibit greatly improved characteristics when compared with those of the normally annealed samples over the temperature region from -150 °C to 90 °C. Specifically, the improvement in the electromechanical coupling constant is quite important for applications such as piezoelectric transducers.

DISCUSION

From the idealized models of PVDF, where lamellar crystallites are distributed in an amorphous matrix,[1,2] it is difficult to understand the observed annealing effects. The X-ray diffraction (half width vs T_a) and dielectric constant data indicate that the annealing brings about increased perfection and lamellar size of the crystallites and an increase in crystallinity. These changes may bring about increased tension on the molecular chains in the amorphous regions. As a result, the elastic modulus should increase. The value of elastic mudulus and P_r should also increase following the increase in crystallinity. Both the increase in crystallinity reflected in the increase in P_r and in the chain tension in the amorphous regions should increase the value of the modulus and e'_{31}. However, the experimental data for c' and e'_{31} shows an opposite annealing temperature dependence. These result strongly suggest that the real system consisting of stretched high temperature annealed PVDF film cannot be fully expressed by the conventional models.

A Model Which Allows Morphological Transformation

The drawing and annealing of polymeric materials has been extensively studied by Geil[15] and Peterlin et. al.[16,17] According to their studies, plastic deformation of nonfibrous semicrystalline polymers destroys the stacks of thin and wide parallel lamellae of the starting material and transforms them into densely packed and well-aligned extremely long and thin microfibrils of the final fibrous structure. They pointed out that the transformation was completed at a draw ratio, λ^*, which is between 8 and 10 in linear polyethylene, about 2.5 in isotactic polypropylene, and between 2 and 3 in nylon 6 or 66.

In the case of PVDF, however, the transformation process has not as yet been clarified. Since the present film is drawn at 100°C by a roller machine to about 5 times the original length, it should not be fully consistent with the lamellar model. Therefore, the present annealing effect may be understood not by using a conventional static model but by using a dynamic model which allows transformations between microfibrils and lamellae.

Figure 11 shows a simplified equivalent circuits which may be used to represent the elastic properties of the film. For simplicity, only two different types of elements are used. One element represents a series connection of amorphous (modulus of c_a) and crystalline (modulus of c_c) regions. A lammellar crystallite or a folded chain crystalline region within a microfibril connected with an amorphous region may be represented by this element. The other element represents a microfibril (modulus of c_{fib}). The elastic modulus of the drawn fibrous structure strongly depends on the draw ratio and has a high value of up to 50 % of that of the ideal crystal lattice in the chain direction, while an isotropic lamellar material has a value about 0.01 c_c.[17] The model represents that the as-stretched film consists of larger amount of fibrous element than annealed film. Annealing brings about a transformation from a microfibril to an amorphous-crystal series structure. According to this model, the experimental results may be interpreted as follows:

The as-stretched film consists of a large fraction of microfibrils and consequently the average intermolecular spacing of chains in the crystalline regions tends to be large (see Fig.

1). The crystallinity is low and consequently the dielectric constant above the glass transition temperature is large. Because of the large fraction of microfibrils, the elastic modulus and piezoelectic stress constant are large.

If a sample is annealed at high temperature, a part of the microfibrils can transform to folded chain crystallites and show better packing of molecular chains. The crystallinity slightly increases and consequently the dielectric constant slightly decreases. As the modulus of the amorphous-crystal series structure ($c_a c_c/(c_a+c_c)$) is less than c_a, the transformation brings about a decrease in bulk modulus which is the sum of those of the two elements. The surface charge induced by an external strain is the sum of contributions of the two elements. When a dynamic strain is applied to the film, it directly produces the same amount of displacement in the microfibril, whereas it produces a reduced displacement in the crystalline region by a factor of $c_a/(c_a+c_c)$ due to the series connection with the amorphous region. Therefore, the transformation brings about a large decrease in bulk piezoelectric stress constant, e'_{31}. This behavior is consistent with that of the experimentally observed values over the normal annealing temperature region from $T_a = 100$ to 160°C.

Anomalous Annealing Effect at Temperatures above 175°C

The annealing effect at temperatures above 175 °C is quite striking. Temperatures from 175 °C to 180 °C are in the melting range of the present PVDF film. Therefore, molecular motion in some crystallites is close to that of the liquid state and consequently recrystallization will easily occur. As pointed out in the explanation of the X-ray diffraction profile, the amount of material which transforms from the phase I to the phase II crystal structure is negligible. The large observed increase in P_r indicates that crystallinity significantly increased during the annealing process. We can estimate the new value of crystallinity to be ~68 % if we assume the crystallinity of the as-stretched sample was ~45 %. This large increase in crystallinity leads to a lower value of dielectric constant but the elastic modulus exhibits a smaller value. These features are quite unique and require further investigation to understand the detailed mechanisms which may be involved. We believe, however, that this may reflect a kind of epitaxial crystal growth which takes place at the interfacial zone between fibrous crystal and amorphous regions.

Because of the large observed increase in P_r which occurs over a narrow range of annealing temperatures, from 170 to 180°C, the value of e'_{31} and d'_{31} also increase quite steeply in the same temperature region. Because of the observed decrease in modulus and increase in P_r, d'_{31} exhibits a value of 27.7 pC/N, the largest of any of the present samples. The important emphasis on the sample annealed at a partially melted annealing temperature is not only its high piezoelectric response but also the excellent aging characteristics of its piezoelectric stress constant and the excellent thermal stability of the mechanical properties of the film.

CONCLUSIONS

The major effect of annealing on the crystalline regions of PVDF is to produce better packing and increased perfection in the crystallites at all annealing temperatures from 100 to 180°C.

The dielectric constant obtained at 20 °C decreases with increasing annealing temperature, which suggests that crystallinity increases as annealing temperature increases.

The elastic modulus decreases with increasing annealing temperature. This is consistent with a model which represents a morphological transformation of microfibrils to lamellar crystals.

The piezoelectric strain and stress constants decrease as the annealing temperature increases up to 160 °C, while the remnant polarization remains almost constant.

The values of P_r, d'_{31} and e'_{31} increase dramatically as the annealing temperature increases from 160 to 180 °C; P_r increases from 56 to 85 mC/m^2, d'_{31} increases from 20.2 to 27.7 pC/N and e'_{31} increases from 51.4 to 65.2 mC/m^2. As a result, P_r and d'_{31} recorded the largest values of all of the unannealed and annealed samples studied. e'_{31} also showed a value close to the largest one, which usually occurs in the unannealed sample, and the best aging characteristics of all. The large value of P_r and the small relaxation strength of the dielectric constant and elastic modulus indicates that the largest crystallinity is approximately 70 %.

Annealing at temperatures in the melting range appears to provide one of the best means for obtaining the highest quality piezoelectric film when applied to highly stretched PVDF film.

ACKNOWLEGMENT

This work was supported in part by the Office of Naval Research.

References

1. M. G. Broadhurst, G. T. Davis, and J. E. McKinney, J. Appl. Phys. 49, 4992 (1978).
2. Y. Wada and R. Hayakawa, Ferroelectrics 32, 115 (1981).
3. K. Koga and H. Ohigashi, J. Appl. Phys. 59, 2142 (1986).
4. H. Kakutani, J. Polym. Sci. 8, 1177 (1970).
5. N. Murayama, J. Polym. Sci. 13, 929 (1975).
6. R. G. Kepler, and R. A. Anderson, J. Appl. Phys. 49, 1232 (1978).
7. J. I. Scheinbeim, K. T. Chung, K. D. Pae, and B. A. Newman, J. Appl. Phys. 50, 6101 (1979).
8. E. L. Nix, L. Holt, T. C. McGrath, and I. M. Ward, Ferroelectrics 32, 103 (1981).
9. K. Matsushige, K. Nagata, and T. Takemura, Jpn. J. Appl. Phys. 17, 467 (1978).
10. J. I. Scheinbeim and K. T. Chung, J. Appl. Phys. 52, 5983 (1981).
11. K. Yamada, M. Oie, and M. Takayanagi, J. Polym. Sci. Polym. Phys. Ed. 22, 245 (1984).
12. A. Sen, J. I. Scheinbeim, and B. A. Newman, J. Appl. Phys. 56, 2433 (1984).
13. T. T. Wang, Ferroelectrics 41, 213 (1982).
14. Y. Takase, H. Tanaka, T. T. Wang, T. Caise, and J. Kometami, Macromolecules 20, 2318 (1987).
15. P. H. Geil, J. Polymer Sci. A2, 3813 (1964), A2, 3835 (1964).
16. A. Peterlin, H. Kiho, R. H. Geil, Polymer Letters 3, 151 (1965), 3, 157 (1965), 3, 257 (1965), 3, 263 (1965).
17. A. Peterlin, J. Appl. Phys. 48, 4099 (1977).

Figure Captions

Figure 1 The X-ray diffraction angle, 2θ, and half width, $\beta_{1/2}$, for the composite (110)(200) reflection of the phase I crystal form plotted as a function of annealing temperature, T_a.

Figure 2 Fiber diagram of the as-stretched film (a) and of the film annealed at 180°C for 2 h (b).

Figure 3 The current density, J, as a function of electric field, E, when the sample is subjected to triangular electric fields with maximum value of 200 MV/m at 20 °C. The thin line, the dotted line and the thick line represent data of the as-stretched sample, of the sample annealed at 160 °C and of the sample annealed at 180°C, respectively.

Figure 4 The electric displacement, D, as a function of electric field calculated from the data in Figure 3. The thin line, the doted line and the thick line represent data of the as-stretched sample, of the sample annealed at 160 °C and of the sample annealed at 180°C, respectively.

Figure 5 The real parts of the dielectric constant, ε', the elastic modulus, c', the piezoelectric strain constant, d'_{31}, the piezoelectric stress constant, e'_{31}, and the remnant polarization, P_r, as a function of annealing temperature. Two different sets of data are presented by circles and triangles, which represent data measured 50 minutes after poling and 90 hours after poling, respectively.

Figure 6 The dielectric constant, ε, as a function of temperature, T, for two samples heat treated at different temperatures of 160°C (thin line) and 180°C (bold line).

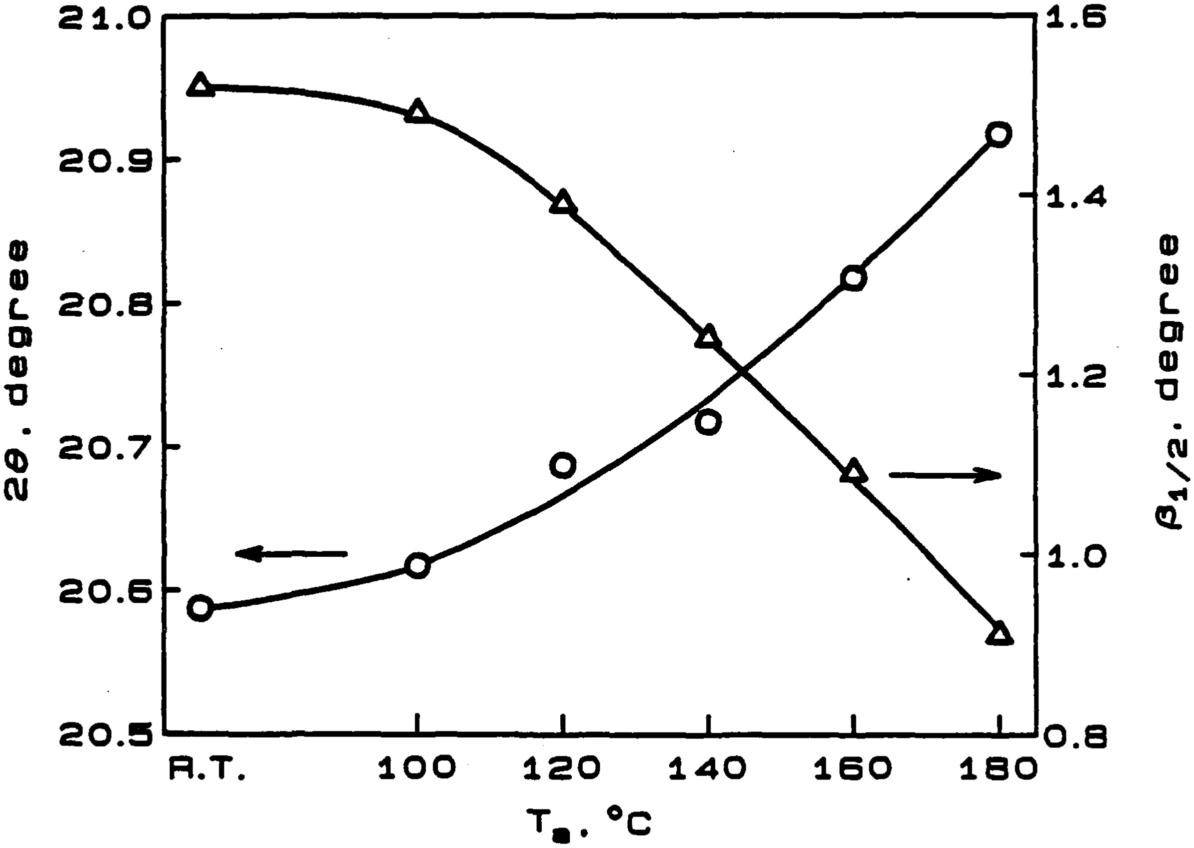
Figure 7 The elastic modulus, c, as a function of temperature, T, for two samples heat treated at different temperatures of 160°C (thin line) and 180°C (bold line).

Figure 8 The piezoelectric strain constant, d_{31}, as a function of temperature, T, for two samples heat treated at different temperature of 160°C (thin line) and 180°C (bold line).

Figure 9 The piezoelectric stress constant, e_{31}, as a function of temperature, T, for two samples heat treated at different temperature of 160°C (thin line) and 180°C (bold line).

Figure 10 The electromechanical coupling constant, k, as a function of temperature, T, for two samples heat treated at different temperature of 160°C (thin line) and 180°C (bold line).

Figure 11 Simplified equivalent circuits which represent the elastic properties of the film. One element represents a series connection of amorphous (modulus of c_a) and crystalline (modulus of c_c) regions, and the other element represents a microfibril (modulus of c_{fib}).



21.0
20.9
20.8
20.7
20.6
20.5
2θ, degrees
1.6
1.4
1.2
1.0
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R.T.
100
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140
160
180
T_a, °C

Fig. 1

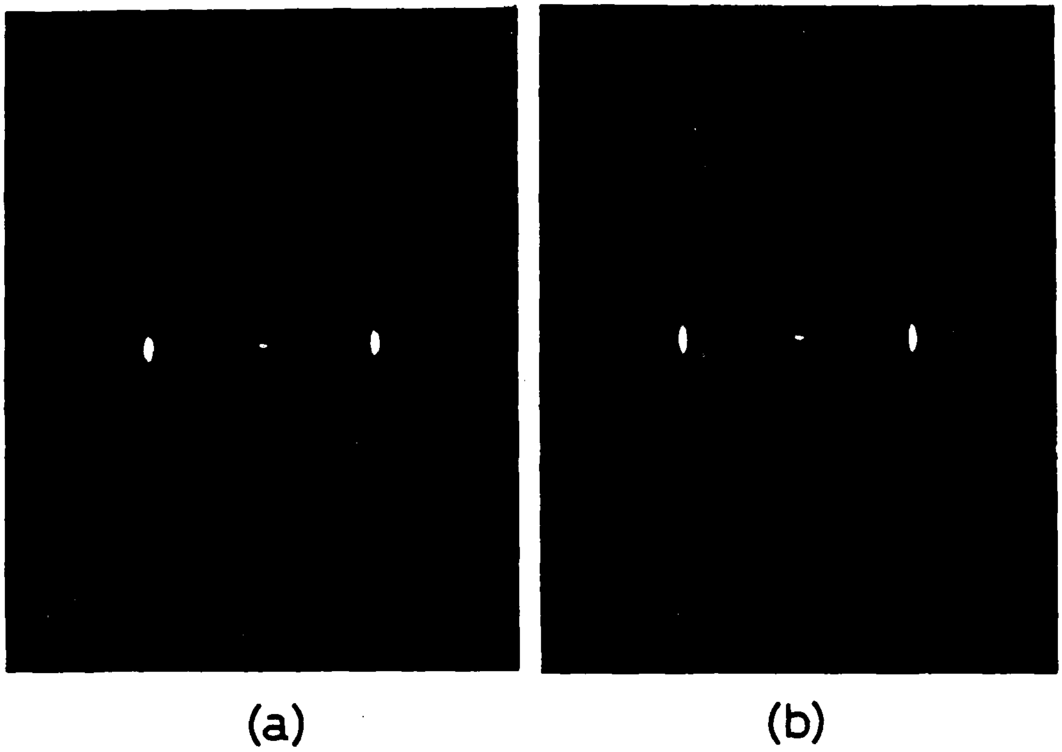
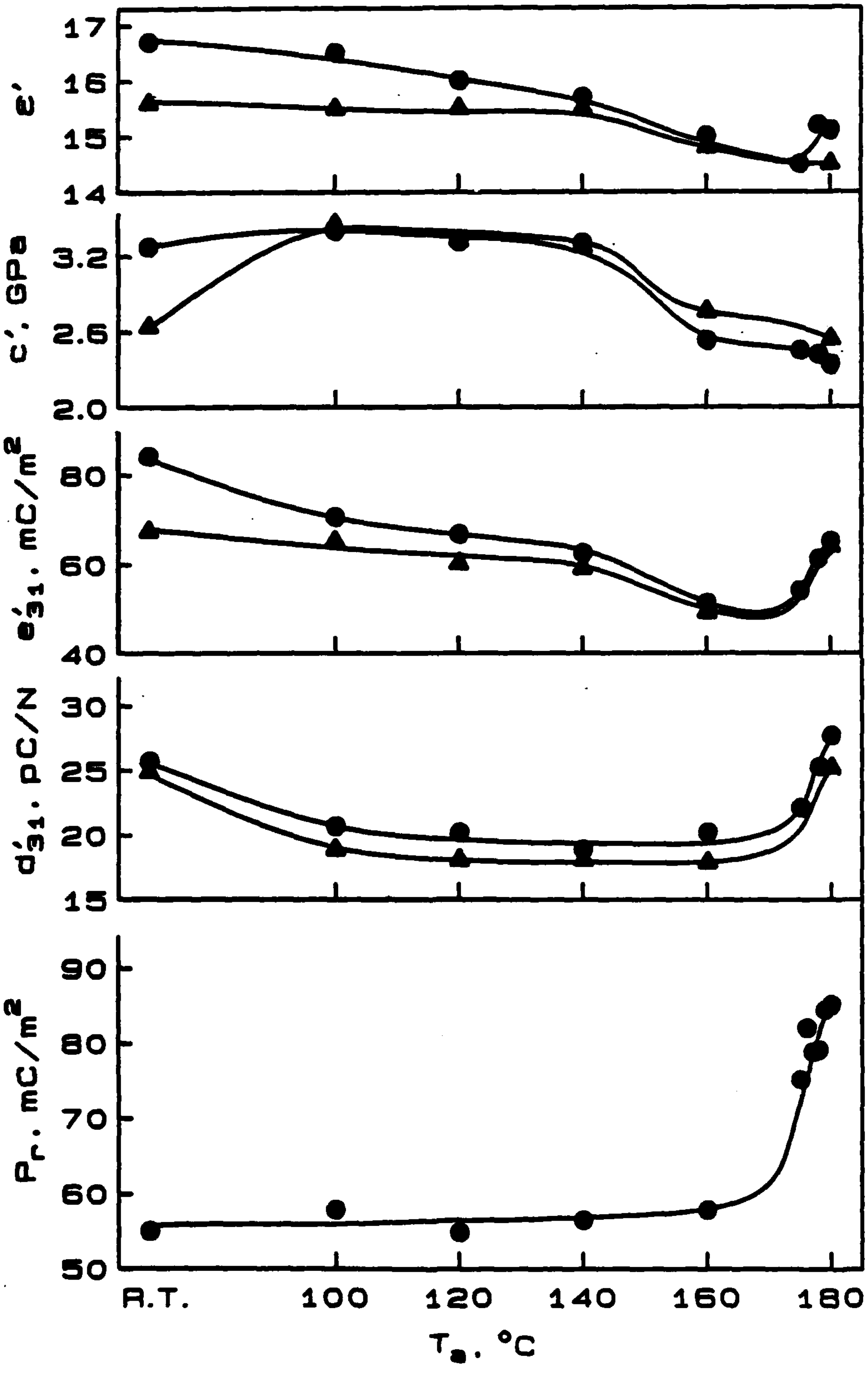

(a) (b)

Fig. 2



ε'
17
16
15
14
c', GPa
3.2
2.6
2.0
e'31, mC/m2
80
60
40
d'31, pC/N
30
25
20
15
Pr, mC/m2
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R.T.
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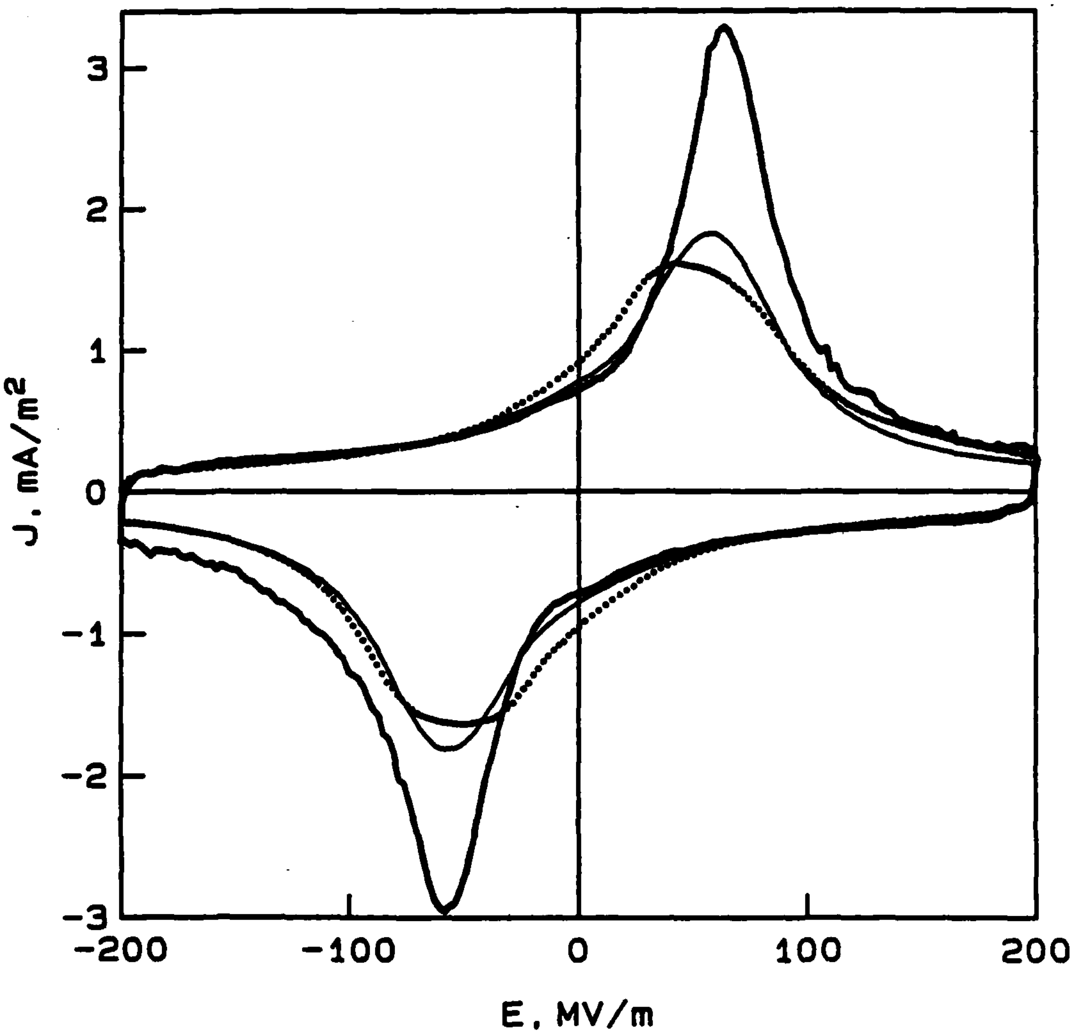
Ta, °C

Fig. 3



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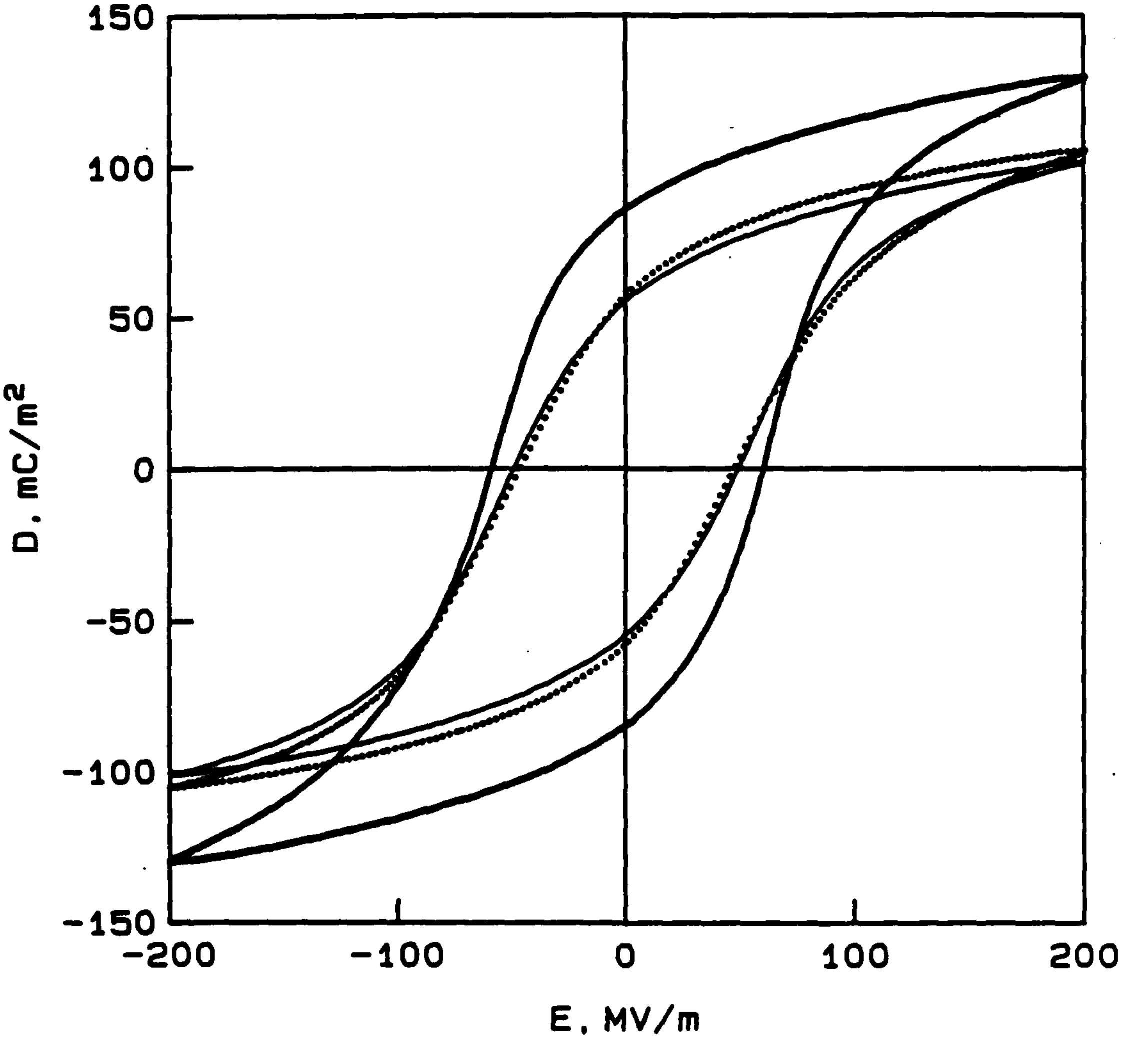

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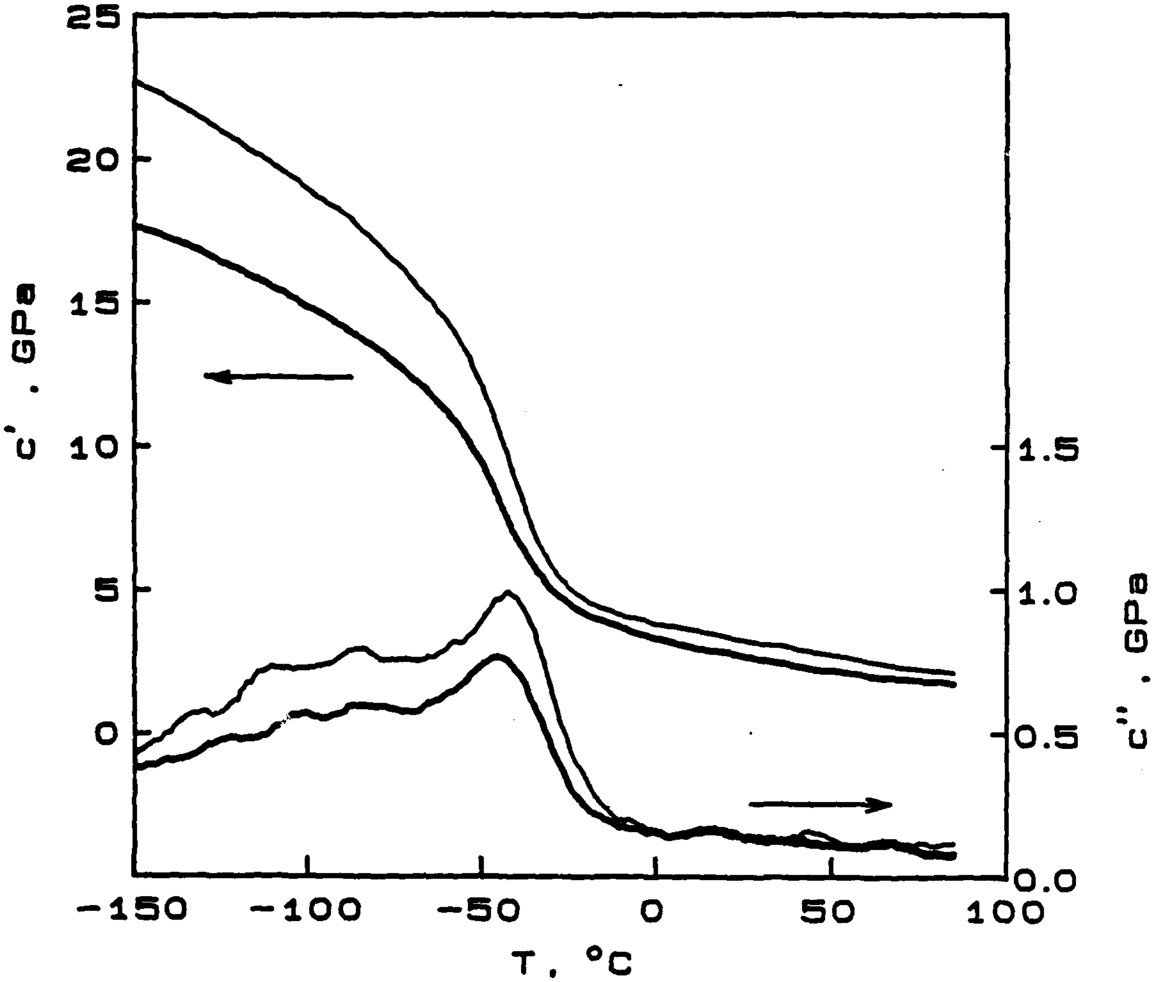

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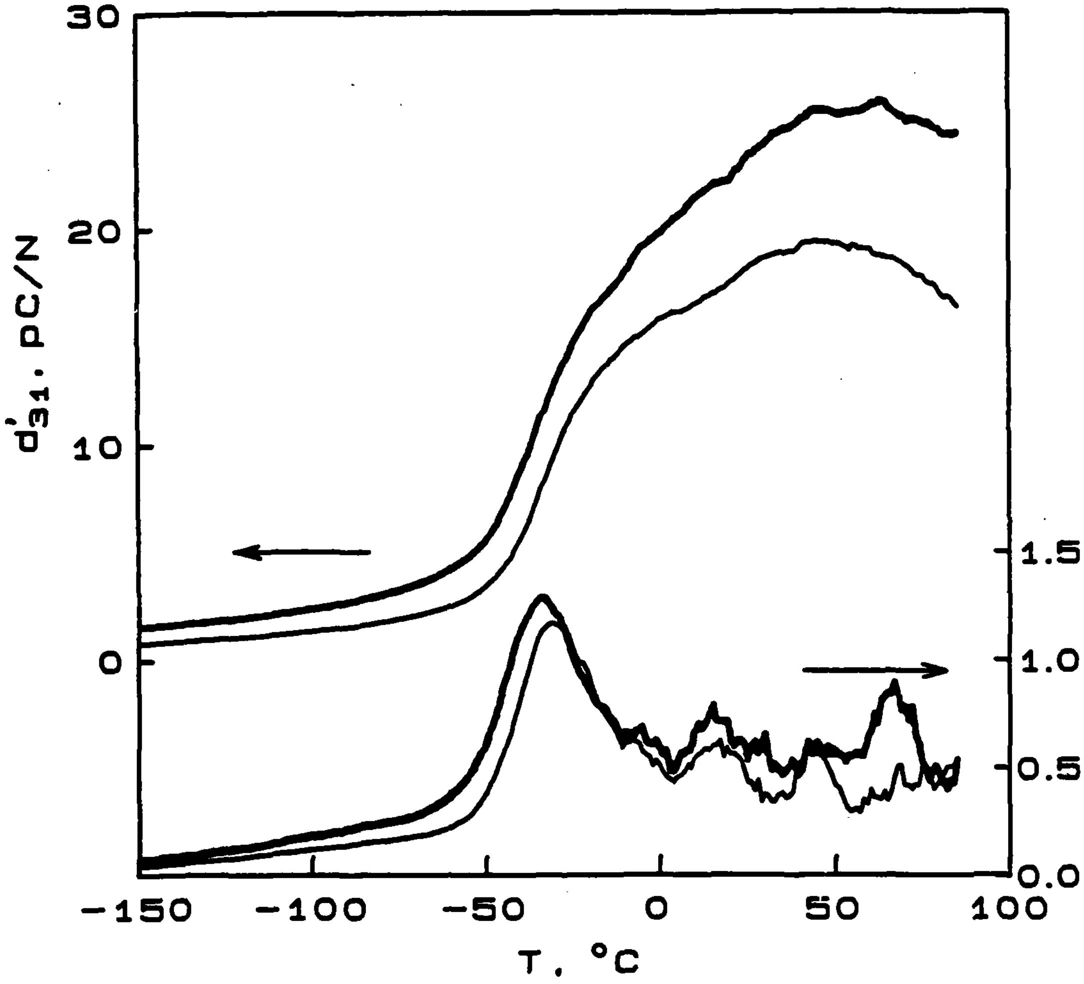

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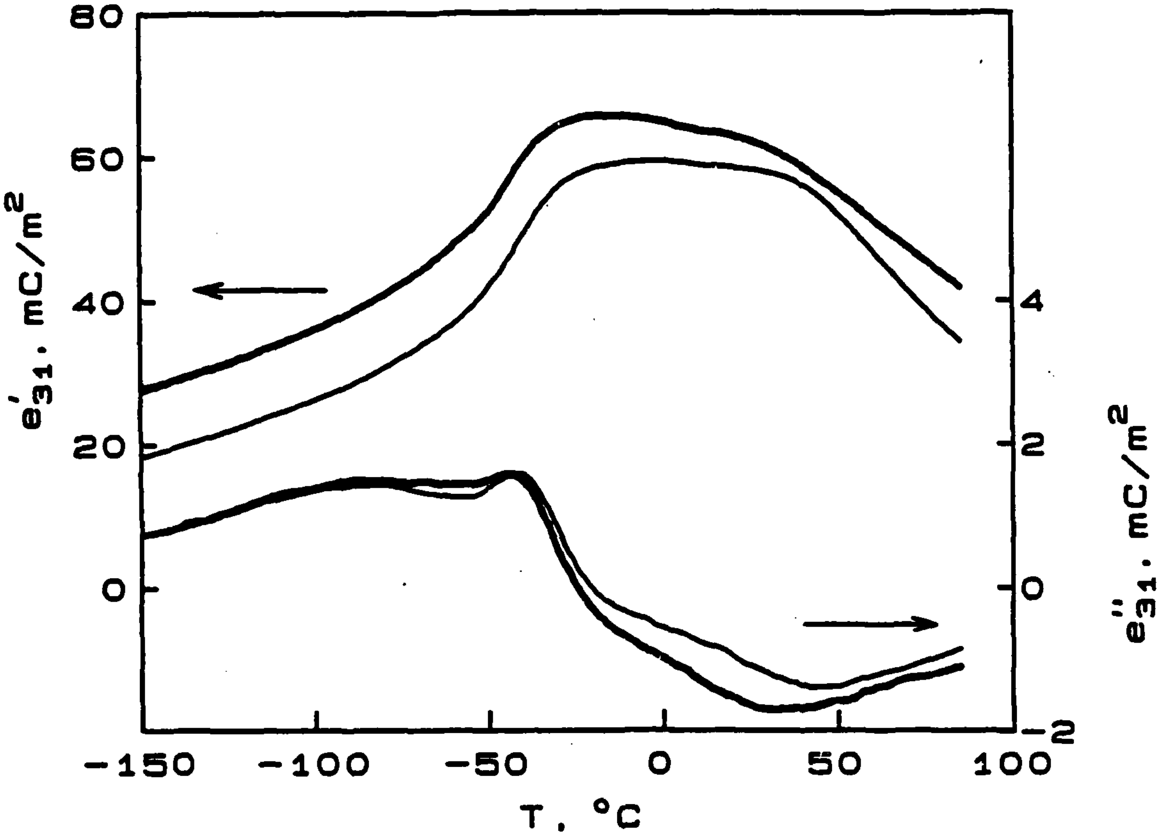

Fig. 8

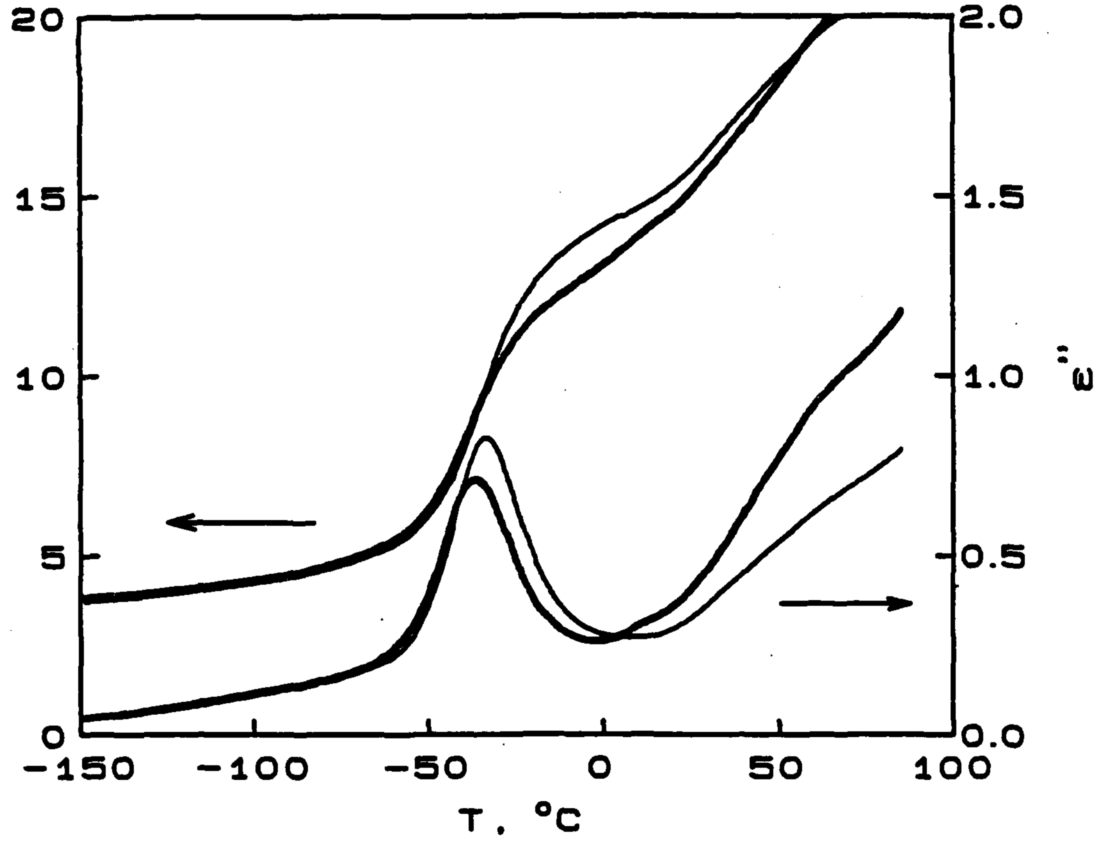

Fig. 9

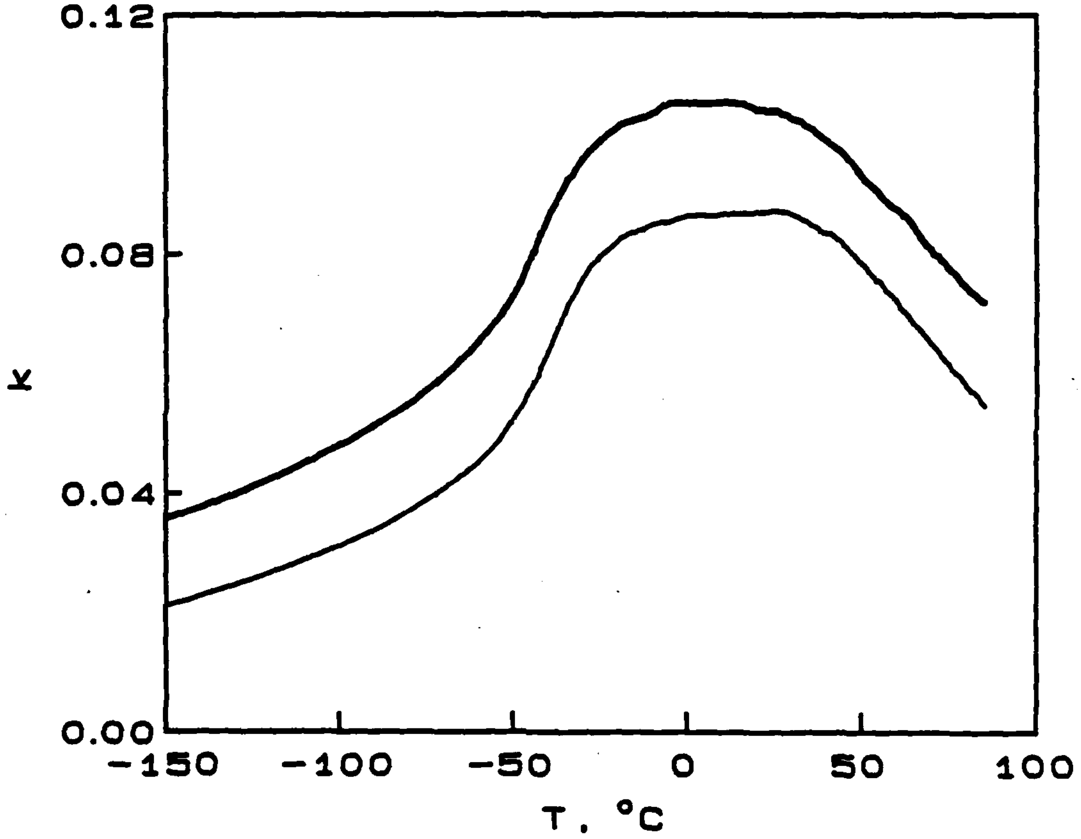

Fig. 10

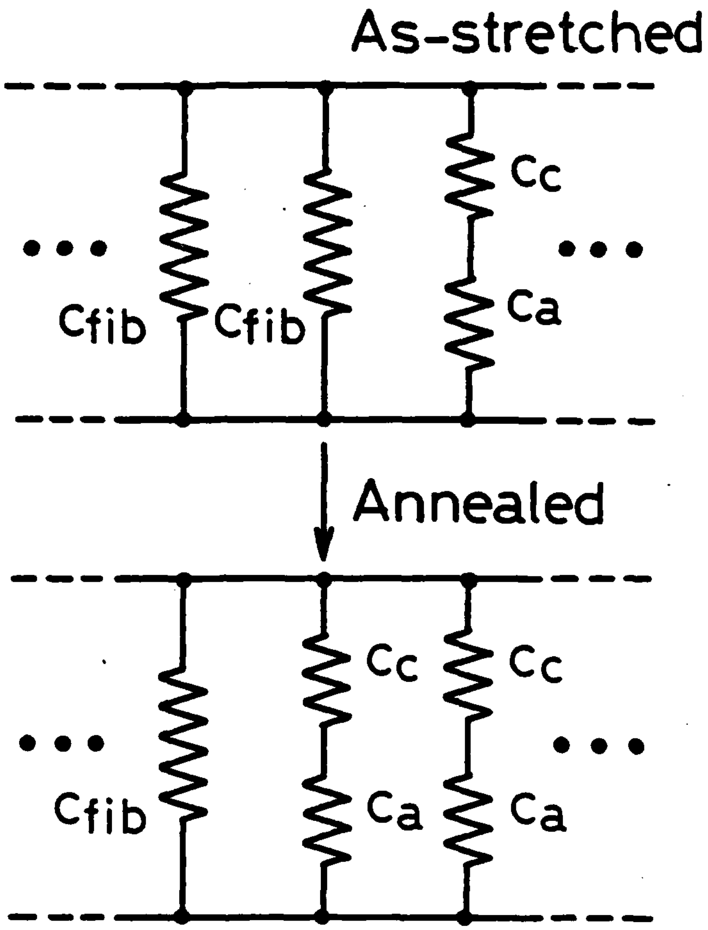

Fig. 11