

## Piezoelectricity in Polyacrylonitrile

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**ABSTRACT:** The piezoelectric and related properties in ion-doped ( $\text{NH}_4\text{NO}_3$ ,  $\text{NaNO}_3$ ) and undoped films of polyacrylonitrile have been measured as a function of temperature. The piezoelectric constants of both ion-doped and undoped films reach a maximum around  $80^\circ\text{C}$  and thereafter decrease markedly with temperature. At about this same temperature, a maximum of thermally stimulated discharge current (TSDC) is also observed with both ion-doped and undoped films. These two effects are thought to have a common origin: the randomization of nitrile dipoles in ordered regions. The piezoelectric constant of pre-stretched films is higher than that for unstretched polyacrylonitrile.

**KEY WORDS** Polyacrylonitrile / Ion-doped ( $\text{NH}_4\text{NO}_3$ ,  $\text{NaNO}_3$ ) Film / Stretched Film / Piezoelectricity / Thermally Stimulated Discharge Current / DC Electric Conductivity /

Piezoelectric properties have been investigated for a variety of polymers.<sup>1,2</sup> Space charges and/or preferred orientation of small parts of macromolecules having non-zero dipole moments are usually considered to be the origin of the residual polarization of electret polymers, and it is their polarization that generates the piezoelectric effect. If residual polarization arises from dipole orientation, a polymer having a large dipole moment may, therefore, have high piezoelectric activity. One polymer demonstrated to have strong piezoelectric activity in its stretched and polarized form is poly(vinylidene fluoride) (PVDF),<sup>3</sup> and it does have a high value of dipole moment, 2.1 Debye units, in its chemical repeat. However, polyacrylonitrile (PAN) side groups have dipole moments of nearly 3.5 Debye units, and these dipoles can be oriented by an applied electrical field.<sup>4,5</sup> Thus, high piezoelectric activity of PAN is also expected.

Because piezoelectricity arises from a combination of dielectric and elastic characteristics in polymer films, it is a rather complicated phenomenon. It should, therefore, exhibit sensitivity to chemical and/or physical structure of a polymer solid. For example, part of the polarization in PAN has been shown<sup>4</sup> to arise from nonpolymeric species which either permanently or transiently carry charges and which, when the specimen is polarized, develop space charging in the specimen. Another part of the polarization in PAN does come from a preferential orientation of nitrile side groups. According to results of infrared internal reflection spectroscopic measurements by Stupp, *et al.*<sup>5</sup> randomization of these oriented dipoles is thermally induced as the temperature is raised above  $90^\circ\text{C}$ . Around this temperature, both dielectric relaxation<sup>6-9</sup> and mechanical relaxation<sup>10-12</sup> have been observed. Therefore, one would expect that the contribu-

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tion to piezoelectric constant due to orientation of dipoles would decay irrecoverably in this temperature region. Many papers concerning the physical structure<sup>13-18</sup> and properties of PAN have been published, but actual piezoelectric behavior of PAN has not been reported in any detail. In this paper, the results of the temperature-dependence of the piezoelectric constants for PAN are reported.

## EXPERIMENTAL

Polyacrylonitrile (PAN) was supplied from Standard Oil Company (Cleveland, OH). The material is reported to have a weight average molecular weight in excess of 35,000. Purification involved the following: PAN powder was first dissolved in dimethylformamide (DMF) at a concentration of 5 wt%, and then it was reprecipitated by pouring the solution into distilled methanol. PAN material doped with NaNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub> was prepared by first dissolving the salt in DMF and subsequently adding it dropwise to the PAN solution in DMF. PAN films were cast on a glass surface from 2 wt% DMF solutions under reduced pressure for 24 h at room temperature. The cast films were then dried in an evacuated oven for 24 h at 40°C. Some films were uniaxially stretched at 90°C and then annealed at 130°C for 30 min. Dimensions of film samples for piezoelectric measurements were 2 cm × 0.4 cm, and thicknesses of samples

ranged from 30 to 54 μm. Gold was evaporated onto both sides of every sample to serve as electrodes, and the area of electrode was 0.21 cm<sup>2</sup>. Dimensions of film samples for thermally stimulated discharge (TSDC) measurements were 2.5 cm × 2.5 cm, with an electrode area of 3.14 cm<sup>2</sup>.

A Rheovibron model DDV-II-B (Toyo Kogyo Co., Japan) was used to measure the piezoelectric-strain constant,  $d_{31}$ , piezoelectric-stress constant,  $e_{31}$ , and elastic constant  $C_{11}$ . The 1-axis is taken along the length (stretching direction), and the 3-axis is along the 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  $1.5 \times 10^{-3}$ ) measured and used as basis for calculating absolute values of  $d_{31}$ ,  $e_{31}$ , and  $C_{11}$ . The piezoelectric polarization was detected using a charge amplifier under short-circuit conditions. This measurement was made in the temperature region between room temperature and about 150°C, with a heating rate of about 1°C/min.

Thermally stimulated discharge current (TSDC) thermograms and direct current (dc) conductivity were recorded with an Electret Thermal Analyzer (Toyo-Seiki, Seisaku-sho, Ltd.). The heating rate was 2°C min<sup>-1</sup>. All specimens that were polarized were held for 30 min under the imposed electrical field of  $5 \times 10^4$  V cm<sup>-1</sup> at 130°C and then cooled at

Table I.  $d_{31}$  of polyacrylonitrile film at 25°C (11 Hz)

Dopant species	Dopant concentration <sup>a</sup>	Poling field	Elongation ratio	$10^8 \times d_{31}$ (cgsesu)		
		V cm <sup>-1</sup>		Room temp.	Around 85°C	Around 120°C
None	—	$5 \times 10^4$	2	1.7	4.3	3.6
None	—	$5 \times 10^4$	1	0.32	0.65	—
NH <sub>4</sub> NO <sub>3</sub>	$2 \times 10^{-4}$	$2 \times 10^4$	2	0.26 (0.65) <sup>b</sup>	0.80 (2.0) <sup>b</sup>	1 (2.5) <sup>b</sup>
NaNO <sub>3</sub>	$2 \times 10^{-4}$	$1 \times 10^4$	1	0.07 (0.35) <sup>b</sup>	0.16 (0.8) <sup>b</sup>	8 (40) <sup>b</sup>
None	—	$10 \times 10^4$	2	3.0	6.3	10.7

<sup>a</sup> Molar concentration units: moles salt per gram PAN. For example,  $1 \times 10^{-4}$  mol g<sup>-1</sup> PAN = 0.85 wt% salt =  $5.3 \times 10^{-3}$  mol/AN residue.

<sup>b</sup> Normalized to be equivalent to a poling field of  $5 \times 10^4$  V cm<sup>-1</sup>.

room temperature under the applied electrical field. The conditions of the specimens are listed in Table I.

## RESULTS

Figures 1 and 2 show the temperature-dependence of the absolute values of dynamic piezoelectric strain constant,  $d_{31}$ , and dynamic piezoelectric stress constant,  $e_{31}$ , for stretched and unstretched PAN films. When tension is given to the specimen at room temperature, negative charge is induced on that surface against which a positive field had been 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°C, both  $d_{31}$  and  $e_{31}$  increase with temperature. However, above 80°C,  $d_{31}$  and  $e_{31}$  decrease remarkably. The piezoelectric constants of stretched specimens show a second peak around 120°C. The piezoelectric constants for a second run, at room temperature, are about 2.5% of those of the first run. The  $d_{31}$ - and  $e_{31}$ -constants of unstretched specimens do not show the second peak, and these values at room temperature are about 20% of initial values for stretched PAN.

Figure 3 shows the temperature-dependence of the absolute values of the dynamic elastic constant  $C_{11}$ , of unstretched film. The remarkable rate of decrease of  $C_{11}$  above 75°C may be due to  $\alpha_a$ -relaxations, as observed by Okajima *et al.*<sup>19</sup> Ishida *et al.*<sup>6</sup> reported a  $\beta$ -relaxation around 60°C (100 Hz) by dielectric measurement, and they attributed it to some local mode relaxation.

Figure 4 represents the temperature-dependence of  $e_{31}$  for both  $\text{NH}_4\text{NO}_3$ - and  $\text{NaNO}_3$ -doped films. The  $e_{31}$  constants decrease steeply above 80°C, in the same manner as those of undoped films. The  $d_{31}$ -constants for each of these samples are listed in Table I. Since either the material doped with ammonium nitrate and stretched or the material

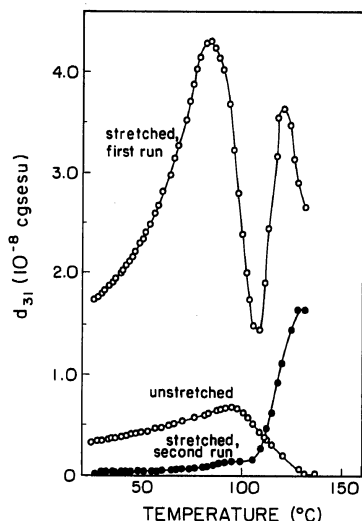


Figure 1. Temperature-dependence of  $d_{31}$ -constants for stretched and unstretched polyacrylonitrile poled at 130°C under  $5 \times 10^4 \text{ V cm}^{-1}$  for 30 min. The stretched specimen was cooled after the first run without an applied field.

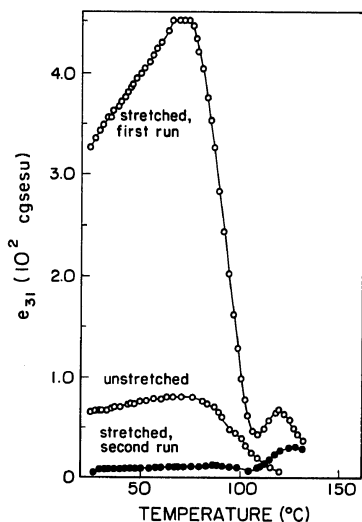
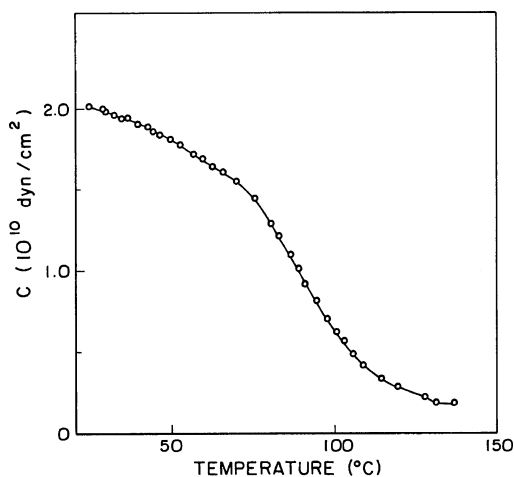
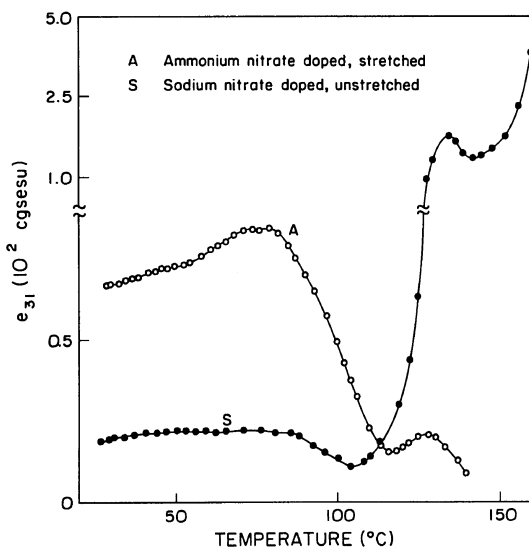


Figure 2. Temperature-dependence of the  $e_{31}$ -constants for stretched and unstretched polyacrylonitrile poled at 130°C under  $5 \times 10^4 \text{ V cm}^{-1}$  for 30 min. The stretched specimen was cooled after the first run without an applied field.

doped with sodium nitrate but not stretched had been polarized under fields,  $E_p$ , of  $2 \times 10^4 \text{ V cm}^{-1}$  and  $1 \times 10^4 \text{ V cm}^{-1}$  respectively, the

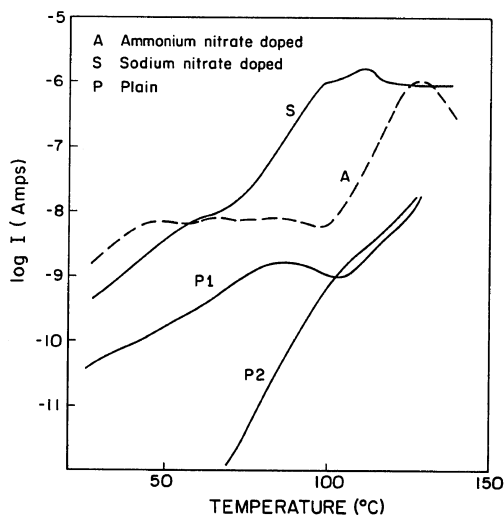


**Figure 3.** Temperature-dependence of the elastic constant,  $C_{11}$ , for unstretched polyacrylonitrile measured at 11 Hz.

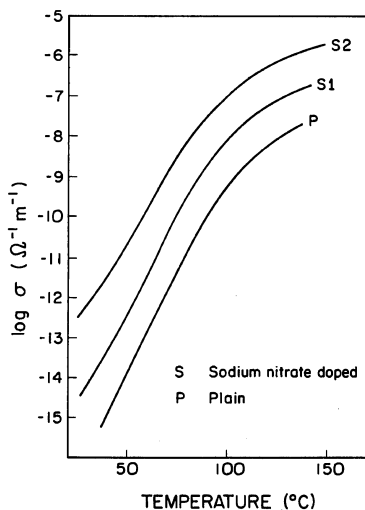


**Figure 4.** Temperature-dependence of the  $e_{31}$ -constants for  $\text{NH}_4\text{NO}_3$ -doped and stretched and  $\text{NaNO}_3$ -doped but unstretched polyacrylonitrile. Specimens were poled for 30 min at  $130^\circ\text{C}$  under  $2 \times 10^4 \text{ V cm}^{-1}$  and  $1 \times 10^4 \text{ V cm}^{-1}$ , respectively.

observed  $d_{31}$ -constants of these PAN preparations are multiplied by normalizing factors of 2.5 and 5, respectively, which are the ratios of  $5 \times 10^4 \text{ V cm}^{-1}$  (the applied electric field in the cases of Figures 1 and 2) to  $E_p$ . It is clear



**Figure 5.** Thermally stimulated depolarization currents from undoped (P) and from ion-doped polyacrylonitrile ( $A=2 \times 10^{-4} \text{ [mol g}^{-1} \text{ PAN] NH}_4\text{NO}_3$  doped film;  $S=2 \times 10^{-4} \text{ [mol g}^{-1} \text{ PAN] NaNO}_3$  doped film) poled at  $130^\circ\text{C}$  under an electrical field of  $5 \times 10^4 \text{ V cm}^{-1}$  for 30 min. P1=the first measurement; P2=the second measurement, cooled after the first run without an applied field. Heating rate was  $2^\circ\text{C min}^{-1}$ .



**Figure 6.** Temperature-dependence of the second run of d.c. conductivity (cooled after the first measurement under an applied field) for  $\text{NaNO}_3$  doped and undoped polyacrylonitrile measured at heating rate of  $2^\circ\text{C min}^{-1}$ . P=undoped film; S1= $2 \times 10^{-5} \text{ [mol g}^{-1} \text{ PAN] NaNO}_3$  doped film; and S2= $5 \times 10^{-4} \text{ [mol g}^{-1} \text{ PAN] NaNO}_3$  doped film. Doped specimens were poled under an electrical field of  $5 \times 10^3 \text{ V cm}^{-1}$ , and undoped films were poled using  $1 \times 10^4 \text{ V cm}^{-1}$ .

from these results that the piezoelectric constants of PAN increase with stretching; polarization by high intensity electrical field also creates increased levels of piezoelectric activity.

Figure 5 shows the thermally stimulated discharge current thermograms of ion-doped ( $2 \times 10^{-4}$  [mol g<sup>-1</sup> PAN] NaNO<sub>3</sub>,  $2 \times 10^{-4}$  [mol g<sup>-1</sup> PAN] NH<sub>4</sub>NO<sub>3</sub>) and plain films polarized at 130°C under an electrical field of  $5 \times 10^4$  V cm<sup>-1</sup> for 30 min. The depolarization currents for both ion doped and plain films show a peak around 90°C. The peak is not observed in the second run, P2. Figure 6 represents the temperature dependence of dc electrical conductivity. The slope of the line changes around 100°C.

## DISCUSSION

The upward trend in piezoelectric strain constant,  $d_{31}$ , for PAN in the vicinity of room temperature is presumably due to the rise in mechanical compliance,  $J_{11}$ , ( $J_{11} = 1/C_{11}$ , where  $C_{11}$  is the elastic constant), with temperature, as shown in Figure 3, because  $d_{31}$  is proportional to  $J_{11}$ , as  $d_{31} = e_{31}J_{11}$ .

Because it is easily found experimentally that unpolarized PAN indeed possesses no appreciable piezoelectric activity, then the magnitude of polarization that can develop in PAN and, more importantly, the nature of this polarization become important in understanding what piezoelectric behavior there is to be measured. Polarization in PAN is commonly taken as arising from a combination of a preferential orientation of dipoles and from space charging effects (unless the space charging creates only mono-polarization). These two effects are additive, and, as such, one expects an increase in net piezoelectricity if the two contributions are of the same sign. Conversely, one expects a decrease in piezoelectricity if these two contributions are of opposite sign. Dipolar polarization has, in fact, been demonstrated,<sup>4,5,20</sup> and it can be

increased by mechanical stretching of the film prior to polarization.<sup>4</sup> Room temperature  $d_{31}$  data (Table I) show the amount by which piezoelectricity responds to this kind of enhancement of polarization.

Attempts in this work to increase polarization by deliberate incorporation of space charges (by ion-doping) yield the surprising result of little, or possibly no, appreciable enhancement of piezoelectric activity! High electrical conductivity of the matrix phase induced by doping ions may decrease the effective electric field applied to the dipoles in the piezoelectric phase. Figure 5 illustrates clearly that incorporation of ions does achieve a large polarization enhancement (more than ten-fold), and the polarization is indeed of the same sign as that due to orientation of dipoles. The reason for this effect is not clear, but the notion that room temperature piezoelectricity in PAN is dominated by dipolar effects is consistent with the observed rapid loss of piezoelectricity above 75°C. Such a feature as this has been observed in many piezoelectric polymers (and is called "piezoelectric relaxation").<sup>21,22</sup> This temperature range coincides quite closely with the known loss of preferred orientation of some nitrile side groups,<sup>20</sup> and so it is proposed that such a local mode process is the cause of this relaxation. An alternative explanation might be an onset of electrical conductivity within the material, which would depress piezoelectric constants.<sup>23,24</sup> The coefficient of expression 1 is applied to bulk  $e$ -constants of materials composed of a continuous matrix phase No. 1 and a dispersed piezoelectrically-active phase No. 2.

$$\frac{C_1}{\alpha C_1 + C_2} \quad (1)$$

where  $\alpha$  is a geometrical factor for phase 1;  $C_1$  and  $C_2$  are electrical capacitances of phase 1 and phase 2, respectively. This coefficient will decrease if charge transport becomes possible in phase 2, through its corresponding increase

in electrical permittivity. Data on conductivity of these PAN materials (Figure 6) show that there is no such abrupt increase in conductivity that could explain the loss of piezoelectric activity in question.

The effect of molecular organization on piezoelectric properties in PAN is important but remains only partly understood. Stretching of specimens, which causes chain alignment plus development of short-range ordering, does clearly enhance room-temperature piezoelectricity into the range of  $3 \times 10^{-8}$  cgsesu. This is similar to what has been observed previously for PVDF, which possesses high piezoelectric activity.<sup>25</sup> Short-range ordering in polarized PAN<sup>20</sup> may be important in controlling both the amount by which dipolar relaxations can occur and the behavior of space charges in polarized and in unpolarized PAN. For example, it has been discussed for some time<sup>13,17,26</sup> that a kind of helical conformation is possessed by PAN chains and that this disposes the nitrile side-groups more-or-less into radial directions. The lateral packing<sup>15,17,18,26</sup> possible with PAN chains is assumed to develop a net dipole moment in the ordered regions. Nevertheless, these ordered regions may represent sites about which Maxwell-Wagner polarization can occur as the result of motion of some space-charging species. It should be noted, however, that the relaxation process occurring at 90°C would not result in a loss of the chain packing pattern of such ordered regions; rather it would simply result in the randomization of dipoles within such regions.<sup>10-13,16</sup> Such local screening polarizations as would form around ordered regions would be expected to decay at 90°C only by the amount by which any net dipole moment of the ordered region relaxes. Phenomenological theories combining effects of multiple contributions to polarization in inhomogeneous systems have been discussed earlier.<sup>27,28</sup>

The exact reasons for the second peak of the piezoelectric constants observed above 100°C

are not clear yet, but it may be associated with the space charge polarization. The depolarization current above 100°C, shown in Figure 5, is also due to space charge.

## CONCLUSIONS

Room temperature piezoelectric activity developed in pure and in ion-doped PAN is due to polarization arising from preferential orientation of nitrile dipoles; the decrease of piezoelectric constant around 90°C is ascribed to the randomization of these nitrile dipoles. The room temperature piezoelectric behavior of ion-doped films ( $\text{NH}_4\text{NO}_3$ ,  $\text{NaNO}_3$ ) is essentially the same as seen in pure PAN, even though thermally stimulated depolarization current data indicate an order-of-magnitude increase in polarization of ion-doped films. Stretching of PAN before polarization is effective in enhancing piezoelectric strain constant, specifically by bringing it into the range of  $10^{-7}$  cgsesu.

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## REFERENCES

1. S. B. Lang, *Ferroelectrics*, **32**, 191 (1981); *ibid.*, **34**, 239 (1981).
2. A. J. Lovinger, *Science*, **220**, 1115 (1983).
3. M. Kawai, *Jpn. J. Appl. Phys.*, **8**, 975 (1969).
4. R. J. Comstock, S. I. Stupp, and S. H. Carr, *J. Macromol. Sci., Phys.*, **B13**(1), 101 (1977).
5. S. I. Stupp and S. H. Carr, *J. Polym. Sci., Polym. Phys. Ed.*, **16**, 13 (1978).
6. Y. Ishida, O. Amano, and M. Takayanagi, *Kolloid Z.*, **172**, 129 (1960).
7. Y. Ishida, M. Matsuo, Y. Ueno, and M. Takayanagi, *Kolloid-Z. Polym.*, **199**, 67 (1964).

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8. L. K. H. Van Beek, *J. Appl. Polym. Sci.*, **9**, 553 (1965).
9. R. Hayakawa, T. Nishi, K. Arisawa, and Y. Wada, *J. Polym. Sci., A-2*, **5**, 165 (1967).
10. Y. Imai, S. Minami, T. Yoshihara, Y. Joh, and H. Sato, *Polym. Lett.*, **8**, 281 (1970).
11. S. Minami, T. Yoshihara, and H. Sato, *Kobunshi Kagaku*, **29**, 114 (1972).
12. K. Miyachi and R. D. Andrews, *Appl. Polym. Sym.*, No. **25**, 127 (1974).
13. C. R. Bohn, J. R. Schaeffgen, and W. O. Statton, *J. Polym. Sci.*, **55**, 531 (1961).
14. J. Koenig, *J. Macromol. Sci., Phys.*, **B4**, 491 (1970).
15. G. Hinrichsen and H. Orth, *Polym. Lett.*, **9**, 529 (1971).
16. G. Hinrichsen, *J. Polym. Sci., C*, **38**, 303 (1972).
17. B. G. Calvin and P. Storr, *Eur. Polym. J.*, **10**, 337 (1974).
18. S. B. Warner, L. H. Peebles, Jr., and D. R. Uhlmann, Office of Naval Research Technical Report No. 1, for Contract N-00014-75-C-0542 (1978).
19. S. Okajima, M. Ikeda, and A. Takeuchi, *J. Polym. Sci., A-1*, **6**, 1925 (1968).
20. S. I. Stupp and S. H. Carr, *Colloid Polym. Sci.*, **257**, 913 (1979).
21. M. Date, S. Takashita, and E. Fukada, *J. Polym. Sci., A-2*, **8**, 61 (1970).
22. T. Furukawa and E. Fukada, *Nature*, **221**, 1235 (1969).
23. T. Furukawa and E. Fukada, *Jpn. J. Appl. Phys.*, **16**, 453 (1977).
24. E. Fukada, H. Ueda, and R. Rinaldi, *Biophys. J.*, **16**, 911 (1976).
25. N. Murayama, *J. Polym. Sci., Phys.*, **13**, 929 (1975); **14**, 989 (1976).
26. P. H. Lindenmeyer, *J. Appl. Phys.*, **34**, 42 (1963).
27. M. Date, *Polym. J.*, **8**, 60 (1975).
28. T. Furukawa, J. Aiba, and E. Fukada, *J. Appl. Phys.*, **50**, 3615 (1979).