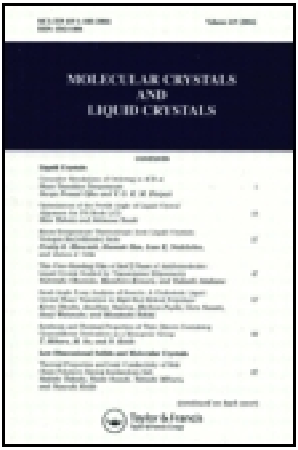

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Pyroelectric and Dielectric Behaviour of the Crystals of The Bis-Toluene Sulphonate Diacetylene Monomer and Polymer

Xiao Ding Quan [a] , David John Ando [a] & David Bloor [a]
[a] Department of Physics, Queen Mary College, Mile End Road, London, E1 4NS, ENGLAND
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PYROELECTRIC AND DIELECTRIC BEHAVIOUR OF THE CRYSTALS OF THE BIS-TOLUENE SULPHONATE DIACETYLENE MONOMER AND POLYMER

XIAO DING QUAN*, DAVID JOHN ANDO AND DAVID BLOOR
Department of Physics, Queen Mary College,
Mile End Road, London E1 4NS, ENGLAND.

Abstract The pyroelectric and dielectric properties of the monomer and partially and fully polymerized crystals of the bis(p-toluene sulphonate) of 2,4-hexadiyne-1,6-diol (TS) were measured along their b-axes from 100 - 300 K. The transition temperatures of the crystals determined from pyroelectric anomalies are similar to those from X-ray and heat capacity determination. The ageing effect of polymer TS crystals has been observed. It is concluded that these crystals lack a Centre of Symmetry.

INTRODUCTION

The presence of pyroelectricity in non-polarised crystals indicates the presence of spontaneous polarisation within the materials and its variation with temperature. Therefore, the observation of pyroelectricity in the toluene sulphonate diacetylene (TS) is apparently in conflict with the centrosymmetric structure determined by X-ray diffraction.

We have made further measurements of the pyroelectric effect in monomer, and partially and fully polymerised crystals of this material, in order to confirm the results of Kiess and Clark[1], and to determine if the monomer and partially and fully polymerised crystals are non-centro-

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*Present Address: Department of Physics, Sichuan University, Chengdu, The People's Republic of China.

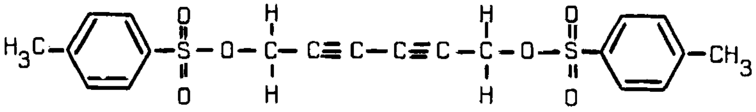
symmetric. Our results reveal a pyroelectric effect along the b-axes of all the monomer, partially and fully polymerised TS crystals studied over the temperature range 100 - 300 K, and enables us to make comparisons with recent observations of phase transitions in similar samples.

Nine months after the first measurements, the sign and magnitude of the pyroelectric coefficient of the polymer TS crystals remain almost unchanged. There are, however, significant changes near the phase transition region and in the temperature at which the pyroelectric current changes its sign as described below.

We have also measured the dielectric properties of the monomer and polymer TS crystals. No dielectric anomaly has been found along either their b-axes or a-axes over the same temperature range.

EXPERIMENTAL

MATERIAL - TS



TS monomer crystals grown from acetone solutions were cut parallel to the (010) plane, i.e. the polymer chains are perpendicular to the contact area, and the samples were thermally polymerized in the solid state at 333 K. The polymerization time, ranging from 5 to 170 hours, depends on the requirements. Silver paste electrodes were spread on opposing (010) surfaces. For pyroelectric measurements the electrode area was typically 0.03 to 0.1 cm^2, and for dielectric measurements, 0.2 - 0.3 cm^2. The thickness of all the samples was about 0.05 cm.

PYROELECTRIC MEASUREMENT

The pyroelectric effect was investigated by using the pyroelectric current method

$$I = dQ/dt = pA\ dT/dt, \qquad (1)$$

and the current was measured with two Keithley Model 610C electrometers. The experimental apparatus is shown schematically in Fig. 1. The magnitude of the pyroelectric signal

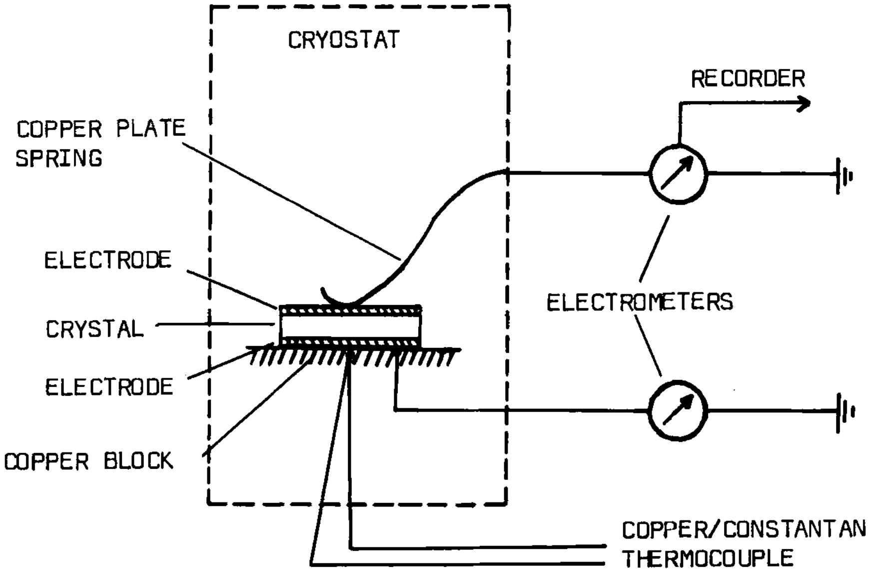


FIGURE 1. Schematic of experimental apparatus.

was of the order of 10^{-13} A, well above the maximum background current, which was less than 2×10^{-14} A.

The crystals were cooled and heated at a quasi-constant rate, and the temperature and its rate of change were monitored by a DTC-2 digital temperature controller. The system was carefully calibrated by using a copper versus constantan thermocouple to correct for a small temperature gradient between the DTC-2 sensor and the sample.

The experimental conditions were:

Temperature range	100 - 300 K,
Temperature change rate	0.6 - 0.15 K/s,
Vacuum pressure of cryostat	$<2 \times 10^{-5}$ torr,
Electric field in the crystals	<1 V/cm.

DIELECTRIC MEASUREMENT

The capacitance C and conductance G were measured at 1 KHz with an autobalance universal bridge (WAYNE KERR B642). The sample holder and measuring conditions were similar to that used in pyroelectric measurements.

The system for the measurements of pyroelectric and dielectric properties were tested by using a $BaTiO_3$ crystal sample.

RESULTS AND DISCUSSION

All the monomer, partially and fully polymerized TS crystals under investigation show a pyroelectric effect along their b-axes over the temperature range 100 - 300 K. The sign of the current for heating is exactly the reverse of that for cooling. An example of the recorded currents (for monomer TS) is shown in Fig. 2. The pyroelectric behaviour of polymer TS crystal is very similar to the results of Kiess and Clarke.[1]

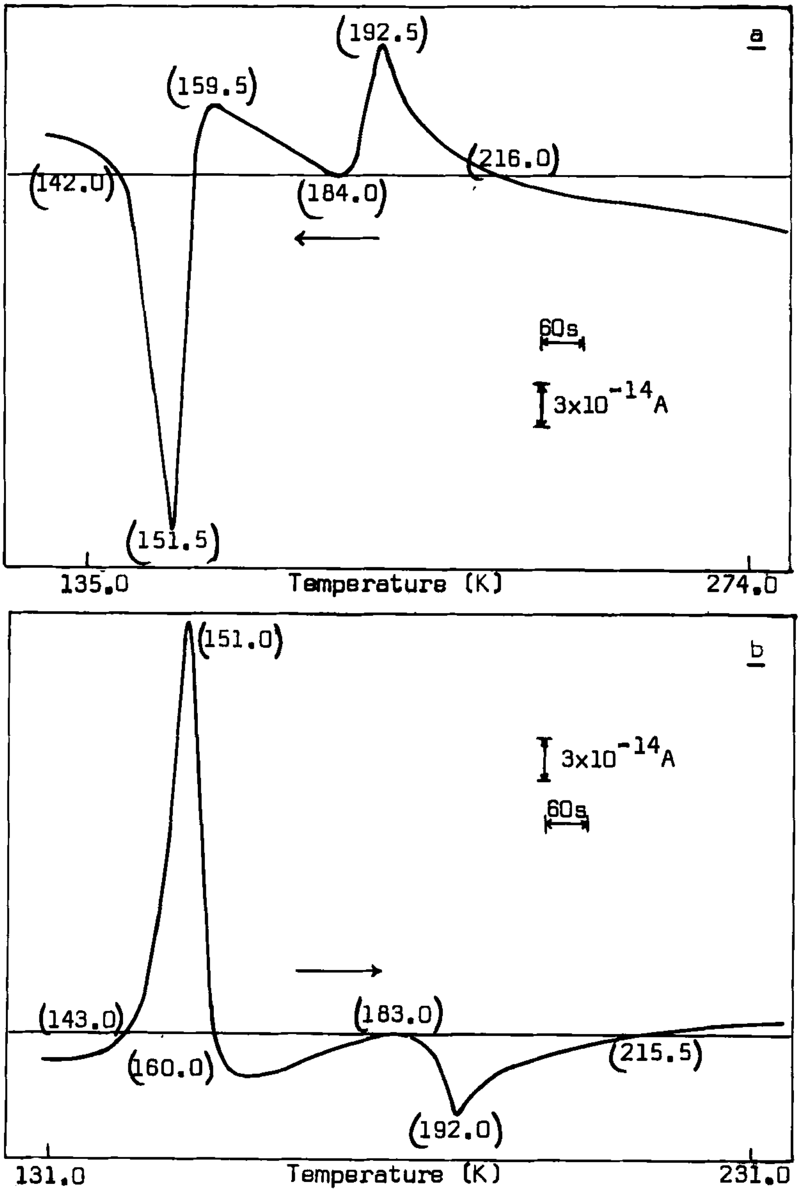


FIGURE 2. The pyroelectric currents recorded from monomer TS crystals in their *b*-axes upon a) cooling and b) heating. The figures in parentheses are the corresponding temperatures.

The pyroelectric coefficient calculated from the recorded currents for monomer, partially and fully polymerized TS crystals in their b-axes are shown in Figs. 3 and 4. The maximum pyroelectric coefficients for polymer TS is (3-4) x 10^{-11} C/cm^2 K, similar to that of the polarized polyvinyl chloride (3 x 10^{-11} C/cm^2 K), but about 2 orders of magnitude smaller than that of polyvinylide fluoride (1.0 - 2.4) x 10^{-9} C/cm^2 K.

The phase transitions obtained from the anomalies of pyroelectric behaviour (see Fig. 5) are in reasonable agreement with X-ray diffraction and specific heat capacity measurements. The two peaks in the pyroelectric coefficient of the crystals polymerised for less than 15 hours at 33 K correspond to the two phase transitions, i.e. the high temperature commensurate phase to an incommensurate phase, and the incommensurate to low temperature commensurate phase. The values of the transition temperatures for TS monomer are 206 and 163 K (from X-ray data[2]), 193 and 157 or 192 and 156 K (from heat capacity data[3,4]) and 192 and 151 K (from our pyroelectric data[5]). The apparent discrepancies probably occur due to the sensitivity of the transition temperatures to traces of polymer or the ageing effects. Our results suggest a lower limiting value for the transition temperature, 195 K, than that observed by Patillon et al, 205 K,

The oscillation of the pyroelectric current near the phase transition (two extrema exist in this temperature region) suggests that two transitions occur, i.e. that an incommensurate phase exists within 4 K of the phase transition temperature reported previously.

By considering the experimental conditions, all the mechanisms, such as injection of charge, preferred orientation of dipoles by external field, dielectric absorption

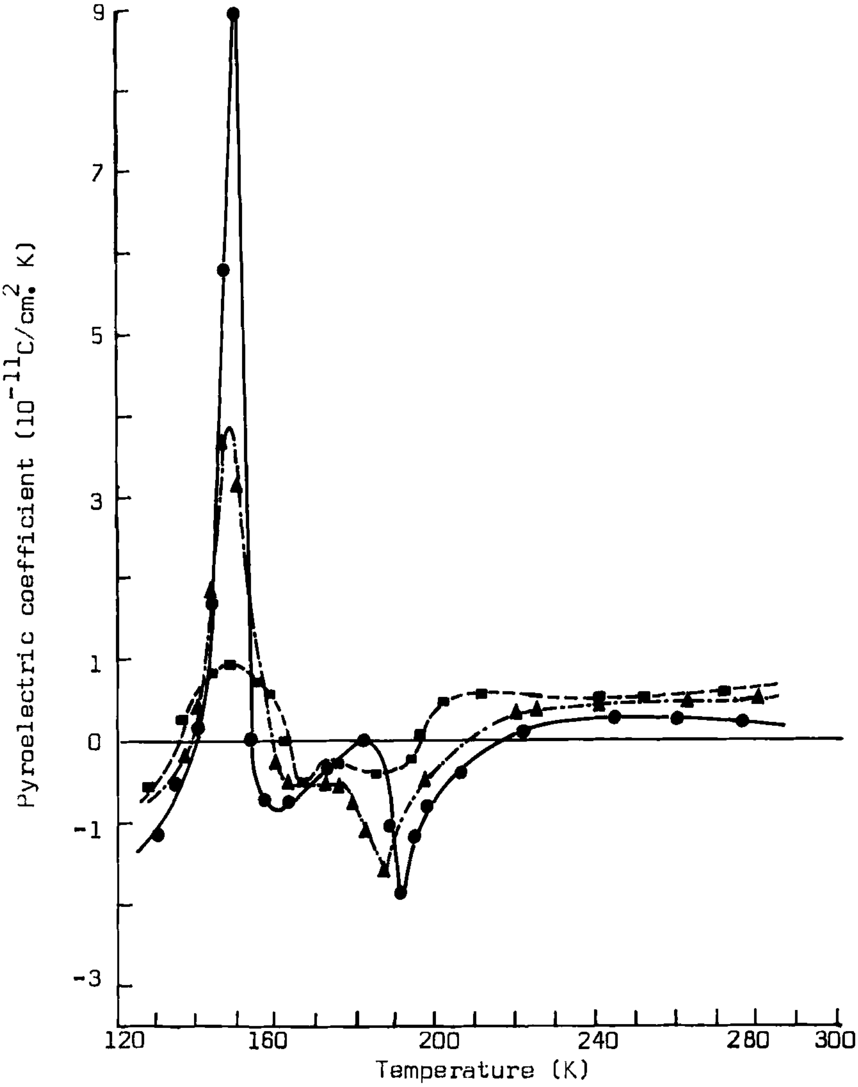


FIGURE 3. The temperature dependence of the component p_b of the pyroelectric coefficient along the b-axis, for TS monomer crystals (●,——), 5 hours partially polymerized TS crystals (▲,—·—·—) and 10 hours partially polymerized TS crystals (■,– – –) (all measured upon heating). (Reproduced with the kind permission of the North Holland Publishing Company.)

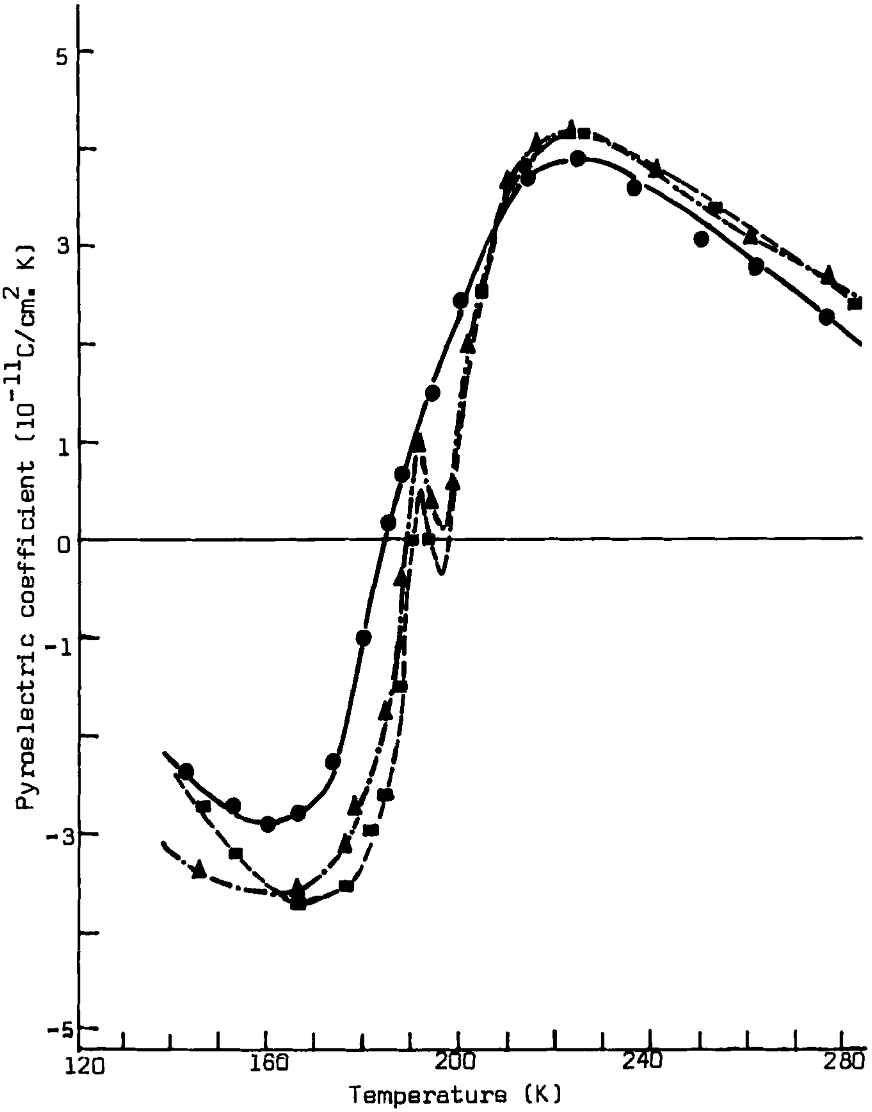


FIGURE 4. The temperature dependence of the component P_b of the pyroelectric coefficient along the b-axis, for TS crystals partially polymerized for 15 hours (●,——), 20 hours (▲,—·—·—) and 72 hours (■,— — —) (all measured upon heating). (Reproduced with the kind permission of the North Holland Publishing Company.)

current, photo-electric current, occurrence of ionic charges on crystal bounding surfaces and their temperature dependence, etc., were excluded to explain the observed current.

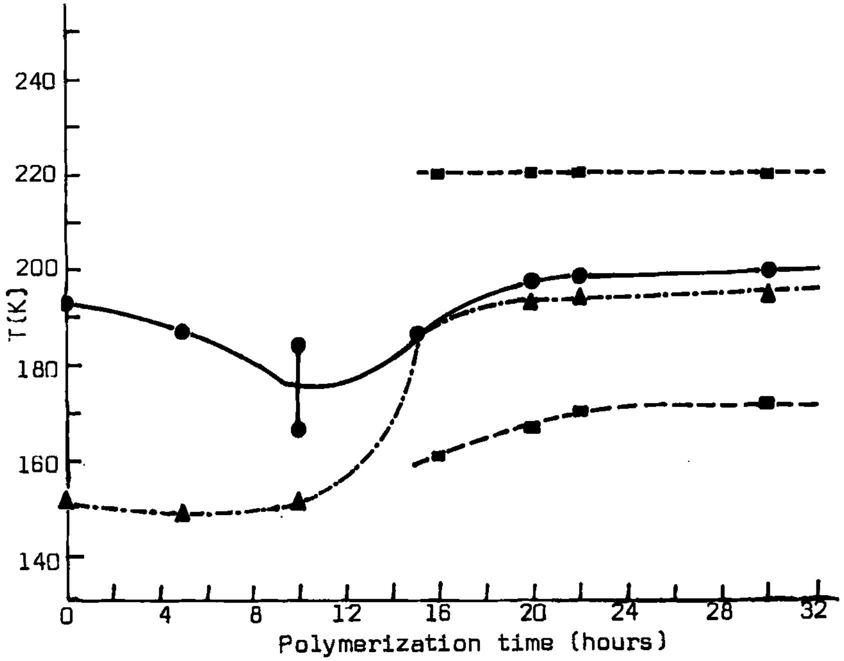


FIGURE 5. The phase transition temperatures as a function of polymerization time at 333 K obtained from the pyroelectric measurements (upper transition, ●,——— ; lower transition, ▲ ,—·—·— ; temperatures corresponding to P_b maxima , ■, — — — —) (Reproduced with the kind permission of North-Holland Publishing Company.)

From the experiments of varying the temperature change rate dT/dt, it is very clear that the current depends on dT/dt (this can also be seen from Fig. 2), and consequently the thermoelectric current is also excluded. Therefore we conclude that the pyroelectric effect in these crystals indicates that the crystals must lack a centre of symmetry.

The marked difference in the pyroelectric behaviour of the monomer and polymer crystals suggests different origins for the non-centrosymmetry. For crystals with low polymer content, the non-centrosymmetry results from the occurrence of the incommensurate phase, which is thought to be either an orientation wave involving torsion of the side groups or a probability wave involving the two different side group configurations[6]. Since the side-groups contain polar SO_2 groups (see crystal structure for details[7]) any perturbation of the structure can give rise to a net dipole for the crystal. The occurrence of domains or the pinning of the incommensurate structure at dislocations are two perturbations which could produce this effect. Since the upper phase transition is nearly second order[8] the effect of perturbations will be weaker than that at the lower phase transition. In addition, at lower transition the wavelength in the incommensurate phase approaches infinity so that any perturbation of the structure would have a much larger effect, as observed experimentally.

The large pyroelectric effect observed over a wide temperature range for crystals with high polymer content is more difficult to explain. It is probably a result of the strain which occurs in partially polymerised crystals due to the mis-match between the monomer and polymer.

The ageing effect of the pyroelectricity of the polymer TS crystals, which were stored in the dark in a refrigerator, has been observed. After 8-9 months of the first measurement (i.e., about one year since the crystal growth), the sign and magnitude of the pyroelectric coefficient of polymer TS crystals was essentially unchanged, but the oscillation of the pyroelectric current near the phase transition region decreases or even completely disappears, and the temperature at which the pyroelectric current changes its sign is lower. The typical pyroelectric current curves recorded on cooling for both surfaces of a polymer TS sample (polymerized at 333 K for 72 hours and stored for 9 months) are shown in Fig. 6. Comparing Fig. 6 with Fig. 4 (the curve for 72 hours polymerization), one can clearly see the difference between them. The loss of the two extrema suggests that the transition from higher temperature commensurate phase to lower temperature commensurate phase occurs continuously.

The dielectric properties of monomer and polymer TS crystals along their b-axes were measured over the temperature range 100 - 300 K. The temperature dependence of the dielectric constant is shown in Fig. 7, together with the results for polymer TS crystals along their a-axes which were converted from the data of Saunders[9]. No dielectric anomaly has been found for monomer and polymer TS crystals in either b-axes or a-axes in the temperature range studied.

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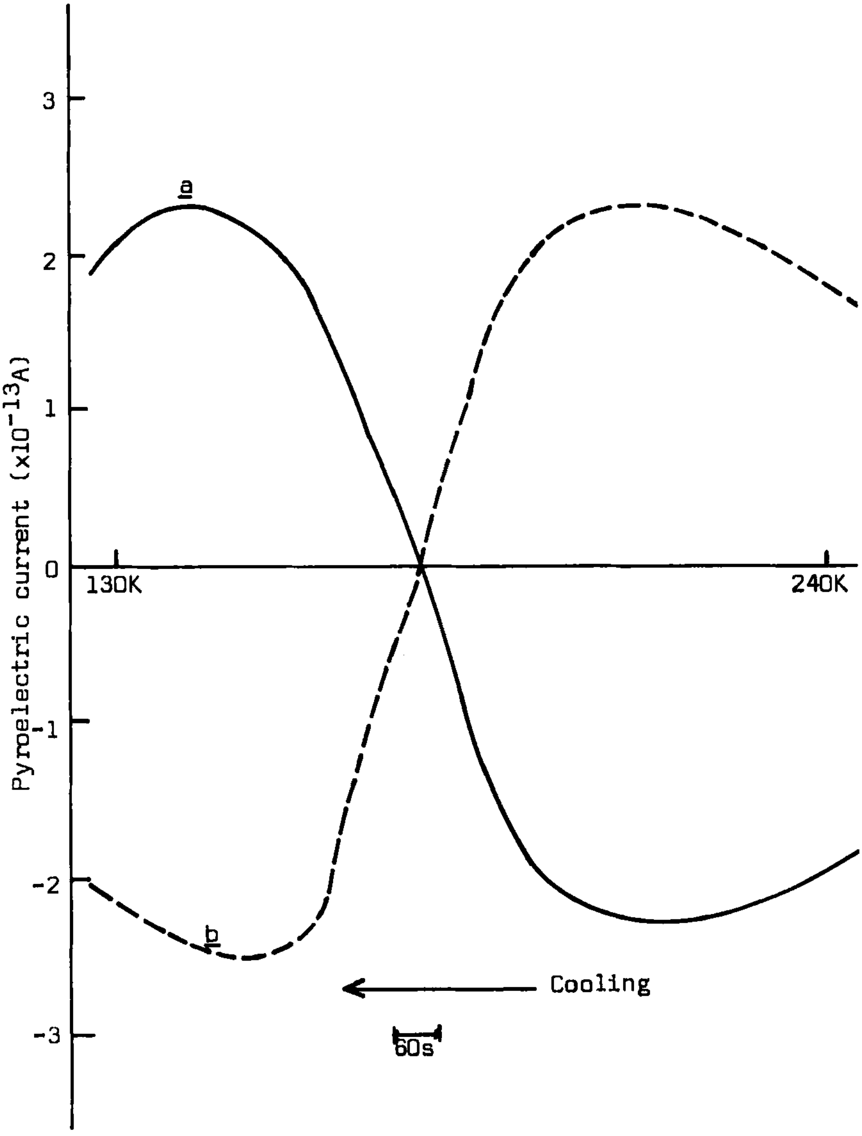

FIGURE 6. Typical recorded curves on cooling for both surfaces of a TS sample polymerized at 333 K for 72 hours; measurements taken after samples had been stored for a period of approximately 9 months.

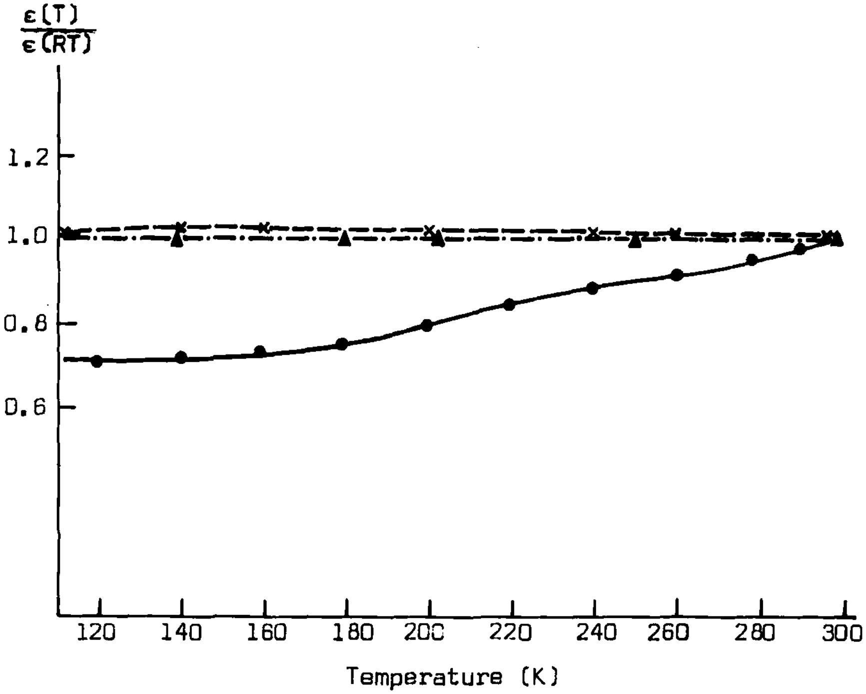

FIGURE 7. The temperature dependence of the dielectric constant of the monomer and polymer TS crystals along their a- and b-axes: ε_a (●, ———), polymer TS crystals, a-axis (coverted from ref. 8); ε_b-p (X, – – – –), polymer TS crystals, b-axis; ε_b-m (▲, —·—·—), monomer TS crystals, b-axis.

REFERENCES

1. H. Kiess and R. Clarke, Phys. Stat. Solidi, A49, 133 (1978).
2. J. N. Patillon, P. Robin, P. A. Albouy, J. P. Pouget and R. Comes, Mol. Cryst. Liq. Cryst. 76, 297 (1981).
3. I. Hatta, T. Nakayama and T. Matsuda, Phys. Stat. Solidi, A62, 243 (1980).
4. M. Bertault, A. Collet and M. Schott, J. Physique-Letters, 42, L131 (1981).
5. D. Q. Xiao, D. J. Ando and D. Bloor, Chem. Phys. Lett., 90, 247 (1982).
6. P. Robin, J. P. Pouget, R. Comes and A. Moradpour, Chem. Phys. Lett., 71, 217 (1980).
7. D. Bloor, D. A. Fisher, D. N. Batchelder, R. J. Kennedy, A. C. Cottle, W. F. Lewis and M. B. Hursthouse, Mol. Cryst. Liq. Cryst., 52, 83 (1979).
8. J. N. Patillon, P. Robin, P. A. Albouy, J. P. Pouget and R. Comes, Mol. Cryst. Liq. Cryst., 76, 297 (1981).
9. G. A. Saunders, Private Communication.