

Smectic C* (of F*)–Smectic A phase transition in side chain polymers investigated by piezoelectric technique

S. Iablonskii and S. Pikin

Institute of Crystallography RAS, 117333 Moscow, Russia, and Dipartimento di Fisica, Politecnico di Torino, 110129 Torino, Italy

A. Sparavigna and A. Strigazzi

Dipartimento di Fisica, Politecnico di Torino, 110129 Torino, Italy

(Submitted 20 December 1994)

Pis'ma Zh. Eksp. Teor. Fiz. **61**, No. 2, 131–136 (25 January 1995)

The measurement of the piezoelectric response, by means of a new technique sensitive to the polar ordering of the polymer liquid crystals, has been used to detect the temperature phase transitions of the ferroelectric chiral side chain polymer P5*M and of the copolymer C25. As a result of these investigations, the sharp jump of the piezoelectric signal has been observed in the vicinity of the smectic C*–smectic A and smectic F*–smectic A phase transitions. In this letter we present a theoretical model, which takes into account the peculiarities of the structure of polymer ferroelectrics, and propose an explanation for the pretransitional behavior in the piezoelectric signal at the transition temperature. © 1995 American Institute of Physics.

Recently a new technique to measure the piezoelectric response of ferroelectric liquid crystal polymers in the glassy and liquid crystalline state has been developed.¹ This technique, which is sensitive to the polar ordering of the material, detects the low frequency complex value of the piezoelectric response $\Pi = V e^{i\Delta\phi}$, which is characterized by an amplitude V and a phase shift $\Delta\phi$. The response Π is proportional to the derivative $\partial P / \partial \sigma$, where P is the spontaneous or induced polarization, and σ is the applied stress. In the case of intrinsic piezoelectricity, the polarization is a function of the tilt angle θ in the smectic phase. In this case the signal can be assumed proportional to ² $\partial \theta / \partial \sigma$.

Here we present the results obtained by applying this technique to the study of the phase transitions of the chiral side chain polymer P5*M and of the copolymer C25. According to Meyer,³ three basic conditions must be kept in order to have ferroelectricity: i) tilted smectic phase, ii) absence of mirror symmetry, and iii) nonzero transverse dipole moment. P5*M and C25 satisfy the three required conditions and show the ferroelectric properties: the phase sequences for these two materials are, respectively:

G1 → smectic C* → smectic A → I (P5*M)

and

G1 → smectic F* → smectic A → I (C25).

A small amount (~1 mg) of the substance was clamped to a cell consisting of two glasses with the inner surfaces of the glasses coated by a conducting film of SnO₂. These

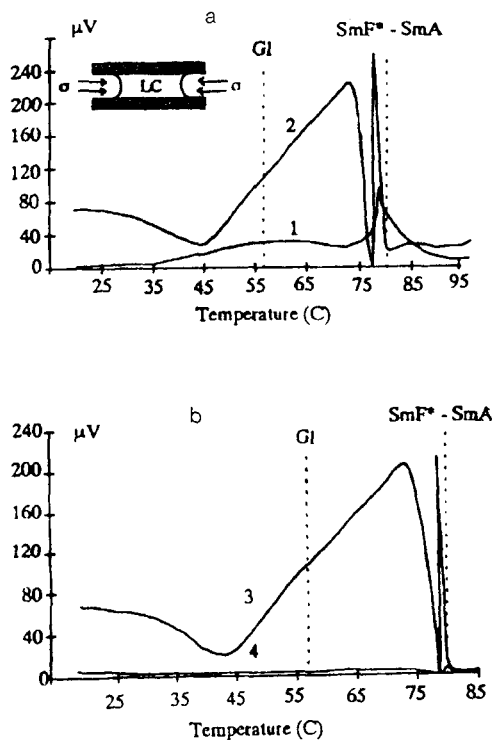


FIG. 1. Amplitude of the piezoelectric response as a function of the temperature for the copolymer C25. a—Curve 1 is the signal for the first scanning without an electric field: curve 2 for the poled sample with a bias of +500 V. The insert shows the measurement cell. b—Curve 3 data for the sample poled by a -500-V bias and curve 4 for an annealed sample. We note that the amplitude of the signal is almost the same for curves 2 and 3.

two electrodes are separated by a 110-micron Teflon spacer and the sample has a disk-like shape. An alternating low frequency (81-Hz) pressure is applied to the edge of the sample (see the inset in Fig. 1a). The piezoelectric response was detected by a lock-in amplifier at the fundamental frequency of the applied field. The resonant frequency of the setup assembly is used in order to subject the sample to the highest pressure. The amplitude of the signal V and the phase shift $\Delta\phi$ were independently recorded as functions of the temperature for different sample conditions: In all experiments we have performed, the heating rate of the sample was held at 3 K/min. Curve 1 in Fig. 1a shows the behavior of the first measurements for a sample of C25 prepared in the absence of an electric field, using a strong temperature gradient perpendicular to the cell plates.

In the same figure, curve 2 shows instead the behavior of the same sample heated to the clearing point and then poled by cooling to room temperature under a dc bias of +500 V. In Fig. 1b, curves 3 and 4 give, respectively, the amplitude V for the same sample polarized by a bias of -500 V and for the annealed sample. The phase shift $\Delta\phi$ of the signal for the same sample, poled by a bias of -500 V, is shown in Fig. 2. The analysis of the phase shift data allows us to identify the phase transition temperature and the glassy transition. The sharp peak in the phase $\Delta\phi$ at 80 $^{\circ}\text{C}$ corresponds to the smectic F*-smectic A transition: The phase shift is due to the drastic changes of the mechanical properties of the material. Near 55 $^{\circ}\text{C}$, the change in the slope of the phase shift signal identifies the glassy transition.

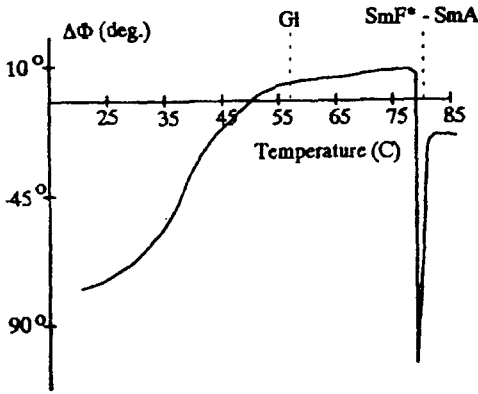


FIG. 2. Phase shift of the piezoelectric response as a function of the temperature for the copolymer C25. Note the change of slope identifying the glass transition and the peak corresponding to the smectic F*–smectic A transition.

In Figs. 3a and 3b the data for the polymer P5*M are shown.

The transition points obtained from our data are in good agreement with those obtained by means of DSC scanning (see Fig. 4). They indicate a slight difference from the data previously reported in Refs. 4 and 5.

Let us now analyze the signal amplitude V , giving special attention to the smectic C*–smectic A or smectic F*–smectic A transitions. From Fig. 1a we see that the signal for the poled C25 sample increases, reaching a maximum in the vicinity of the transition from the ferroelectric phase to the paraelectric phase A and sharply decreases to zero value near 77 °C after a sharp peak is reached at 79 °C. A similar situation is seen for P5*M (see Fig. 3).

This behavior can be explained by taking into account the peculiarities of the structure of ferroelectric polymers which are subjected to an elastic stress. Measuring the amplitude V as a function of temperature, we observe the effect of elastic stress on the phase transition $A \leftrightarrow C^*$ ($A \leftrightarrow F^*$). This effect is reflected in the displacement δT_c of the transition temperature T_c , $\delta T_c \sim -\sigma$. Thus, the tilt angle θ and the bulk polarization P are functions of the variable $t + \sigma$, where $t \sim (T - T_c)$. The dependence $P(t + \sigma)$ promotes the temperature dependence of the “piezoelectric” coefficient $\partial P / \partial \sigma$. In the case of helicoidal structure of the chiral smectic C* phase, the bulk polarization is equal to zero. Under the action of sufficiently strong external electric field E the sample is polarized, and a certain bulk polarization is stored after switching off the field due to the existence of various structural defects. In fact, this bulk polarization is smaller than a nominal one, it is heterogeneous, and it has a finite time of life. Because of these circumstances, in ordinary low-mass ferroelectric liquid crystals (FLC) the measured response $\partial P / \partial \sigma$ has a typical broad peak in a certain temperature range below the T_c point. We note that such a temperature behavior differs from the dependence $\partial P / \partial \sigma \sim \partial \theta / \partial \sigma \sim t^{-1/2}$, which could be in homogeneously polarized FLC. The polymer FLC have a very similar temperature dependence of this response in the same temperature range, but we see also a very pronounced difference in the response of polymer FLC in a narrow temperature interval near the T_c point, where another rather sharp peak is observed systematically.

For the phase transition smectic F*–smectic A the second peak is sharper and taller

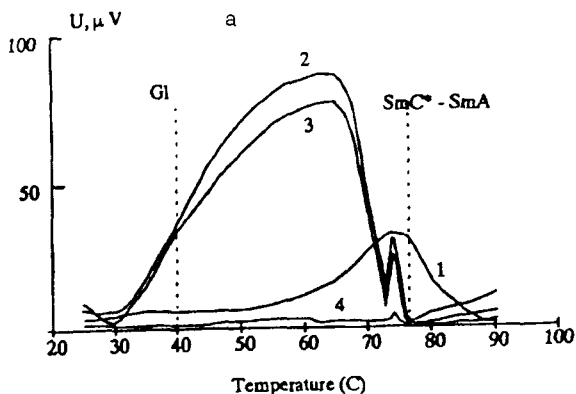
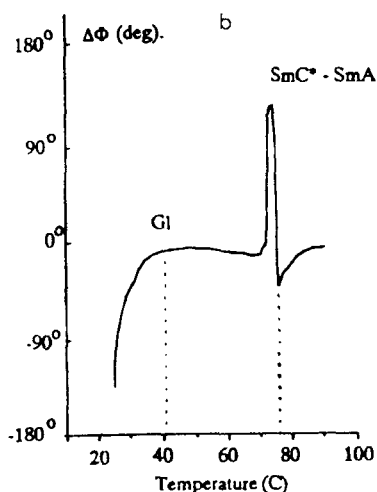


FIG. 3. a—Amplitude of the piezoelectric response for the polymer P5*M. Curve 1 corresponds to the first scanning without an electric field. Curves 2 and 3 are data for a poled sample with a bias of +500 V and -500 V, respectively. Curve 4 is obtained for the annealed sample. b—Phase shift for P5*M.



than that for the transition smectic C*—smectic A in the presence and in the absence of an electric field. In the absence of an external electric field the peak is smaller and broader than in the presence of a field. In our opinion, the appearance of the second peak is connected with the occurrence of a first-order phase transition in each substance at a nominal transition temperature T_c (for example, F*—A transition) or at a temperature near the nominal transition temperature (for example, C*—A transition). The first-order phase transitions smectic F*—smectic A were found to occur in some low-mass liquid crystals.^{6,7} The first order C*—A phase transition occurs less frequently.⁸ Pure thermodynamics and composite peculiarities of polymer liquid crystals can give rise to first-order phase transitions in polymer tilted smectics with chiral molecules. The pyroelectric measurements in the polymer ferroelectric liquid crystal P5*M (Ref. 9) did not show the existence of some jumps of the spontaneous polarization, which could be characteristic of a first-order transition. It seems that the pyroelectric method is not as sensitive in this case as the piezoelectric method. To measure the polarization jump by the pyroelectric method at the transition temperature, we should have a power w and time width τ of the laser

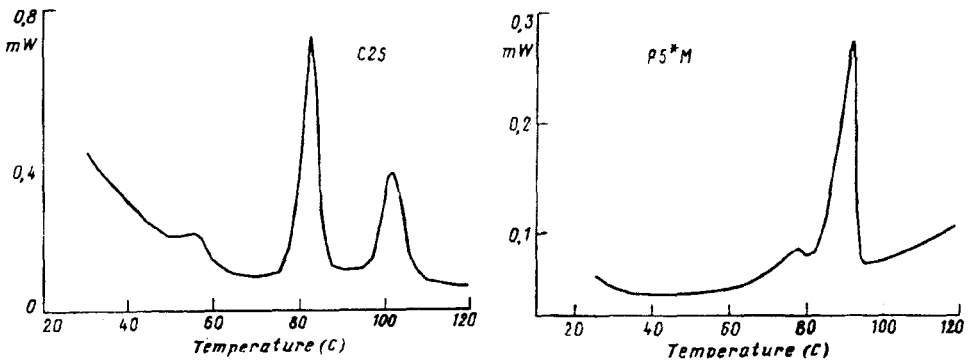


FIG. 4. Examples of DSC heating curves for C25 and P5*M.

pulses such that the value $w\tau$ would be larger than the transition latent heat Q . In contrast, the temperature cannot be changed because of the heat loss in the first-order transition. The piezoelectric method is free from this shortcoming, because the temperature is always fixed at the mechanical stress action, which changes only the transition point T_c . Thus, the method proposed by us can detect ordinary first-order phase transitions attributable to the symmetry properties of liquid crystals. The shape of this second peak in the response $\partial P/\partial\sigma$ can be controlled by the structure of the polymer ferroelectrics. Such materials generally have some distributions of amorphous and crystalline regions of various sizes d (Ref. 10). The ferroelectric phase transitions, in fact, take place in each crystalline region and both the transition point and the character of the transition depend on the size d and the boundary conditions.¹¹ In such a case the phase transitions in very small smectic C* crystalline regions must be changed dramatically in the vicinity of the T_c point if, for example, there are interactions of the spontaneous polarization P_s with some subsurface fields E_s at the boundaries of the smectic C* regions. These surface interactions can be ignored in large areas, but for small ones the quantity E_s/d plays the role of a bulk field E (see Fig. 5). It was shown for the chiral smectic C* that a sufficiently strong bulk field changes the character of the phase transition in the vicinity of the T_c point from a second-order to a first-order phase transition.^{12,13} The first-order transition from the homogeneous C* state to the helicoidal C* state must occur at the temperature $t^* \sim -E^{2/3}$ if the values of E are larger than the tricritical value E_{tc} , $E_{tc}^{2/3} \sim Kq^2$, where K is the elastic constant, and q is the inverse pitch. The corresponding jumps in the angle θ and the polarization P_s are proportional to $E^{1/3}$ at $t=t^*$ (Refs. 12 and 13).

Thus, if there are many small regions with $d < d_c$ and $d_c \sim E_s/E_{tc} \sim E_s q^{-3}$ in the polymer FLC sample, then for the response $\partial P/\partial\sigma$ we can expect the existence of a close to δ -function peak at $t=t^*$, which is imposed on the broad, smooth peak mentioned above. If the subsurface field E_s is small and the wave number q is large, i.e., the critical size d_c is very small, then the number of regions exhibiting the first-order transition is small, and the corresponding additional peak must be weak. The width of such a peak depends on the distribution of regions of size $d < d_c$. We conclude that a preliminary

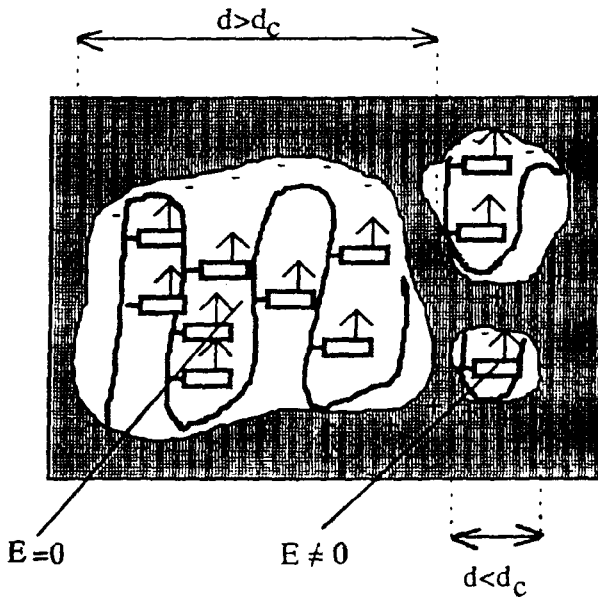


FIG. 5. Distribution of smectic C* regions in the polymers FLC. In small regions with dimension less than the critical size a bulk electric field E which influences the phase transition is present.

treatment of the sample strongly influences the response measurements, because it accounts for the distribution of regions of different sizes and changes the boundary conditions of the regions and their helicoidal structure. Our measurements clearly show this dependence of the response on the sample treatment. The action of strong external electric field E makes this first-order transition effect more pronounced, because the larger quantity of such regions can undergo a first-order transition. The corresponding peak in the piezoelectric response must be strong. The macropolarization is smaller at lower temperatures and therefore the response decreases quickly (see curves 1 in Fig. 1a and Fig. 3a).

In the case of a phase transition smectic F*–smectic A, which can be a first-order phase transition in the absence of electric fields, all the effects considered above must be more pronounced and the corresponding peaks must be sharper than those in the previous case. In small areas, the tilt angle jumps and the corresponding critical values of the untwisting fields must be larger than in the large regions. Therefore, the interval of sizes d in which twisting occurs is larger, and consequently the temperature interval in which the macropolarization is zero is wider in the presence of an external field. This can explain the steep decrease of the response in a narrow temperature interval, when the temperature decreases (see curve 2 in Fig. 1a and curve 3 in Fig. 1b). The smoother temperature behavior of a relatively weak peak in the absence of an external field (see curve 1 in Fig. 1a) shows, in our opinion, the existence of a similar distribution in the size of regions in the chiral smectics F*. It is known¹⁴ that some mechanical movements can result in a certain untwisting of the polarization helix. Therefore, a weak piezoelectric response can be observed in the C* and F* phases even in the absence of external fields at lower temperatures (see curves 1 in Fig. 1 and Fig. 3).

The response time for small regions can be much less than for big regions because of smaller scales of the heterogeneity in the first case and larger effects of the polymer viscosity in the second case this time being changed by a jump at the first-order phase transition temperature. This can explain the characteristic change of the response phase with temperature in our experiments: almost from the in-phase response above the t^* point to the counterphase response below the t^* point.

We conclude that the proposed method of measurements of the electric response to mechanical stresses can give sufficiently extensive information about the structure and properties of polymer FLC with a sensitivity much higher than that of other techniques like those of pyroelectric or differential scanning calorimetry.

The authors are greatly indebted to Dr. M. V. Kozlovskii (Institute of Crystallography, Russian Academy of Sciences) for furnishing the samples.

- ¹S. V. Yablonskii, E. I. Katz, and M. V. Kozlovskii *et al.*, *Mol. Materials* **3** (1994).
- ²L. M. Blinov and V. G. Chigrinov, *Electrooptic effects in liquid crystal materials*, Springer-Verlag, New York, 1994.
- ³R. B. Meyer, L. Liebert, L. Strzelecki, and P. Keller, *J. Phys. (Paris) Lett.* **36**, L-69 (1975).
- ⁴M. V. Kozlovsky, S. G. Kononov, and L. M. Blinov, *Eur. Polym. J.* **28**, 907 (1992).
- ⁵M. V. Kozlovsky, K. Fodor-Csorba, L. Bata, and V. P. Shibaev, *Eur. Polym. J.* **28**, 901 (1992).
- ⁶C. Rosenblatt and J. T. Ho, *J. Physique* **44**, 383 (1983).
- ⁷D. M. Potukuchi, R. Bhaskara, N. V. S. Rao, and V. G. K. M. Pisipati, *Zeit. Naturf.* **44 A**, 23 (1989).
- ⁸K. Satyendra, *Phys. Rev. A* **23**, 3207 (1981).
- ⁹V. P. Shibaev, M. V. Kozlovskii, N. A. Platé, *et al.*, *Polym. Sci. USSR* **29**, 1616 (1987).
- ¹⁰R. Anderson, R. Kepler, and R. Lagasse, *Ferroelectric* **33**, 91 (1981).
- ¹¹E. M. Terent'ev and S. A. Pikin, *Macromol. Chem., Rapid Commun.* **4**, 739 (1983).
- ¹²A. Michelson and D. Cabib, *J. Phys. (France) Lett.* **38**, L-321 (1977).
- ¹³S. A. Pikin, *Structural Transformation in Liquid Crystal*, Gordon and Breach Science Publishers, N. Y., 1991.
- ¹⁴P. Pieranski, E. Guyon, and P. Keller, *J. Physique* **36**, 1005 (1975).

Published in English in the original Russian journal. Reproduced here with stylistic changes by the Translation Editor.