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# SMECTIC C* (OF F*) - SMECTIC A PHASE TRANSITION IN SIDE CHAIN POLYMERS INVESTIGATED BY PIEZOELECTRIC TECHNIQUE

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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 phase temperature 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.

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, sensitive to the polar ordering of the material, detects the low frequency complex value of the piezoelectric response $\Pi = Ve^{i\Delta\phi}$, characterized by an amplitude $V$ and a phase shift $\Delta\phi$: the response $\Pi$ is proportional to the derivative $\partial P/\partial s$ where $P$ is the spontaneous or induced polarization and $\sigma$ is the applied stress. In the case of intrinsic piezoelectricity, the polarization is function of the tilt angle $\theta$ in the smectic phase and in this case, the signal can be assumed also proportional to $\partial\theta/\partial\sigma$ [2].

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 have to be kept in order to have ferroelectricity: i) tilted smectic phase, ii) absence of mirror symmetry and iii) non zero transverse dipole moment. P5*M and C25 satisfy the three required conditions and show ferroelectric properties: the phase sequences for these two materials are respectively:

$$\mathrm{Gl} -> \mathrm{SmecticC}^* -> \mathrm{SmecticA} -> \mathrm{I} \qquad (\mathrm{P5^*M})$$

and

$$\mathrm{Gl} -> \mathrm{SmecticF}^* -> \mathrm{SmecticA} -> \mathrm{I} \qquad (\mathrm{C25})$$

A small amount ($\sim$ 1 mg) of substance has been clamped into a cell composed by two glasses with the inner surfaces of glasses coated by a conducting film of $SnO_2$. These two electrodes are separated by a 110 microns teflon spacer and the sample assumes a disk-like form. An alternating low frequency (81 Hz) pressure is applied to the edge of the sample (see insert in fig.1*a*) and the piezoelectric response has been detected at the fundamental frequency of the applied field by

a lock-in amplifier. The frequency used is the resonant frequency of the set-up assembly, in order to have on the sample the highest pressure. The amplitude of the signal $V$ and the phase shift $\Delta\phi$ has been independently recorded as a function of the temperature for different sample conditions: in all experiments we have performed, the heating rate of the sample was fixed to 3K/min. Curve *1* in fig.1*a* shows the behaviour of the first measurements for a sample of C25 prepared in absence of electric field using a strong temperature gradient perpendicular to the cell plates.

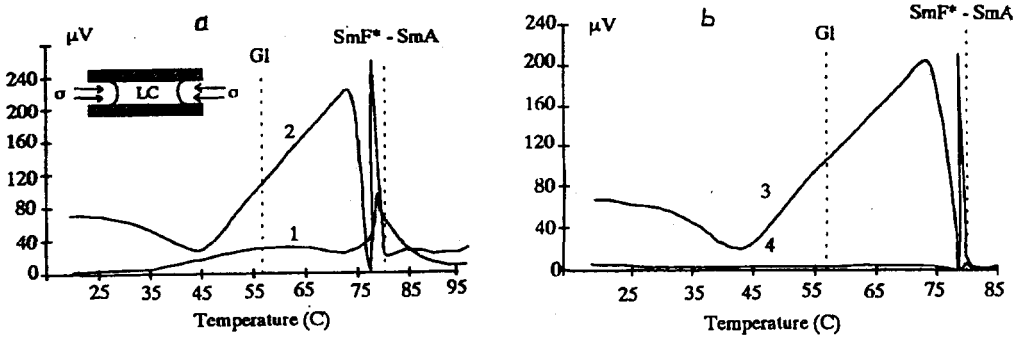


Fig.1. Amplitude of the piezoelectric response as a function of the temperature for the copolymer C25. *a* – Curve *1* is the signal for the first scanning without electric field: curve *2* for the poled sample with a bias of +500V. The insert shows the measurement cell. *b* – Curve *3* data for the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

In the same figure, curve *2* shows instead the behaviour of the same sample heated up to the clearing point and then poled by cooling down to room temperature under a d.c. bias of +500V. In fig.1*b*, curves *3* and *4* give respectively the amplitude $V$ for the same sample polarized by a bias of –500V 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°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. Around 55°C, the change of the slope in the phase shift signal identifies the glassy transition.

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

The transition points obtained by our data are in good agreement with those obtained by means of DSC scanning (see fig.4) but show slight difference with data previously reported in Ref.[4, 5].

Let us now analyse the signal amplitude $V$ giving special attention to the smectic C* – smectic A or smectic F* – smectic A transitions. From fig.1*a*, one can see that the signal, for the poled C25 sample, increases reaching maximum at the vicinity of transition from ferroelectric phase to paraelectric phase A and sharply decreases to zero value at around 77°C. After, a sharp peak is obtained at 79°C. Similar situation is seen for the P5*M (see fig.3).

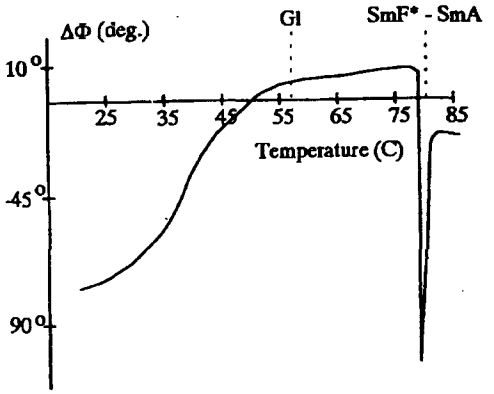


Fig.2. Phase shift of the piezoelectric response as a function of the temperature for the copolymer C25. Note the change of slope identifying the glass transition and the peak corresponding to the smectic F* – smectic A transition

This behaviour can be explained by taking into account the peculiarities of the structure of ferroelectric polymers, subjected to an elastic stress. Actually, 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 $\delta T_c$ of the transition temperature $T_c$, $\delta T_c \sim -\sigma$. Thus, the tilt angle $\theta$ 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 typical broad peak in some temperature range below $T_c$ – point. One should note that such a temperature behaviour 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 show the very similar temperature dependence of this response in the same temperature range, but one can see also the very pronounced difference in response of polymer FLC in a narrow temperature interval near $T_c$ – point where the another more or less sharp peak in observed systematically.

For the phase transition smectic F* – smectic A, this second peak is more sharp and tall than for the transition smectic C* – smectic A in presence as well in absence of electric field. In absence of the external electric field a peak is rather smaller and broader than in presence of field. In our opinion the appearance of the second peak is connected, in fact, with the occurrence of first-order phase transitions in both substances at a nominal transition temperature $T_c$ (for example F* – A transition) or at a temperature near the nominal one (for example C* – A transition). The first-order phase transitions smectic F* – smectic A are known in some low mass liquid crystals [6, 7]. The first order C* – A phase transition occurs more seldom [8]. Pure thermodynamics reasons as well as composite peculiarities of polymer liquid crystals can give rise to the first-order phase transitions in polymer tilted smectics with chiral molecules. The pyroelectric measurements in the polymer ferroelectric liquid crystal P5*M [9] did not show the existence of some jumps of the spontaneous polarization, which could be characteristic for the

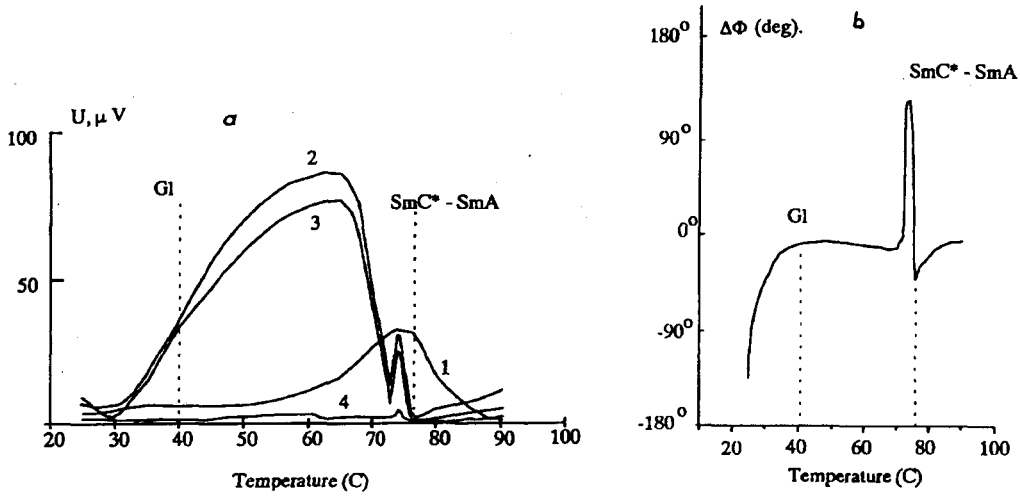


Fig.3. *a* – Amplitude of the piezoelectric response for the polymer P5*M. Curve *1* corresponds to the first scannig without electric field. Curves *2* and *3* are data for poled sample with bias respectively of +500V and –500V. Curve *4* is obtained for the annealed sample. *b* – Phase shift for P5*M

first-order transition. It seems that the pyroelectric method is not so sensitive for these aims as the piezoelectric one. Really, to measure the polarization jump by the pyroelectric method at the transition temperature, one should have such power $w$ and time width $\tau$ of laser impulses so that the magnitude $w\tau$ would be larger the transition latent heat $Q$. In the opposite case, the temperature cannot be changed due to the heat loss on the first-order transition. The piezoelectric method is free from this shortcoming because the temperature is always fixed at mechanical stress actions, which change only the transition point $T_c$. Thus, the presented method can detect ordinary first-order phase transitions occurring due to the symmetry properties of liquid crystals. The form of this second peak in the response $\partial P/\partial\sigma$ can be controlled also by peculiarities of the structure of

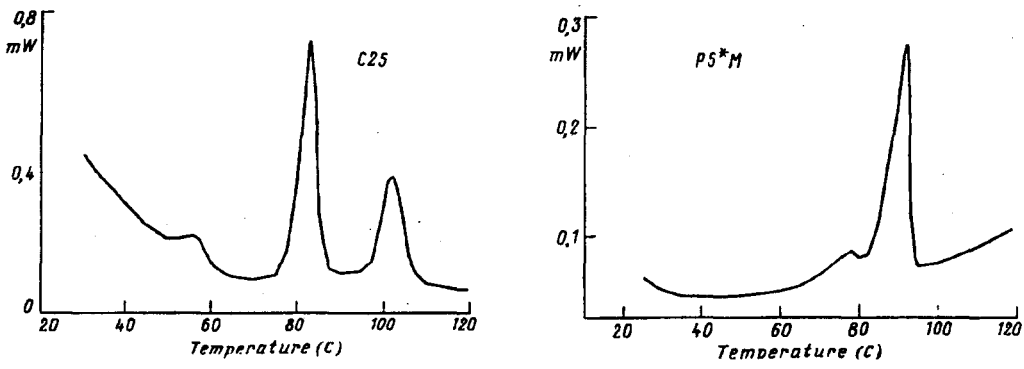


Fig.4. Examples of DSC heating curves for C25 and P5*M

polymer ferroelectrics. Really, such materials have, as a rule, some distributions of amorphous and crystalline areas of various sizes $d$ [10]. The ferroelectric phase transitions, in fact, take place in each crystalline area 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 areas must be changed dramatically in the vicinity of $T_c$-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* areas. These surface interactions can be neglected for large areas, but for small ones, the magnitude $E_s/d$ plays the role of a bulk field $E$ (see fig.5). It was shown for the chiral smectic – C* that sufficiently strong bulk field changes the character of the phase transition in the vicinity of $T_c$ – point from a second- to a first-order 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 values of $E$ are larger than the tricritical one $E_{tc}$, $E_{tc}^{2/3} \sim K\,q^2$, where $K$ is the elastic constant, $q$ is the inverse pitch. The corresponding jumps in the angle $\theta$ and polarization $P_s$ are proportional to $E^{1/3}$ at $t = t^*$ [12, 13].

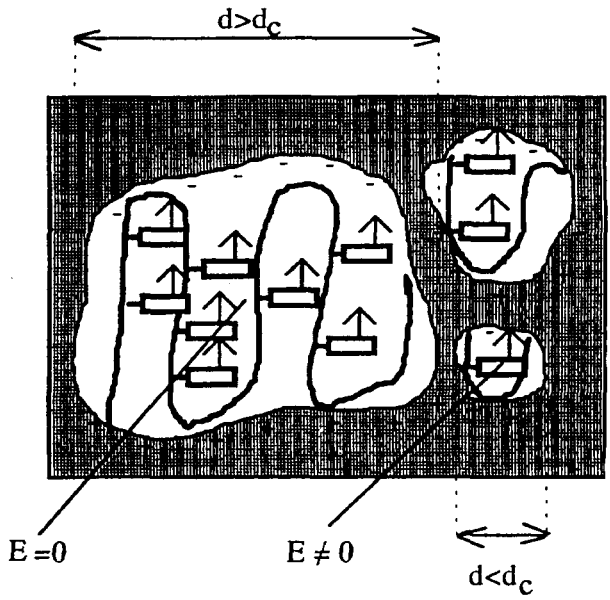


Fig.5. Distribution of smectic-C* crystalline areas in polymers FLC. In small regions with dimension less than a critical one, a bulk electric field $E$ is present that influences the phase transition

Thus, if there is a big amount of small areas with $d < d_c$, $d_c \sim E_s/E_{tc} \sim E_s q^{-3}$, in the polymer FLC sample, then, for the response $\partial P/\partial\sigma$, one can expect the existence of almost $\delta$-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 quantity of areas exhibiting the first-order transition is small, and the corresponding additional peak must be weak. The width of such a peak depends on the areas distribution on sizes $d < d_c$. One can conclude that a preliminary treatment of the sample strongly influences the response measurements because it prepares the areas distribution on sizes and changes the boundary conditions for areas 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 areas can undergo the first-order transition, the corresponding peak in the piezoelectric response must be strong. The macropolarization is smaller at lower temperatures and therfore the response decreases quickly (see curves *1* in fig.1*a* and in fig.3*a*).

In the case of phase transition smectic F* – smectic A, which can be of the first-order in absence of electric fields, all the effects considered above must be more pronounced and the corresponding peaks must be more sharp than in the previous case. In small areas, the tilt angle jumps and corresponding critical values of untwisting fields must be larger than in big ones, 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 presence of 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.1*a* and curve *3* in fig.1*b*). The more smooth temperature behaviour of the relatively weak peak in absence of external field (see curve *1* in fig.1*a*) shows, in our opinion, the existence of a similar distribution on area sizes in the chiral smectics F* also. It is known [14] that some mechanical movements can result in a certain untwisting of the polarization helix, therefore some weak piezoelectric response can be observed in C*- and F* phases even in absence of external fields at lower temperatures (see curves *1* in fig.1 and fig.3).

The response time for small areas can be much less than for big areas because of smaller scales of a heterogeneity in the first ones and larger effects of the polymer viscosity for the second ones, this time being changed also 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 an in-phase response above $t^*$-point to a counter-phase response below $t^*$-point.

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

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