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Ferroelectric liquid-crystalline polymethacrylates

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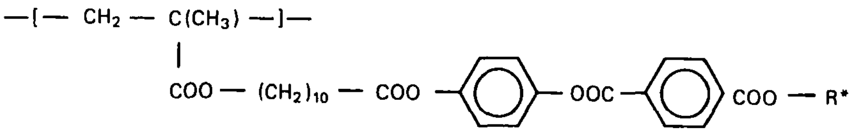
The ferroelectricity in the chiral smectic C phase of two comb-shaped liquid-crystalline polymers with a methacrylic main chain, phenyl benzoate side groups and chiral fragments of different types have been studied using the pulse pyroelectric method. The spontaneous polarization, pyroelectric coefficient and some relaxation times associated with two different molecular motions have been evaluated.

1. Introduction

In previous papers [1, 2] we have developed a new approach with which to create ferroelectric polymers by means of chemical binding of polymer chains with molecules of low molar mass liquid crystals forming the chiral smectic C phase. A sketch of the dipole moment ordering of the side mesogenic groups in these polymers and their helical twisting in the smectic layers of the S_C^* phase are shown in figures 1 (a) and (b). About a dozen or so comb-shaped polymers with the mesogenic side groups mimicking low molar mass chiral smectic C have recently been synthesized [3–6]. The molecular structure of these polymers should predetermine the appearance of spontaneous polarization. Nevertheless up until now the detailed investigation of the ferroelectric behaviour of such polymeric chiral smectics C has not been carried out.

This paper describes the results of a study of the spontaneous polarization, P_S the pyroelectric coefficient, γ, and the relaxation times, τ, connected with two different molecular modes of motion of two comb-shaped polymethacrylic liquid-crystalline polymers with phenylbenzoate mesogenic fragments and different terminal chiral groups in the side branches:



Polymer	R*
P5*	$-CH_2-C^*H(CH_3)-C_2H_5$
P6*Cl	$-CH_2-C^*HCl-CH_2-C-CH(CH_3)_2$

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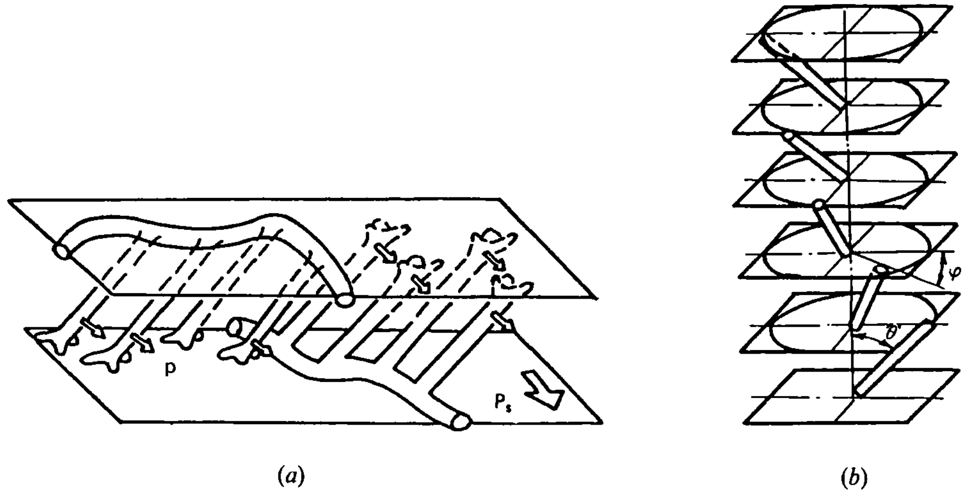


Figure 1. Sketches showing the dipole moment, *p*, ordering of the side mesogenic groups in the smectic layers of the S_C^* phase of a chiral polymer (the arrow P_s shows the direction of the spontaneous polarization) (*a*) and the helical twisting of mesogenic molecules in the smectic layers of the S_C^* phase (for simplicity the main chains are omitted) (*b*).

2. Experimental

The synthesis and structure of polymers I and II have been described [2]. The ratio of the weight average molar mass (M_w) to the number average molar mass (M_n) of the polymers has been determined by the combined GPC–light scattering technique (Waters-40; Milton Ray, U.S.A.). The phase transition temperatures, heats of transition and some molecular characteristics of the polymers studied are presented in the table.

The spontaneous polarization, P_s, of the polymers has been determined using the pyroelectric method [7]. The pyroelectric coefficient of the polymers was measured from the pyroelectric response of a liquid-crystalline sample to heat pulses from a Nd-glass laser. The spontaneous polarization P_s was calculated by integrating the curve, $\gamma(T)$, using the relation $\gamma(T) = dP_s/dT$ and taking into account the noise effects.

The relaxation time for the pyroelectric response, τ_θ, associated with changing the tilt angle θ of the mesogenic groups (see figure 1 (*b*)) has been calculated according to [7] from oscillograms of the damping of the pyroelectric response to a heat pulse. The relaxation times of spontaneous polarization, τ_φ^t, and τ_φ^u associated with the twisting or untwisting processes of the helicoidal chiral smectic C structure were obtained from damping or growing curves of the pyroelectric response to a standard heat pulse after switching an external electric field off or on.

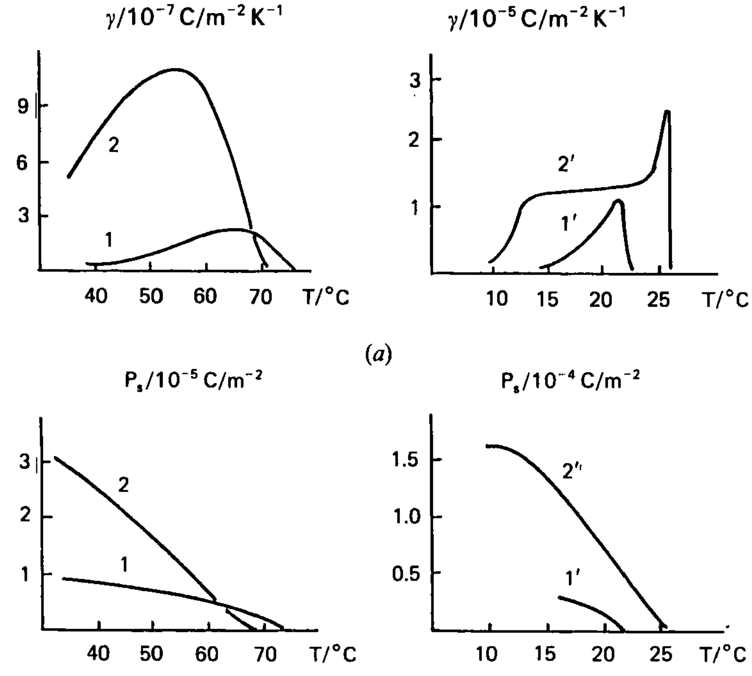
As we can see from the table both polymers, according to X-ray data, form a layered tilted chiral smectic C structure; a sketch of the mesogenic arrangement is shown in figure 1 (*b*). We can see that all of the mesogenic groups are arranged in layers. The existence of the chiral centres leads to an asymmetry in the hindered rotation of mesogenic molecules around their long axes and as a consequence to a twisting of the molecular long axes in one layer in relation to those of the neighbouring layer at an angle φ. The ordering of the transverse dipole moments results from the ordering of the short axis of the mesogenic molecules. All of the dipole moments

Some properties of ferroelectric liquid crystal polymers.

Polymer	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	Glass temperature T_g/°C	Transition temperatures and heats of transition	Mesogenic group tilt angle at 20°C
P5*	48000	4·1	45	$S_C^* \xleftrightarrow[1{\cdot}6\,\mathrm{kJ/mol}]{73°\mathrm{C}} S_A \xleftrightarrow[4{\cdot}4\,\mathrm{kJ/mol}]{85°\mathrm{C}} I$	24°
P6*Cl	31000	3·1	50	$\begin{tikzcd} S_C^* \arrow[rr, "79°\mathrm{C}", "6{\cdot}2\,\mathrm{kJ/mol}"'] & & I \arrow[dl, "79°\mathrm{C}\ 3{\cdot}4\,\mathrm{kJ/mol}"] \\ & S_A \arrow[ul, "71°\mathrm{C}\ 2{\cdot}8\,\mathrm{kJ/mol}"] & \end{tikzcd}$	34°

in the layer are turned in the same direction. But each dipole moment is turned at a certain angle with respect to the preceding one, so that on average the dipole moments are compensated. The helixal structure is electrically neutral.

The spontaneous polarization results on applying an electric field in the direction perpendicular to the helix axis. Figure 1 (*a*) shows the appearance of the spontaneous polarization in the single smectic layer of the comb-shaped polymer. The results of studying the ferroelectric properties of polymers P5* and P6*Cl (and also of the corresponding monomers) are presented in figure 2. Both the monomers and the polymers studied in the temperature region of the chiral smectic C phase manifest the pyroelectric effect and possess a spontaneous polarization.



(*a*)

(*b*)

Figure 2. Temperature dependence of the pyrocoefficient, γ, (*a*) and the spontaneous polarization, P_s, (*b*) for polymers P5* (1), P6*Cl (2) and their monomers M5* (1′), M6*Cl (2′).

The values of the pyroelectric coefficient calculated for both polymers reach a plateau with increasing external electric field up to $E_{\text{unw}} \sim 10$ MV/m. We can see from figure 2 (*a*) that the curve of the spontaneous polarization $P_s(T)$ for P5* (curve 1) in the temperature region 30–70°C and especially in the vicinity of S_C^*–S_A transition looks like the curve in figure 3 showing the tilt angle versus temperature. It means that the values of P_s grow proportionally with increasing the tilt angle of the mesogenic fragments relative to the normal to the smectic plane. For both polymers the shapes of the curves showing the temperature dependence of the spontaneous polarization and the pyroelectric coefficient are similar to those for low molar mass ferroelectric liquid crystals, distinguished at the same time by a lengthening of these curves along the temperature axis. However the values of spontaneous polarization of the polymers studied are three to five times less than the corresponding values for the monomers. It

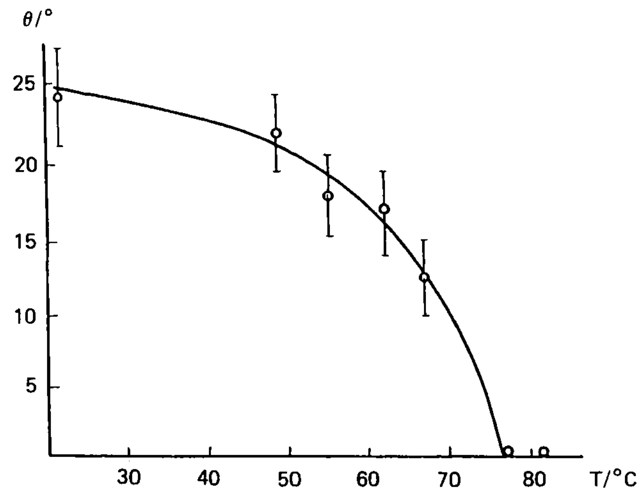


Figure 3. The temperature dependence of mesogenic group tilt angle θ, for polymer P5*.

should be noted that for both the polymers and the low molar mass ferroelectric liquid crystals the spontaneous polarization grows with increasing transverse dipole moment of the mesogenic side chains and decreasing the distance between the dipole group and the chiral centre; the maximal values of P_S for P6*Cl is about three to five times greater than the corresponding values for P5*. At the same time the values of P_s and γ for the monomers are very close to those for typical low molar mass ferroelectric liquid crystals $P_s \approx 10^{-4}\,\mathrm{C\,m^{-2}}$ and $\gamma \approx 10^{-5}\,\mathrm{C\,m^{-2}\,K^{-1}}$.

For the ferroelectric liquid-crystalline polymers P5* and P6*Cl we have studied the temperature dependences of two relaxation times connected with two types of molecular motions: the change of the tilt angle of the mesogenic side chains and the change of the (azimuthal) helicoidal twist angle φ by switching an external electric field off or on (see figure 1 (*b*)). The relaxation time for the pyroelectric response, τ_θ, corresponds to the former motion, the relaxation times of twisting, τ_φ^{t}, and untwisting, τ_φ^{u}, the helix to the latter. As we see from figure 4, passing to the polymer P5* from its monomer the relaxation time, τ_θ, increases by about a factor of four. This seems to be explained by the high viscosity of the polymer liquid crystal phase and slowing down of all the relaxational processes due to the presence of long polymer chains chemically linked with the mesogenic groups. The τ_θ values of P6*Cl in vicinity of the phase transition S_C^*–S_A were evaluated as approximately 60–80 μs, i.e. twice as large as the corresponding value for monomer (34 ± 4 μs). So the substitution of the 2-*S*-methylbutyl chiral terminal fragment of the mesogenic group by the 2-*S*-chloro-4-methylpentyl group both in the polymer and in the monomer results in a pronounced decrease of the τ_θ values. This can be caused as for the larger spontaneous polarization of chlorine-containing monomer and polymer, by just the difference in the geometrical shape of the chiral fragment.

Figure 5 presents the relaxation times for helicoidal twisting τ_φ^{t} and untwisting τ_φ^{u} for the polymer P6*Cl as a function of temperature. τ_φ^{t} somewhat exceeds τ_φ^{u} over the whole temperature range studied. The increase of both τ_φ with decreasing temperature obeys the Arrhenius law

$$\tau_\varphi = \tau_\varphi^0 \exp(E_A/RT),$$

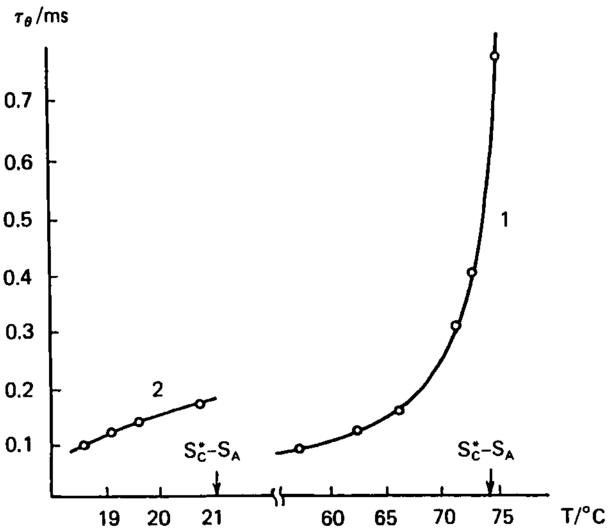


Figure 4. The temperature dependence of the relaxation time for the pyrocoefficient, τ_θ, for polymer P5* (1) and its monomer M5* (2).

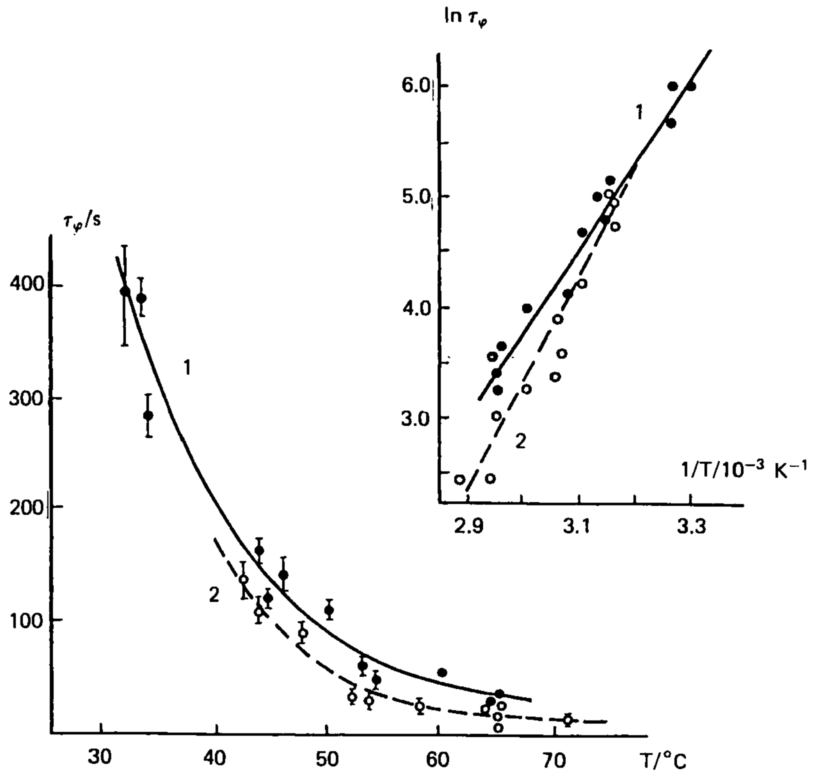


Figure 5. The temperature dependence of the relaxation time for helix twisting $\tau^{t}_{\varphi}(1)$ and untwisting $\tau^{u}_{\varphi}(2)$ for polymer P6*Cl.

as can be seen from figure 5. The activation energy for the twisting process, E_A^t, estimated from this equation is equal to 66 $\pm$ 4 kJ/mol and for the untwisting process E_A^u is 77 $\pm$ 10 kJ/mol; these values coincide within the accuracy of the measurements.

The technique used only permits us to give the upper limit of the corresponding relaxation times for the monomer: $\tau_\varphi^{t,u} \leqslant 5$ s. It is known, however, that relaxation times connected with twisting and untwisting of the helicoidal structure for typical low molar mass ferroelectric liquid crystals are in the range 10^{-4}–10^{-3} s [8, 9]. At the same time the reorientational processes in the smectic and nematic polymeric phases and the processes of untwisting the helicoidal structures, in a cholesteric phase of comb-shaped liquid-crystalline polymers have been characterized by relaxation times of 10^1–10^2 s (depending on the degree of polymerization) and activation energies of the order of 50–200 kJ/mol (depending on the mesophase types and some other factors) [10, 11].

The comparison of τ_θ with τ_φ^t and τ_φ^u for the polymer P6*Cl shows that the main chain is greatly involved in the motion associated with the change of the azimuthal angle φ, than with the motion associated with the change of the tilt angle. This can be explained by the scale difference of these motions: the change of the azimuthal angle takes place over a distance of about the helicoidal pitch (300 nm), at the same time the change of the tilt angle of the mesogenic fragments occurs within the limits of smectic layer thickness (3 nm). As a result the τ_θ values of polymers P5* and P6*Cl exceed the corresponding values of the low molar mass ferroelectric liquid crystals by two to four times whereas the τ_φ values are exceeded by five to six orders of magnitude.

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