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Liquid Crystal Polymers

Thermotropic Liquid Crystalline Polymers.
16. Chiral Smectics "C" with Spontaneous Polarization

V. P. Shibaev[1], M. V. Kozlovsky[1], L. A. Beresnev[2], L. M. Blinov[2], N. A. Platé[1]

[1] M. V. Lomonosov Moscow State University, Moscow, USSR

[2] A. V. Shubnikov Institute of Crystallography, Academy of Sciences, Moscow, USSR

Summary

Liquid crystalline comb-like polymers with spontaneous polarization are described.

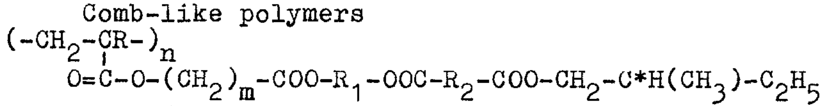
Introduction

Studying structure and properties of liquid crystalline (LC) polymers with mesogenic side groups simulating different structural types of low molecular weight liquid crystals (1), we turned our attention to polymer chiral smectics. Such compounds are of interest because of their ability to ferroelectric properties arising from the hypothesis on symmetry of ferroelectric low molecular weight liquid crystals (2,3). Layered smectic phase, being built from chiral (optically active) molecules having long axes tilted to layer plane is the best known to manifest the dipole ordering. The only symmetry element of such structures is polar two-fold axis along the layers and normal to the molecular tilt plane. Transverse dipole moment of chiral molecules determines the spontaneous polarization along this axis. For low molecular weight liquid crystals such type of symmetry is realized in chiral tilted smectics (Sm C* and some other modifications of smectics).

For the polymeric liquid crystals tilted smectic phase Sm C formation was also observed (4,5). That's why assumption could be made that the introduction of chiral mesogenic groups into linear or comb-like macromolecules of tilted smectic phases should lead to the polymers being able to spontaneous polarization.

Results and Discussion

Comb-like polymers



$$\begin{array}{l}(-CH_2-\underset{|}{C}R-)_n\\ \quad O{=}C-O-(CH_2)_m-COO-R_1-OOC-R_2-COO-CH_2-C^*H(CH_3)-C_2H_5\end{array}$$

where $m = 6-12$, which we synthesized, meet the requirements mentioned above because they have an asymmetric atom C* in a macromolecule of polymer tilted smectic (5).

From the calorimetric, optical microscopic and X-ray data two smectic phases were found in one of such polymers to exist:

$$\text{Glassy state} \xleftrightarrow{20\text{-}30°C} \text{Sm C}^* \xleftrightarrow{73\text{-}75°C} \text{Sm A} \xleftrightarrow{83\text{-}85°C} \text{Isotropic melt}$$

where Sm A - the smectic A phase with side chains normal to the layer plane (the interlayer distance of 3.6 ± 0.2 nm) and Sm C* - smectic C phase with tilted side chains, the long axis tilt angle to the layer plane normal being equal to $21 \pm 4°$ at 25°C (the interlayer distance of 3.2 ± 0.1 nm). The Sm C* structure is frozen in polymer glass upon cooling below glass point transition T_g.

The value of spontaneous polarization P_s was calculated upon integrating the experimental temperature dependence of the pyroelectric coefficient $\gamma = dP_s/dT$, measured from the pyroelectric response of a liquid crystalline layer to heat pulses from a Nd-glass c.w. laser having duration $t_0 \approx 0.1$ ms.

The temperature dependence of pyrocoefficient $\gamma(T)$ for one of the chiral polymers is shown on Fig.1 as well as the spontaneous polarization $P_s(T)$ calculated upon integrating the curve $\gamma(T)$, reduced to zero polarizing voltage U.

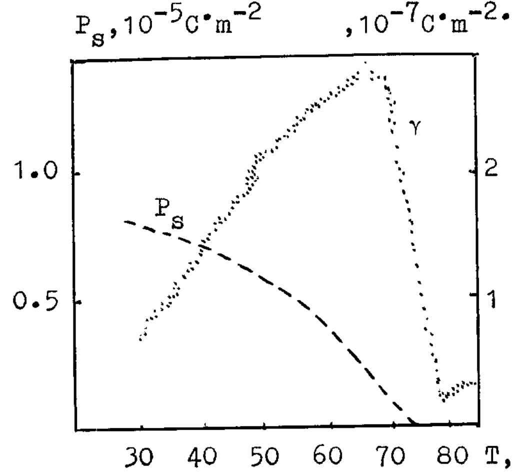


Fig.1. The temperature dependence of pyrocoefficient γ (T) and spontaneous polarization P_s(T) for one of chiral synthesized polymers.

The maximum value of P_s in the Sm C* phase is equal to $(0.8\text{-}0.9) \cdot 10^{-5}$ C·m^{-2}. Such a value is characteristic for typical low molecular weight LC ferroelectrics (see, for example, data for esters (6)).

Let us mention some particularities of these LC polymers.

a) The relaxation time τ of the spontaneous polarization, estimated from the oscillogram of pyroelectric response (7) is of the order of 100 μs well below the Sm C* - Sm A transition point and reveals a fast growth in the vicinity of this point reaching 1 ms just at the Sm C* - Sm A transition. This reminds the behavior of the soft mode in solid ferroelectric near the Curie point. Large relaxation time τ in LC polymers which exceeds τ value for low molecular weight ferroelectric liquid crystals by two orders of magnitude may be connected with high viscosity of polymeric mesophase and with thermal disordering of the large molecular ensembles tied by polymeric chains.

The large value of τ is the reason for an absence of the sharp maximum $\gamma(T)$ at the point Sm C* - Sm A which is characteristic for classical LC ferroelectrics, since heat pulse duration t_0 is too small to ensure steady-state heating conditions, and therefore the amplitude of response U_m, and hence $\gamma(T)$, is going down linearly with the ratio τ/t_0 (8).

b) After switching off the external polarizing voltage and making short circuit of the cell electrodes pyroelectric response remains constant for more than 5 minutes. This is indicative of the small value of elasticity coefficients and the large values of viscosity coefficients as compared with classical LC ferroelectrics.

c) Preliminary experiments show the preservation of the spontaneous polarization in a rather wide temperature interval including room temperature.

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