# Antiferroelectric achiral mesogenic polymer

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## Abstract

X-ray structure determination and pyroelectric measurements have been carried out on mesogenic mixtures composed of an achiral side-chain polymer and its monomer. The mixtures show antiferroelectric polarization hysteresis loops in the mesophase which was shown to be a bilayered smectic C. The results obtained on polymer–monomer mixtures are interpreted in terms of the smectic C structure with alternating tilt which, from a symmetry standpoint, is allowed to be antiferroelectric.

## 1. Introduction

Chiral liquid crystalline phases such as tilted smectics $C^*$, $F^*$, $I^*$, etc., both low molecular mass and polymer, manifest ferroelectric [1,2] and antiferroelectric [3,4] properties. In these mesophases the spontaneous polarization arises as a secondary order parameter due to a molecular tilt with respect to the smectic layer normal and the $P_S$ vector lies in the plane of a smectic layer perpendicular to the tilt plane.

Despite the fact that there exist a variety of achiral (with, at least, one mirror symmetry plane) *crystalline* ferroelectrics, mostly inorganic ones, a search for the achiral analogues of *mesomorphic* ferro- and antiferro-electrics is still a challenge to both theoretical and experimental researchers. Prost and Barois [5] predicted a "longitudinal" ferroelectric where the spontaneous polarization arises due to the dipole–dipole interaction and directed along the normal to the smectic layers. Ferroelectric and anti-ferroelectric ordering may arise due to specific inter-molecular interactions which favour parallel alignment of electric dipoles as was discussed in Ref. [6]. In an achiral substance the $P_S$ vector must lie in the mirror plane; within this plane it is allowed to be oriented at any angle with respect to the layer normal. In a tilted smectic phase, for example, the polarization may arise due to an alternation of the tilt direction in neighbour smectic layers as was discussed by Brand, Cladis and Pleiner [7,8]. Ferroelectric order has also been predicted for achiral discotic mesophases formed by bowl-like molecules [9].

Recent experiments on low molecular mass polyphilic compounds [10] seem to be in accordance with theoretical predictions. However, neither ferro-nor antiferro-electric properties have been observed in achiral mesogenic polymers. Moreover, to our knowledge, there have been no reports even on crystalline polymer antiferroelectrics. Here we present an example of the antiferroelectric behaviour of a mesogenic mixture composed of an achiral side-

chain polymer and its (also achiral) monomer. None of the two counterparts alone manifests this behaviour.

## 2. Experimental

An anomalous electric behaviour has been observed in mixtures of several achiral side-chain methacrylate and acrylate polymers with their monomers. Here we present data only for the polymer–monomer pair PM6R8–M6R8, Fig. 1, at various monomer content. The molecular weight of the polymer was 81500. Sacharimetry technique showed no trace of the optical activity of monomer and polymer solutions in conventional solvents. All the details related to the synthesis of the monomer and its polymerization and characterization will be published elsewhere.

X-ray measurements were performed using a two-circle STOE diffractometer with a linear position-sensitive detector for data collecting (Cu K$\alpha$ radiation) [11] and a KARD diffractometer with a two-coordinate detector [12] for small and wide scattering angle ranges, respectively.

To study the antiferroelectric behaviour of our materials we used a pulse pyroelectric technique described in detail earlier [13]. A 100 $\mu$s pulse of a Nd$^{3+}$ YAG laser was used to provide a small local temperature change $\Delta T$ in a sample. Laser radiation ($\lambda = 1.06$ $\mu$m) was partly absorbed in ITO layers. The pyroelectric response was measured as a pulse

voltage across the load resistor $R_L = 100$ k$\Omega$ with a wide band amplifier and a storage oscilloscope. A dc field of various strengths was applied to the sample in order to measure hysteresis loops in coordinates pyroresponse–bias voltage.

Our cells consisted of two ITO covered, non-treated glass plates with 10 $\mu$m thick teflon spacers. The cells were filled by substances in the isotropic phase, mostly by pressing the substance between the two electrodes. Cells were placed in a thermal jacket with optical windows.

The temperature dependence of the spontaneous polarization (on an arbitrary scale) was calculated by integrating the pyroelectric voltage which is proportional to the pyroelectric coefficient $\gamma$, according to ($T_i$ is the transition temperature to the isotropic phase):

$$P_s(T) = \int_{T_i}^{T} \gamma(T) \, dT. \tag{1}$$

Then the correct scale for $\gamma$ and $P_s$ was introduced by comparison of the pyroelectric response at a certain temperature with the value measured for a well known ferroelectric liquid crystal.

Strictly speaking, Eq. (1) is valid only for the field off regime. When an external dc field is applied to prepare a ferroelectric monodomain or to "unwind" an antiferroelectric, what is really measured is the total polarization $P = P_s + P_i$ where $P_i$ is the field induced contribution, observed, for example, in the isotropic phase. Since $P_i$ is much smaller than $P_s$ we can use Eq. (1) for the measurements of $P_s$ in the "unwound" antiferroelectric phase.

## 3. Results

Fig. 2 shows the pyroelectric coefficient and macroscopic polarization as functions of temperature for mixtures of PM6R8 and M6R8 at various concentrations (in wt%) of the monomer. All the measurements have been carried out on cooling under dc bias field $E = 12$ V/$\mu$m. At zero field no pyroelectric response is observed on cooling from the isotropic phase. With the bias field applied the field induced pyroresponse (and polarization) in the isotropic phase ($T > 170°C$) is still negligible for all of the mixtures,

**M6R8**

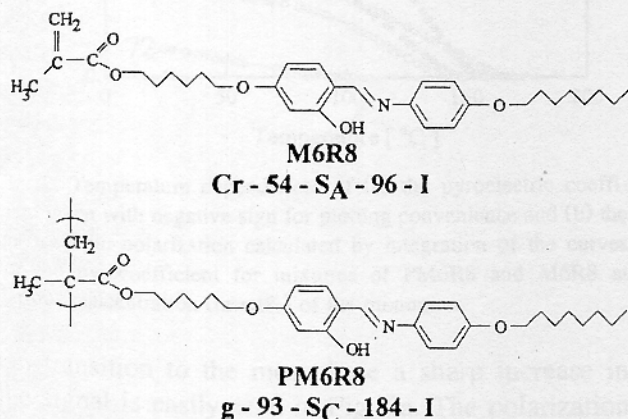**Cr - 54 - S$_A$ - 96 - I**

**PM6R8**

**g - 93 - S$_C$ - 184 - I**

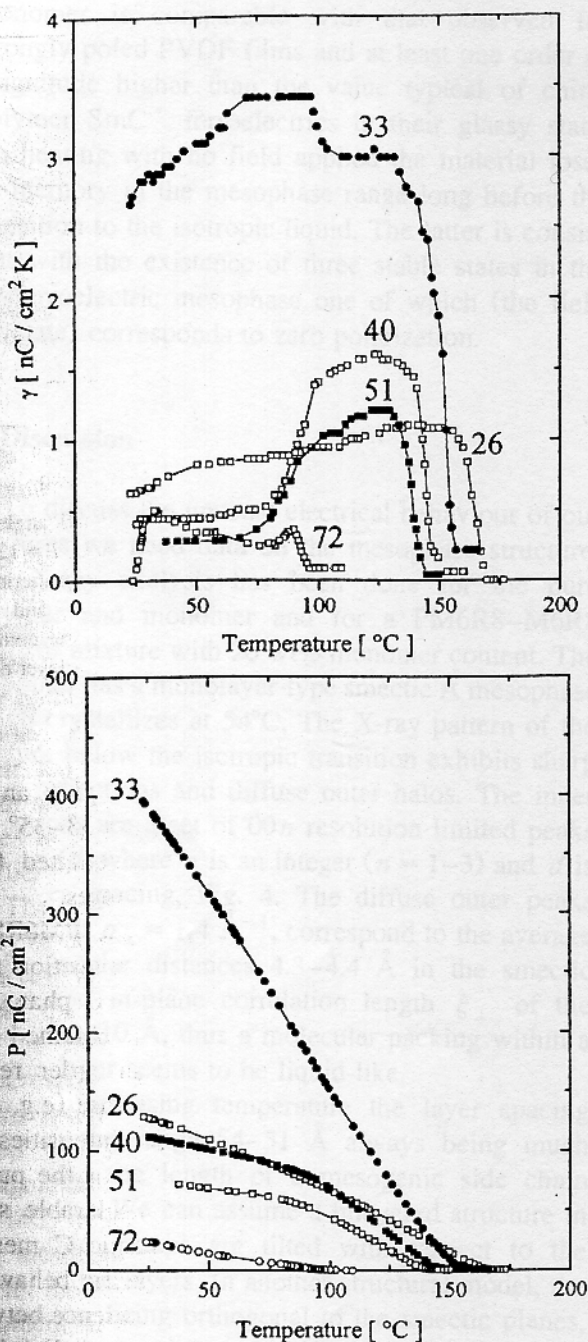Fig. 1. Chemical formulae and phase transition temperatures for the polymer and monomer.

Fig. 2. Temperature dependences of (a) the pyroelectric coefficient taken with negative sign for plotting convenience and (b) the macroscopic polarization calculated by integration of the curves for the pyrocoefficient for mixtures of PM6R8 and M6R8 at various concentration (in wt%) of the monomer.

On transition to the mesophase a sharp increase in the signal is easily seen in Fig. 2a. The polarization permanently increases on cooling although its growth is less pronounced in the glassy state. The value of

the macroscopic polarization both in the mesophase and in the glassy state has a well pronounced maximum as a function of monomer concentration. Neither the monomer nor pure polymer shows pyroelectric response and the optimum response is achieved for a mixture with approximately 33% of the monomer.

The voltage dependence of the macroscopic polarization in the mesophase is extremely nonlinear. At low voltages the field induced polarization increases linearly with field and rapidly relaxes after the field is switched off. However, above a certain threshold the polarization grows in a superlinear way and the field induced state remains for half a minute or so. At these voltages, a double hysteresis loop in "dc bias–pyroresponse" coordinates is easily measured, Fig. 3. Each of the subsequent points in the loop has taken half a minute after application of the corresponding voltage. Such loops are typical of antiferroelectrics: they correspond to three stable states, one with zero polarization (the field off state) and two states with the spontaneous polarization oriented along the two possible directions of the external field. No electrooptical response has been observed under an ac or dc voltage.

In the glassy state the pyroelectric response remains stable for a long time. Some of our samples stored at room temperature keep their polarization for almost a year. The best magnitude of the pyrocoefficient in the glassy state, $\gamma = 24 \ \mu C/m^2$ K mea-
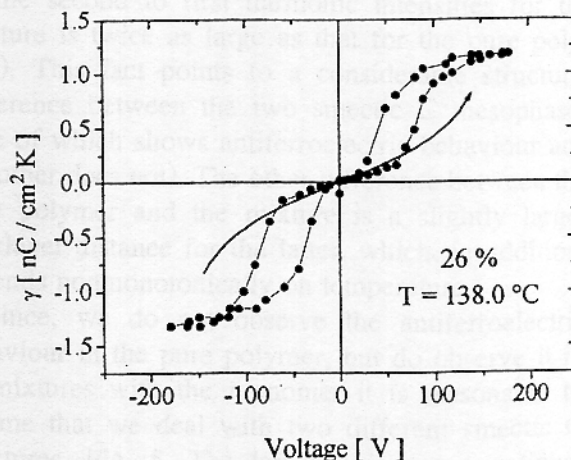


Fig. 3. A quasi-static antiferroelectric loop in the coordinates dc bias voltage–pyroelectric coefficient for PM6R8–M6R8 mixture with 26 wt% of the monomer.

sured for a PM6R8–M6R8 mixture with 33% of the monomer is comparable with that observed for strongly poled PVDF films and at least one order of magnitude higher than the value typical of chiral polymer SmC* ferroelectrics in their glassy state. On heating with no field applied the material loses its memory in the mesophase range long before the transition to the isotropic liquid. The latter is consistent with the existence of three stable states in the antiferroelectric mesophase one of which (the field off state) corresponds to zero polarization.

## 4. Discussion

To discuss the unusual electrical behaviour of our mixtures we need data on the mesophase structure. The X-ray analysis has been done for the pure polymer and monomer and for a PM6R8–M6R8 (74:26) mixture with 26 wt% monomer content. The monomer has a monolayer-type smectic A mesophase which crystallizes at 54°C. The X-ray pattern of the mixture below the isotropic transition exhibits sharp inner reflections and diffuse outer halos. The inner reflections are a set of $00n$ resolution limited peaks at $2\pi n/d$, where $n$ is an integer ($n = 1–3$) and $d$ is the layer spacing, Fig. 4. The diffuse outer peaks centered at $q_\perp \approx 1.4$ Å$^{-1}$, correspond to the average intermolecular distances 4.3–4.4 Å in the smectic planes and in-plane correlation length $\xi_\perp$ of the order of 6–10 Å, thus a molecular packing within a smectic layer seems to be liquid-like.

With decreasing temperature the layer spacing varies in the range 54–51 Å always being much larger than the length of a mesogenic side chain ($L \approx 33$ Å). We can assume a bilayered structure in which side groups are tilted with respect to the normal to the layers. In another structural model, the side chains, being orthogonal to the smectic planes, would partly overlap each other. In order to make a choice from the two structural models, two-dimensional X-ray patterns from oriented films in the glassy state have to be analyzed, Fig. 4 (inset). It is clearly seen that the outer reflections are split into two intense spots lying on opposite sides of the equator line ($q_\perp$ direction). This points to a tilt of the side groups with respect to the normal to the layers. The azimuthal angles of the intensity maxima
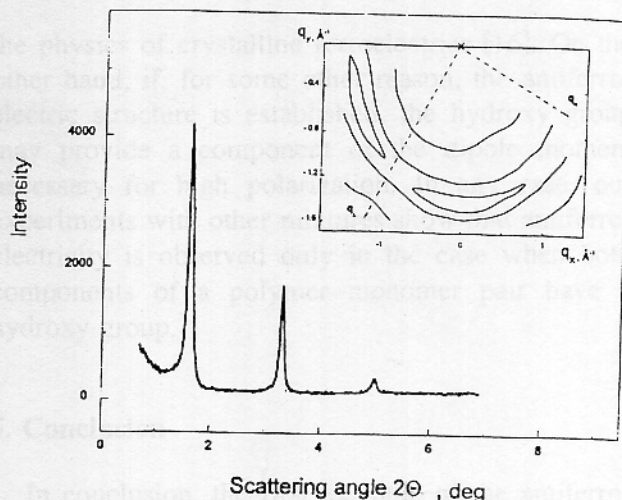


Fig. 4. X-ray diffraction patterns in the small angle scattering regions for a PM6R8–M6R8 (74:26) mixture, $T = 120°C$. Inset: X-ray diffraction patterns in a wide angle scattering regions. Frozen bilayer smectic C phase, $T = 20°C$, $q_x$ and $q_y$ are the coordinates of the two-dimensional detector, the components of the scattering wave vector $q_\parallel$ and $q_\perp$ lie along layer normals and in the plane of smectic layers respectively.

with respect to the $q_\perp$ direction give an average value of molecular tilt angle $\beta \approx 33–35°$ in good agreement with the tilt angle calculated from the layer spacing data at low temperatures.

Thus, according to X-ray data, PM6R8–M6R8 (75:25) mixture shows a phase transition from the isotropic into a bilayered smectic C phase. Similar X-ray diffraction data have been obtained for pure polymer PM6R8. However, high order reflections are more pronounced for the mixture (e.g. the ratio of the second to first harmonic intensities for the mixture is twice as large as that for the pure polymer). This fact points to a considerable structural difference between the two smectic C mesophases (one of which shows antiferroelectric behaviour and the other does not). The other difference between the pure polymer and the mixture is a slightly larger interlayer distance for the latter, which, in addition, depends nonmonotonically on temperature.

Since, we do not observe the antiferroelectric behaviour in the pure polymer, but do observe it in its mixtures with the monomer it is reasonable to assume that we deal with two different smectic C structures, Fig. 5. The left one is a conventional smectic C with a uniform tilt in neighbour layers and free rotation of mesogenic groups around their long
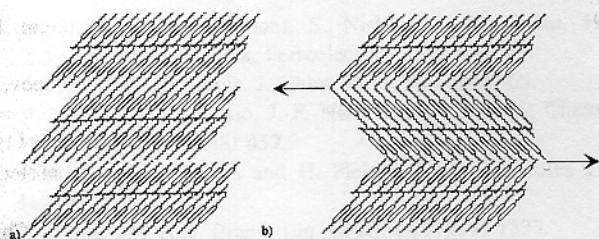
Fig. 5. Two possible packings of the mesogenic groups of a side-chain polymer in the bilayer smectic C phase: (a) uniform tilt; (b) alternating tilt with in-plane antiferroelectric order.

axes (liquid-like layers). We assume that the pure polymer has this structure. On addition of the monomer the structure of the mesophase converts into the smectic C structure with alternating molecular tilt, Fig. 5b. Indirectly, the appearance of this structure is confirmed by an increase in the second order X-ray reflection intensity, see also Ref. [14]. In our opinion, the monomer fills an extra free volume, hinders the rotation of the mesogenic units around their long axes and induces the smectic structures with alternating tilt. The role of the monomer additives in provoking new structures has been reported earlier [15].

The field behaviour of the alternating tilt structure may be described as follows. In the field off state the macroscopic polarization is zero. With increasing field, the bilayers with in-plane polarization opposite to the field reorient in the field direction and a macroscopic polarization appears. Two field directions result in two quasi-stable states and a double loop typical of antiferroelectrics. The maximum magnitude of the macroscopic polarization measured ($4 \, mC/m^2$) may be accounted for if we assume that all mesogenic units of both polymer and monomer (with molecular weight about 500) have their dipole moment projections on the field direction of about 1 debye which is quite reasonable. On transition to the glassy state, a field induced macroscopic polarization becomes frozen and the material manifests pyroelectric response comparable with that typical of crystalline polymer ferroelectrics [16].

It is much more difficult to understand the molecular mechanism of the phenomenon. In our opinion the hydroxy group may play a crucial role. On one hand, it may be conductive to in-layer polar packing due to dipole–dipole interaction well known from

the physics of crystalline ferroelectrics [16]. On the other hand, if, for some other reason, the antiferroelectric structure is established, the hydroxy group may provide a component of the dipole moment necessary for high polarization. In any case, our experiments with other mixtures show that antiferroelectricity is observed only in the case when both components of a polymer–monomer pair have a hydroxy group.

## 5. Conclusion

In conclusion, the first example of the antiferroelectric behaviour of mesogenic mixtures composed of an achiral side-chain polymer and its monomers is presented. The mixtures show antiferroelectric hysteresis curves in the mesophase whereas none of the two counterparts alone manifests this behaviour. The results are interpreted in terms of the smectic C structure with alternating tilt which, from the symmetry viewpoint, is allowed to be antiferroelectric. The monomer additive to a polymer is assumed to be provoking the alternating tilt structure. The mixtures, being cooled to the glassy state under a dc electric field applied, reveals high pyroelectric coefficient comparable to that observed in proper polymer ferroelectrics.

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