

Antiferroelectric behaviour of achiral mesogenic polymer mixtures

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X-ray structure determination and pyroelectric and piezoelectric measurements have been carried out on mesogenic mixtures composed of achiral side chain polymers and their monomers. Certain mixtures show antiferroelectric polarization hysteresis loops in the mesophase which was shown to be a bilayered smectic C, while the two components of the mixtures taken alone show no antiferroelectricity. The results obtained on the polymer-monomer mixtures are interpreted in terms of the smectic C structure with alternating tilt which, from a symmetry viewpoint, is allowed to be antiferroelectric. The antiferroelectric mixtures, on being cooled to the glassy state under a d.c. electric field applied, reveal high pyroelectric coefficients with prospects for application as IR detectors.

1. Introduction

Since the beginning of this century achiral (with mirror symmetry) crystalline ferro- and antiferro-electrics have been investigated very extensively [1]. As a rule, they manifest so-called *proper* ferroelectricity when the spontaneous polarization arises as a primary order parameter due to dipole-dipole interactions, although there are some examples of *improper* crystalline ferroelectrics where P_S is a secondary order parameter. Among proper ferroelectrics there have been found crystalline polymers such as polyvinylidene fluoride (PVDF) and its copolymers. Weak ferroelectric properties have also been observed in an achiral lamellar mesophase, that is in a non-crystalline material [2].

On the other hand, chiral tilted mesophases (C^* , F^* , I^* , etc.), including those of polymers, manifest both ferroelectric [3, 4] and antiferroelectric [5, 6] properties. The mechanism of ferroelectricity in these systems is quite specific: a tilt of elongated chiral molecules, that is the order parameter of a tilted phase, results in a polar ordering of their short axes (and their transverse dipole moments) perpendicular to the tilt plane. The P_S vector lies in the plane of a smectic layer perpendicular to the tilt plane. Such materials also belong to the class of improper ferro- and antiferro-electrics.

A search for *achiral* analogues of *mesomorphic* ferro- and antiferro-electrics is still a challenge to researchers, both theoreticians and experimentalists. Prost and Barois [7] predicted a 'longitudinal' proper ferroelectric where

the spontaneous polarization arose due to the dipole-dipole interaction, is directed along the normal to the smectic layers and is allowed even in the smectic A phase. Improper ferroelectric and antiferroelectric ordering may arise due to specific intermolecular interactions which favour parallel alignment of electric dipoles as was discussed in [8, 9]. In a tilted smectic phase of a non-chiral substance, the P_S vector must lie in the tilt plane. It might be at a certain angle to the layer planes [8] or lie in the layer plane, as was discussed theoretically by Brand, Cladis and Pleiner [10, 11]. Ferroelectric order has also been predicted for non-chiral discotic mesophases formed by bowl-like molecules [12].

Few recent experiments seem to be in accordance with such theoretical predictions. An achiral mesophase composed of so-called polyphilic compounds [8] manifests a rather small P_S value [2] of the order of 10 nC cm^{-2} . Much higher P_S magnitudes, of the order of 100 nC cm^{-2} have been reported by Swager *et al.* at the Budapest International Liquid Crystal Conference [13] for discotic (bowl-like) mesogens. However, ferro- or antiferro-electric properties were never observed in achiral mesogenic polymers. Moreover, to our knowledge, there have been no reports on crystalline polymer antiferro-electrics (all copolymers of PVDF are ferroelectric). In our search for novel polar materials we have found, rather unexpectedly, an interesting system with very unusual properties [14]. Here we present the first example of antiferroelectric behaviour of mesogenic mixtures composed of an achiral side chain polymer and its monomer. Of particular interest is the fact that neither

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Table 1. Phase transition temperatures (°C) and molecular weights for the polymers investigated.

Polymer	Phase behaviour	\bar{M}_w	\bar{M}_w/\bar{M}_n
PM6R8	g 93 S _c 184 I	81·500	2·1
PM6R6	g 82 S _c 157 S _A 173 I	54·300	2·4
PM6B8	g 80 S _c 161 I	64·500	1·9
PA6R8	g 60 S _c 180 I	85·200	5·8

Table 2. Phase transition temperatures (°C) and molecular lengths L (Å) for the monomers investigated.

Monomer	Transition temperatures	L
M6R8	Cr 54 S _A 96 I	34·0
M6R6	Cr 63 S _A 95 I	31·5
M6B8	Cr 71 S _A 114 I	34·0
A6R8	Cr 59 S _A 119 I	32·5
C11R8	Cr 60 S _A 119 I	35·2

for the polymers, as well as the transition temperatures determined by DSC and microscopic observations are summarized in table 1. The transition temperatures and molecular lengths (calculated with standard computer simulation software) of the corresponding monomers are given in table 2. A detailed description of the synthesis and characterization of intermediate and end products will be presented elsewhere [16].

In the most important cases (PM6R8, M6R8, their mixture in a 74:26 ratio and polymer PM6B8), X-ray structure determinations have been carried out. X-ray measurements were performed using a two-circle STOE diffractometer with a linear position-sensitive detector for data collection (CuK_α radiation) [17]. The longitudinal resolution was at the level $\Delta q_{\parallel} = 4 \times 10^{-3} \text{ \AA}^{-1}$ (full width at half maximum, FWHM). The components of the diffraction vector q_{\parallel} and q_{\perp} were parallel and perpendicular to the layer normal, respectively: $q = (4\pi/\lambda) \sin \theta$ (θ is scattering angle and λ is the wavelength of the radiation). Thus measurements of the longitudinal correlation length were limited by the value $\xi_{\parallel} = 2/\Delta q_{\parallel} \approx 500 \text{ \AA}$.

An X-ray study in the wide scattering angle region ($q_{\perp} \geq 1 \text{ \AA}^{-1}$) provides data on the positional correlations in the plane of the smectic layers. These measurements were performed using flat-plate photographs and a KARD diffractometer with a two-coordinate detector [18, 9]. To derive the intensity contour maps from the two-dimensional images, the following procedure was used. First the number of radial cross-sections with an azimuthal step of 5° was recorded. The intensity distribution in each cross-section was divided into discrete groups from 1 to 4 (the maximum intensity was set

equal to 4). In this way contours of equal intensity in gradations 1, 2 and 3 were displayed.

X-ray diffraction measurements were performed both on powder specimens (thin-wall glass capillaries) and on well oriented thin films. Oriented samples were prepared using the shear alignment technique. The polymer was placed between two glass plates and heated to the temperature of the mesophase, close to the transition into the isotropic liquid. Then, to provide a shear, the cover glass was repeatedly (and circularly) moved relative to the substrate. On fast cooling to room temperature, oriented textures with the smectic planes parallel to the film surface were maintained. The resulting films had thicknesses from 50 to 100 μm .

3. Electric measurements

To study the electric behaviour of our materials we used two techniques very sensitive to the incidence of any (spontaneously or field induced) polarized state, namely measurements of the pyroelectric and piezoelectric response. Cells consisted of two ITO covered, untreated glass plates with teflon spacers of thickness about 8 and 110 μm for pyroelectric and piezoelectric measurements, respectively. The cells were filled with materials in the isotropic phase either by capillary forces (for thin cells it takes about an hour) or by pressing the substance between the two electrodes. Cells were placed in a thermal jacket with optical windows.

For pyroelectric measurements, we used a pulse technique described in [19] in detail. A 100 μs pulse of a Nd³⁺ YAG laser was used to provide a small local temperature change ΔT in a sample. Laser radiation ($\lambda = 1.06 \mu\text{m}$) was partly absorbed in the ITO layers. The pyroelectric response was measured as a pulse voltage across the load resistor $R_L = 100 \text{ k}\Omega$ using a wide band amplifier and a storage oscilloscope. D.c. fields of various strengths were applied to the sample in order to measure hysteresis loops in pyroresponse-bias voltage coordinates. The data were recorded and processed with an IBM/PC computer.

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 γ , according to equation (1) (T_i is the transition temperature to the isotropic phase):

$$P_s(T) = \int_{T_i}^T \gamma(T) dT \quad (1)$$

Then the correct scale for γ and P_s was introduced by comparison of the pyroelectric response at a certain temperature with the value measured for a known ferroelectric substance [20] in a new cell made from the

X-ray measurements do not reveal broadening of $00n$ peaks or any additional diffuse scattering from admixed monomers. This means that the monomers randomly occupy the bilayers formed by the polymer matrix. No indication was found of any segregation of mixture components or phase separation.

With decreasing temperature, the layer spacing calculated from figure 2 varies with temperature in the range of 54–51 Å, being always much larger than the length of a mesogenic side chain ($L \approx 33$ Å). This implies some form of bilayer arrangement of the side groups in the smectic planes. We can assume a bilayer structure in which the 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, might partly overlap each other (in an interdigitated structure). In order to make a choice between the two structural models, two-dimensional X-ray patterns from oriented films had to be analysed, see figure 4. It is clearly seen that the outer reflections are split into two intense spots lying to the right and left 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 for the spots with respect to the q_{\perp} direction give an average value of the molecular tilt angle β . Note, that in orthogonal smectics, the outer reflections are always centred at the equator line. The tilt angle derived from the X-ray scattering, $\beta = 35\text{--}39^\circ$, is in good agreement with the tilt angle calculated from the layer spacing data at low temperatures: $\beta = \arccos d/2L \approx 33\text{--}35^\circ$.

Thus, according to the X-ray data, the PM6R8-M6R8 (74:26) mixture shows a phase transition from the

isotropic into a bilayered smectic C phase. The X-ray studies were also carried out separately on pure polymer PM6R8 and its monomer M6R8. In the only mesophase found in the monomer, the smectic phase interlayer spacing $d \approx 35$ Å is very close to the molecular length $L \approx 33$ Å; thus, according to the X-ray and optical data, this phase should be referred to as smectic A. The polymer was shown to have the same bilayered smectic C phase as the (74:26) mixture. However high order reflections are more pronounced for the mixture (e.g. the ratio of the second to the first harmonic intensities for the mixture is twice as large as that for the pure polymer). In addition, in the pure polymer, the interlayer spacing monotonically decreases with temperature, consistent with an increase in the tilt angle. In the mixtures with the monomer, the interlayer distance is slightly larger and depends non-monotonically on temperature. The temperature behaviour of the interlayer distance has been measured for two mixtures, PM6R8-M6R8 (74:26) and (67:33) (the latter has even more pronounced antiferroelectric properties). For instance, in mixture (67:33), with decreasing temperature the interlayer distance changes non-monotonically: first, in the range 160–100°C it increases (from 53 to 55 Å), then in the range 100–25°C, it decreases (down to 51 Å in the glassy state). Both the more pronounced high order reflections and the anomalous increase in the spacing of the C phase close to the transition into the isotropic state point to a specific mutual packing of the monomer molecules and the side chain groups of the polymer that is strongly dependent on temperature.

Therefore, we conclude that both the pure polymer and its mixtures with the monomer have a bilayer struc-

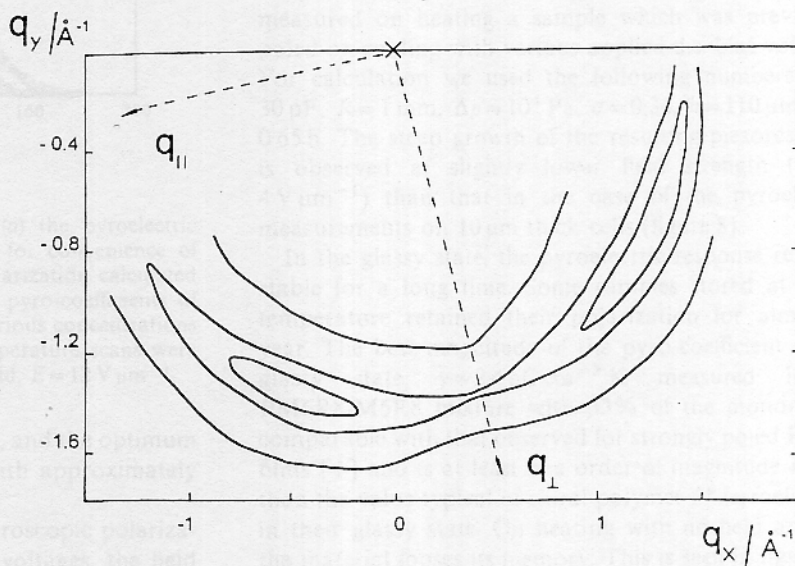


Figure 4. X-ray diffraction patterns in the wide angle scattering region for an oriented film of a PM6R8-M6R8 (75:25) mixture; frozen bilayer smectic C phase, $T = 20^\circ\text{C}$. q_x and q_y are the coordinates of the two-dimensional detector; the components of the scattering wave vector q_{\parallel} and q_{\perp} lie along the layer normals and in the plane of the smectic layers, respectively. The small angle peaks shown in figure 2 are omitted because of the intensity scale difference.

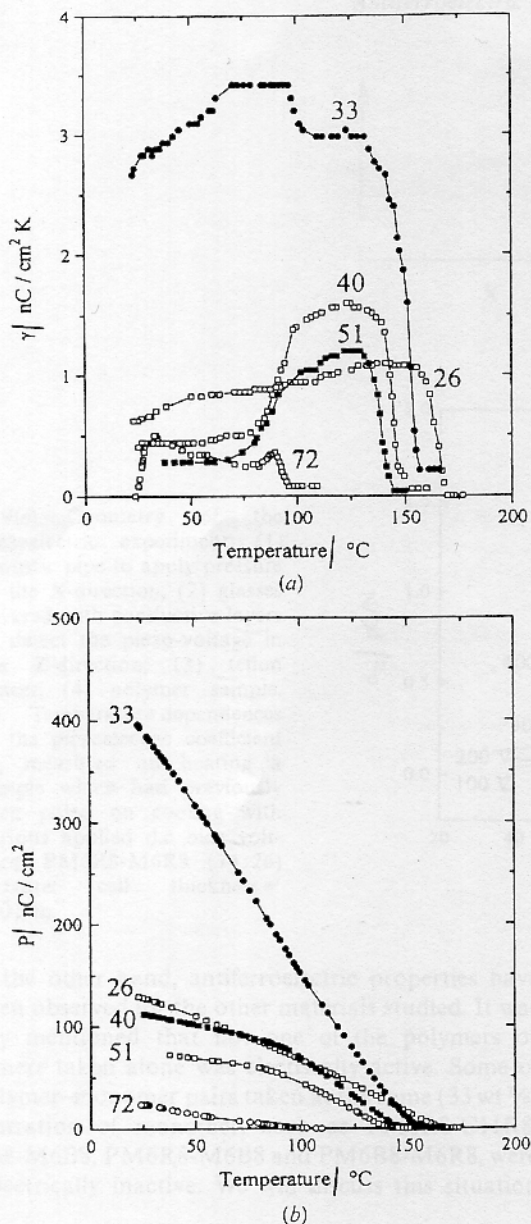


Figure 6. Temperature dependences of (a) the pyroelectric coefficient taken with negative sign for convenience of plotting and (b) the macroscopic polarization calculated by integration of the curves for the pyro-coefficients of mixtures of PM6R8 and M6R8 at various concentrations (in wt %) of the monomer. The temperature scans were made on cooling under a d.c. bias field, $E = 12 \text{ V } \mu\text{m}^{-1}$.

polymer shows a pyroelectric response, and the optimum response is achieved for a mixture with approximately 33% of the monomer.

The voltage dependence of the macroscopic polarization is extremely non-linear. At low voltages, the field

induced polarization increases linearly with field and rapidly relaxes after field switching off. However, above a certain threshold the polarization grows in a super-linear way, and the field induced state has a certain memory (about half a minute). At these voltages, a double hysteresis loop expressed in coordinates of 'd.c. bias-pyroresponse' (instead of polarization, in conventional techniques) is easily measured, as shown in figure 8. Each of the consecutive points in the loops shown was 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 with the spontaneous polarization oriented along two possible directions of the external field. The essential difference of our system from solid and liquid crystalline (chiral) antiferroelectrics is the rather slow response. It should be mentioned that no electro-optical response has been observed under either a.c. or d.c. voltage.

Strong field non-linearity was confirmed by measurements of the piezoelectric response of a PM6R8-M6R8 (74:26) mixture (figure 9(a)). As has been shown in detail [22], the piezoelectric coefficient in a glassy state can be calculated from the experimentally available piezoelectric voltage U by the following simple formula:

$$d_{31} = \frac{UC}{4LR\Delta p} \quad (2)$$

where C is the capacity of the cell and cables, R is the radius of the polymer disk-shaped sample, Δp is the pressure difference and L is the penetration length of the deformation, dependent on the thickness of the sample h and Poisson ratio σ . Figure 9(b) shows the temperature dependences of piezoelectric coefficient d_{31} measured on heating a sample which was previously poled on cooling with various applied d.c. bias voltages. For calculation we used the following numbers: $C = 30 \text{ pF}$, $R = 1 \text{ mm}$, $\Delta p = 10^4 \text{ Pa}$, $\sigma = 0.34$, $h = 110 \text{ } \mu\text{m}$, $L = 0.65 \text{ h}$. The steep growth of the resulting piezoresponse is observed at slightly lower field strength (about $4 \text{ V } \mu\text{m}^{-1}$) than that in the case of the pyroelectric measurements on $10 \text{ } \mu\text{m}$ thick cells (figure 8).

In the glassy state, the pyroelectric response remains stable for a long time. Some samples stored at room temperature retained their polarization for almost a year. The best magnitude of the pyro-coefficient in the glassy state, $\gamma = 2.4 \text{ nC cm}^{-2} \text{ K}$ measured for a PM6R8-M6R8 mixture with 33% of the monomer is comparable with that observed for strongly poled PVDF films [1] and is at least one order of magnitude higher than the value typical of chiral polymer S_{C}^* ferroelectrics in their glassy state. On heating with no field applied, the material loses its memory. This is seen in figure 10,

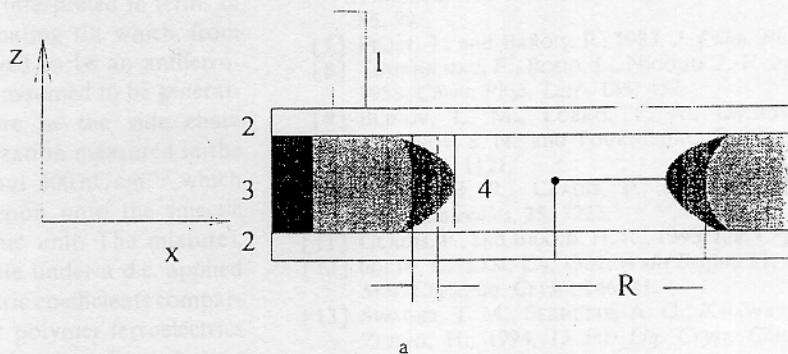
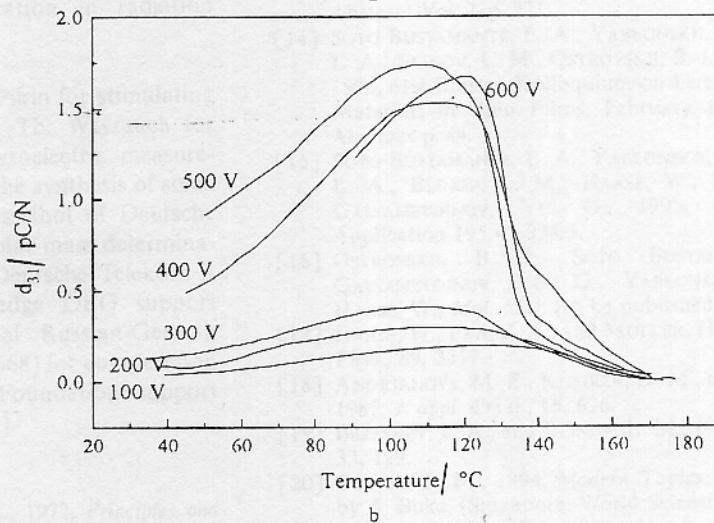


Figure 9(a). Geometry of the piezoelectric experiment: (1) acoustic pipe to apply pressure in the X-direction; (2) glasses covered with conductive layers to detect the piezo-voltage in the Z-direction; (3) teflon spacer; (4) polymer sample. (b). Temperature dependences of the piezoelectric coefficient d_{31} measured on heating a sample which had previously been poled on cooling with various applied d.c bias voltages; PM6R8-M6R8 (74:26) mixture; cell thickness = 110 μm .



On the other hand, antiferroelectric properties have not been observed for the other materials studied. It was already mentioned that not one of the polymers or monomers taken alone was electrically active. Some of the polymer-monomer pairs taken at the same (33 wt %) concentration of monomer, such as PM6R8-C11R8, PM6B8-M6B8, PM6R8-M6B8 and PM6B8-M6R8, were also electrically inactive. We will discuss this situation below.

5. Discussion

Our experimental results on achiral PM6R8-M6R8 mixtures are consistent with either of the two antiferroelectric structures shown in figures 5(b) and 5(c). Indeed X-ray data on the mesophase unambiguously show the typical bilayered smectic C structure which is allowed to be polar only in the case when polarization lies in the tilt plane. However, the pure polymer PM6R8 also has a smectic C structure, but is electrically inactive. It is reasonable to assume that the pure polymer has the conventional structure, shown in figure 5(a). Therefore, a role of the monomer additive is to induce one of the smectic structures with alternating tilt. This role of the

monomer additives in generating new structures has been reported before [26].

In the field off state, the macroscopic polarization in the mesophase 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 (400 nC cm^{-2}) may be accounted for if we assume that all the mesogenic units of both polymer and monomer (with molecular weight about 500) have dipole moment projections on the field direction of about 1 D, which is quite reasonable. On transition to the glassy state, the field induced macroscopic polarization becomes frozen in and the material manifests a pyroelectric response comparable with that of typical, proper polymer ferroelectrics. At the moment we cannot make a choice between the structures shown in figures 5(b) and 5(c); both are consistent with our data.

It is much more difficult to understand the molecular mechanism of the phenomenon. Let us note first that antiferroelectricity is observed only in the case when

liquid-like layers. The results are interpreted in terms of a smectic C structure with alternating tilt which, from the symmetry viewpoint, is allowed to be an antiferroelectric. The monomer additive is assumed to be generating the alternating tilt structure in the side chain polymer. The macroscopic polarization measured in the mesophase reaches values of about 300 nC cm^{-2} which require a dipole moment projection onto the smectic plane of about 1 D per mesogenic unit. The mixtures, on being cooled to the glassy state under a d.c. applied electric field, reveal high pyroelectric coefficients comparable to those observed in proper polymer ferroelectrics and raising prospects for application in radiation detectors [15].

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