

# Antiferroelectricity in achiral mesogenic mixtures of organic materials

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## Abstract

To clarify the mechanism involved in the appearance of antiferroelectric properties in mixtures of polymers containing achiral mesogenic side chains and their monomers, X-ray investigation was carried out in pyroelectrically active samples. The thermal stability of such systems is also reported. The X-ray investigation shows that in highly concentrated mixtures of monomer in polymer, a segregation of the excess of monomer from an optimized ratio (33% monomer/polymer) occurs. © 2000 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

To date, the investigation of ferro- or antiferroelectricity in liquid crystalline materials has always been related to the presence of at least one chiral center in the molecules. In our search for novel polar materials, we have found an interesting system with very unusual properties [1], i.e. they possess no chirality at all. The system consists of mixtures of a side-chain liquid crystalline polymer with its monomer (see Fig. 1). The main chain is mainly methacrylate or acrylate. It is of particular interest that none of the two counterparts manifests this

behavior if isolated. Each one of the samples in a concentration range between 15% and 75% of monomer in polymer shows double polarization hysteresis curves in the smectic C phase typical for antiferroelectric materials [1]. 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.

After cooling from the isotropic to the glassy state under an applied electric d.c. field, the samples reveal a high pyroelectric response. The pyroelectric signal of the samples was high enough to be comparable with that of low molar mass ferroelectric liquid crystals and achiral ferroelectric polymers such as PVDF. The maximum macroscopic polarization obtained from pyroelectric measurements was around 400 nC/cm<sup>2</sup> [2] and corresponds to a 33% w/w of the monomer in polymer. The behavior just de-

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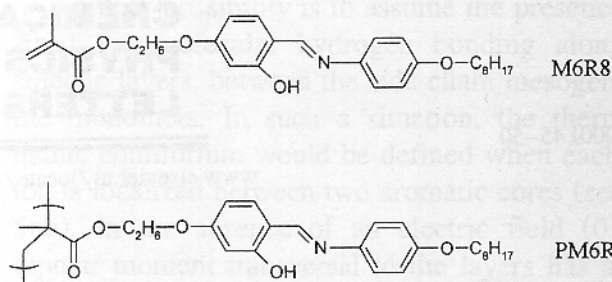


Fig. 1. First investigated mixture components of liquid crystals, monomer (M6R8) and polymer (PM6R8) without chirality showing antiferroelectric behavior.

scribed may be useful in applications such as radiation detectors [3].

The design of these new materials presents advantages that will allow the development of new technology. Materials with a high enough purity with specific features are necessary to improve the properties of existing devices. They can be used as pyro- or piezoelectric sensors in mining, seismology, etc.

The aim of this work is to have a deeper knowledge of the investigated mixtures having high amounts of monomer beyond the 33% considered as the optimized monomer/polymer ratio. This will clarify the decrease in the observed pyroelectric response for high concentration of monomer and therefore increase our knowledge of the involved mechanism for the appearance of antiferroelectricity.

## 2. Experimental

Thermal gravimetric analysis (Perkin Elmer, TGA-7) was carried out in order to study thermal stability of both monomer and polymer. The heating rate was 10°C/min and the heating process, under nitrogen atmosphere, reaches 380°C.

The phase transition temperatures (see Fig. 2) and corresponding enthalpies (see Table 1) for the investigated mixtures were obtained from differential scanning calorimetry data (Perkin Elmer, DSC-7). The presented values correspond to the first heating and cooling process. In Fig. 2 the open circles (○) belong to the phase transition for the polymer mixture PM6R8-M6R8 and polymer alone (PM6R8). The full circles (●) belong to the phase transitions detected by DSC in mixtures having a higher amount

of monomer and the monomer alone (M6R8). These transitions correspond to the excess of monomer in the mixtures that are segregated from the ideal polymer/monomer ratio (2:1).

By heating, all the mixtures have a clearing point between 140°C and 180°C. The presence of monomer in the mixtures becomes evident for monomer concentrations over 20% where a new phase transition at around 50°C is observed. A second phase transition (approx. at 100°C) is detected when the amount of monomer exceeds 35%. On cooling, for mixtures with up to 35% of monomer, the phase transitions at ~50°C is no more observed. For higher concentrations of monomer both transitions detected during the first heating are also present (see Table 1). This last situation remains for subsequent heating-cooling cycles of the samples.

Previous investigations [1–3] showed that on cooling down starting from the temperature where this new phase appears, the pyroelectric activity in the sample decreases substantially. The resulting good agreement between the pyroelectric measurements and the obtained phase transitions for the mixtures need to be explained. Thus, for a clear understanding of the nature of this non-antiferroelectric behavior, samples that contain 48% (PM6R8-48), 58% (PM6R8-58) and 80% (PM6R8-80) of monomer were investigated by means of X-ray diffractometry.

X-ray experiments were carried out focusing a horizontal two-circle X-ray diffractometer (STOE STADI 2) with a linear position sensitive detector (STOE mini PSD) for the data collection.

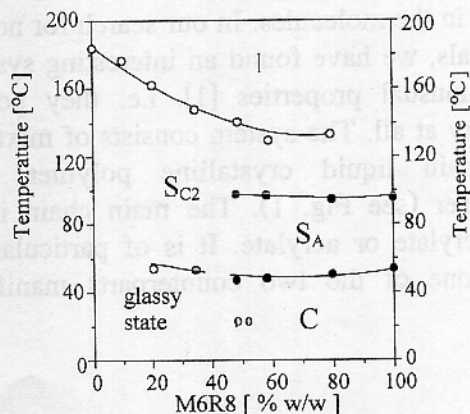


Fig. 2. Phase diagram for mixtures of PM6R8 and M6R8. ○, PM6R8-M6R8 mixtures; ●, M6R8.

Table 1

Phase transition temperature for different polymer–monomer mixtures. The informed enthalpy belongs to the  $S_A$  phase (if present) and the  $S_{C2}$  phase, respectively, whereas in the monomer it corresponds to the transition  $S_{A-I}$ \*

Mixture	Mesophase (°C) (Heating)	Enthalpy (J/g)		
		$C-S_A$	$S_A-S_{C2}$	$S_{C2}-I$
PM6R8	g-93.0- $S_{C2}$ -184.0-I			16.2
PM6R8-9	g-n.d.- $S_{C2}$ -175.9-I			19.4
PM6R8-20	g-54.2- $S_{C2}$ -162.7-I	3.6		19.1
PM6R8-35	g-53.0- $S_{C2}$ -143.5-I	14.5		12.7
PM6R8-48	g-47.4- $S_A$ -100.9- $S_{C2}$ -138.9-I	25.5	3.0	12.0
PM6R8-58	g-48.4- $S_A$ -99.7- $S_{C2}$ -131.1-I	31.2	4.3	10.9
PM6R8-80	g-50.5- $S_A$ -99.6- $S_{C2}$ -132.7-I	49.4	8.5	3.4
M6R8	C-54.0- $S_A$ -96.0-I	77.4	11.4*	

Mixture	Mesophase (°C) (Cooling)	Enthalpy (J/g)	
		$S_A-S_{C2}$	$S_{C2}-I$
PM6R8-9	g-55.5- $S_{C2}$ -173.3-I		20.1
PM6R8-20	g-56.7- $S_{C2}$ -165.1-I		19.8
PM6R8-35	g-53.3- $S_{C2}$ -157.2-I		13.8
PM6R8-48	g-50.7- $S_A$ -103.2- $S_{C2}$ -142.5-I	2.6	9.5
PM6R8-58	g-54.2- $S_A$ -97.9- $S_{C2}$ -144.7-I	4.0	9.7
PM6R8-80	g-50.0- $S_A$ -93.8- $S_{C2}$ -131.3-I	8.3	3.7

n.d.: non-determined.

The temperature dependence of the  $d$ -values is shown in Fig. 3a. From the data it can be seen that the interlayer distance increases with higher monomer concentration. Therefore, the intensity of the pyroelectric signal is related to the presence of a maximum in the  $d$ -values.

As the interlayer distance increases from an optimum polymer/monomer ratio of 2:1 and a length of 54 Å, the intensity of the pyroelectric signal decreases. The temperature variation of the intensity ratio  $I_2/I_1$  for the first two harmonics from the diffraction peaks also correlates with the temperature dependence of the layer thickness in the samples (see Fig. 3b).

### 3. Discussion

Total thermal degradation for the polymer PM6R8 was observed between 380°C and 490°C. The monomer M6R8 decomposes between 310°C and 440°C. The thermal stability at a constant temperature for PM6R8 was tested at 160°C for at least 5 h without noticeable decomposition. This ensures the

reliability of the sample composition for all the experiments carried out.

As was previously described for the mixtures with more than 35% of monomer, in the first heating, DSC experiments show the appearance of two new phase transitions. They are settled at around the same position as the transition temperatures for the monomer alone, i.e. 54°C (crystal- $S_A$ ) and 95°C ( $S_A-I$ ).

The enthalpies associated with the phase transitions at around 100°C and 50°C increase as the amount of monomer in the mixture grows (see Table 1). So, the lower ranges of monomer concentrations have also associated low enthalpy values but cannot be observed. The summation of the enthalpies for both transitions, at ~100°C and at the clearing point, have a more or less constant value of 12 J/g. This fact may indicate the existence of certain interactions between the mixture components.

We found from X-ray measurements for the sample PM6R8-80 that in the temperature region of the non-pyroelectric phase, clearly a new diffraction peak at 34 Å occurs. It is located between the first (001) and the second reflex (002) (see Fig. 4a). This new

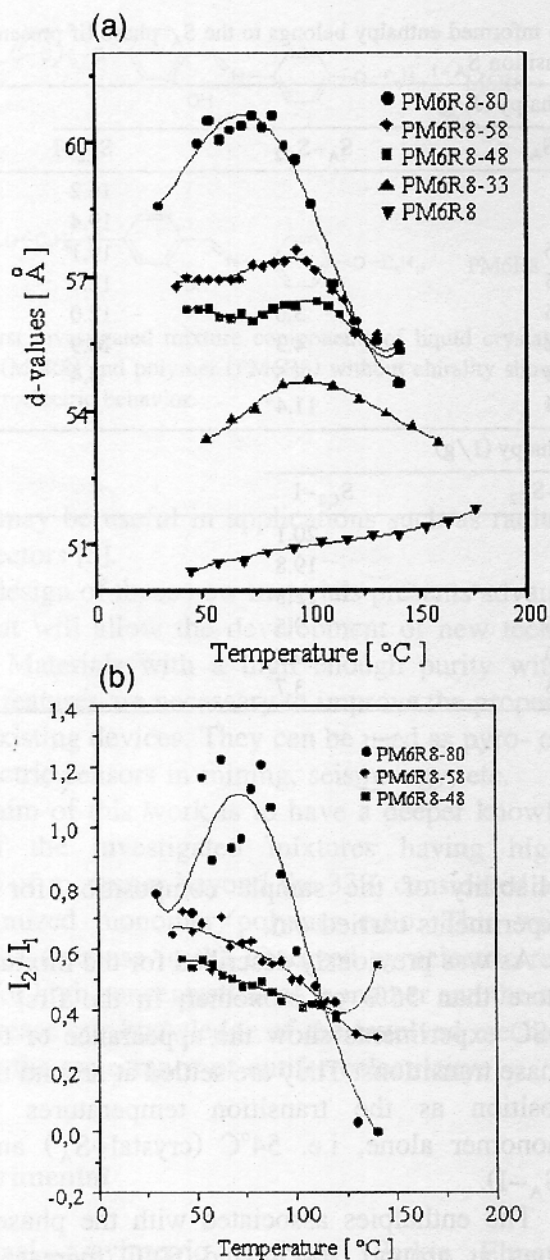


Fig. 3. Temperature dependence of (a) the interlayer distance for PM6R8 and mixtures of PM6R8 with 80%, 58%, 48% and 33% of monomer and (b) relative intensities of 002(I<sub>2</sub>) to 001(I<sub>1</sub>) reflexes for mixtures of PM6R8 with 80%, 58% and 48% of monomer.

reflex appears only between the temperatures belonging to the phase transitions C–S<sub>A</sub> and S<sub>A</sub>–I for the monomer alone. This peak can be associated with the segregation of the free monomer in excess of the finest value (33% of monomer guest in the polymer).

Fig. 4b shows the interlayer distance dependence with the temperature for the first and second reflex

belonging to the polymer. The new reflex at around 33 Å is also drawn. The dependence of this peak on temperature is slightly different as compared with the related behavior of the interlayer distance for the monomer alone [1]. In the later case, this dependence has a better linear fit.

More in depth investigations of these mixtures are necessary to clarify this behavior. Nevertheless, it is possible to assume the coexistence of two different smectic phases at low temperature. One of them belongs to the smectic A phase that corresponds to the excess of monomer. The other one corresponds to the bilayered smectic C<sub>2</sub> phase from the optimal mixture composition. At high temperature, it exists only as the bilayered smectic C<sub>2</sub> phase influenced by

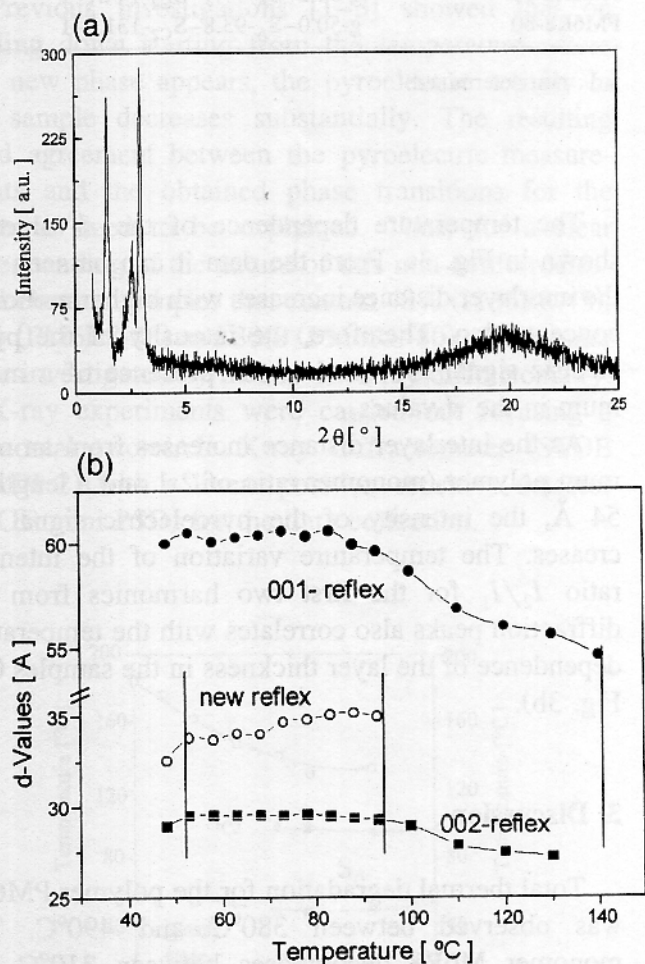


Fig. 4. (a) Diffraction reflexes in the non-pyroelectric phase for PM6R8-80 at 78 °C. (b) Temperature dependence of the interlayer distance for the first (001), second (002) and the new reflex in the mixture PM6R8-80.

the excess of monomer. The effect of this excess is a diminution of the interlayer distance when heating the sample to the isotropic state as shown in Fig. 3a.

The segregation of the monomer in excess of the optimal composition occurs, by cooling, at the phase transition at around 100°C. At lower temperature, the pyroelectric signal decreases due to the appearance of the smectic A phase. In the ideal case, we assume that in the field off state, the macroscopic polarization in the smectic C2 phase is zero. Increasing the field, the bilayers with in-plane polarization opposite to the field reorient in the field direction and a macroscopic polarization appears. For mixtures with higher monomer contents, in the region where the two phases are present, the amount of mixture constructing the SC2 phase behaves as just discussed for the ideal case with 33% of monomer content. The segregated monomer builds a smectic A phase that is

paraelectric and therefore is not influenced by the applied electric field and does not contribute to the observed signal. Then the amount of mixture that forms the ideal ratio of 33% monomer in polymer is responsible for the observed pyroelectric response and the monomer in excess is segregated.

The mechanism involved in the appearance of antiferroelectricity seems to be related to the presence of a herringbone structure frozen by the main chain [1,2]. However, hydrogen bridges through the salicylaldehyde groups present in both, polymer side chains and monomers are so far crucial for the observed high values of the pyroelectric signal [1]. Therefore, the discussion concerning the hydrogen bond formation is of primary importance. Two different models can be postulated. The first one, presented in Fig. 5a, involves inter- and intramolecular hydrogen bridges present in the mesophase.

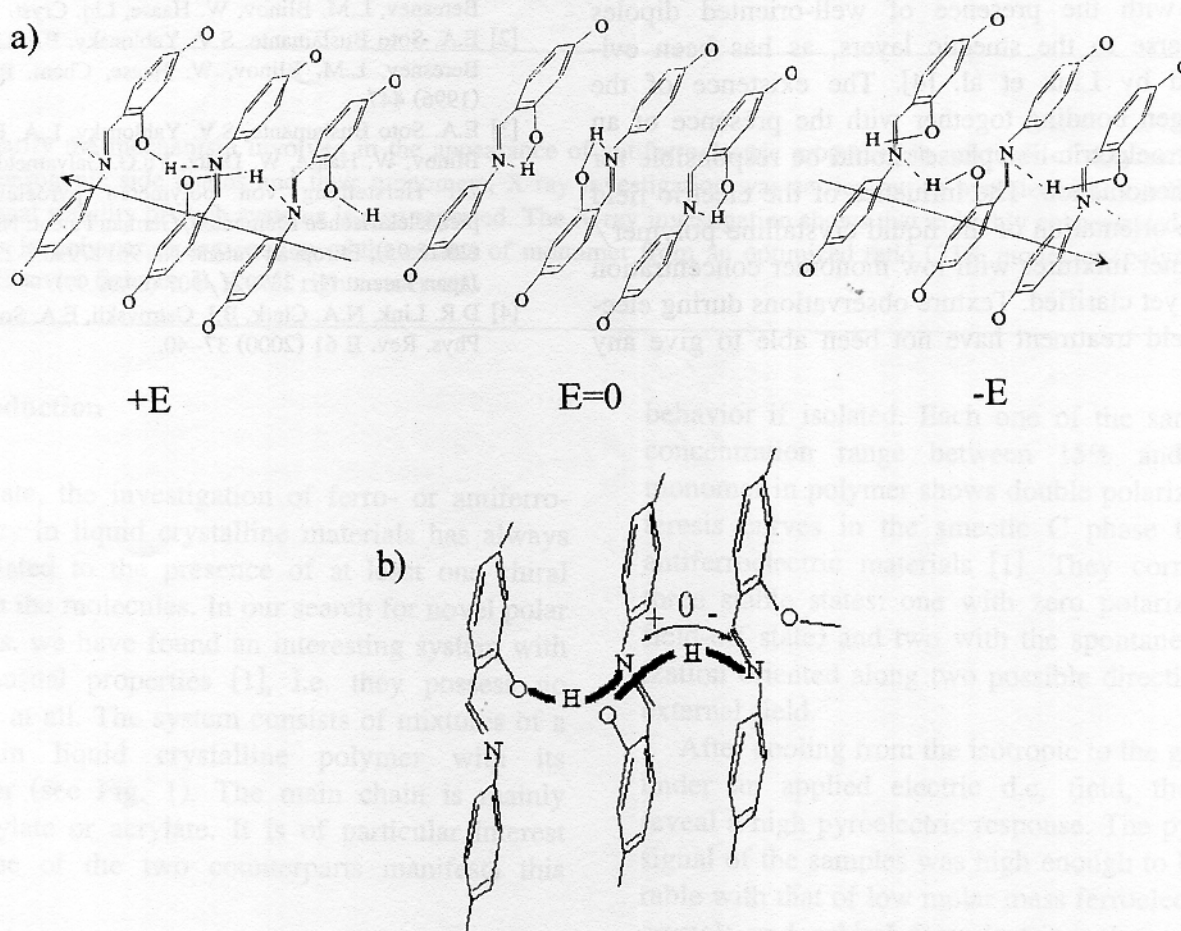


Fig. 5. (a) Proposed model for the observed polarization via reorientation of the hydrogen bridges present in the smectic layers. (b) Proposed model for the observed polarization through fixed intermolecular hydrogen bridges in the presence of an applied electric field (+ and -) and without a Bias field (0).

Another possibility is to assume the presence of a fixed intermolecular hydrogen bonding along the smectic layers, between the side chain mesogens and the monomers. In such a situation, the thermodynamic equilibrium would be defined when each proton is localized between two aromatic cores (see Fig. 5nb). In the absence of an electric field (0), the dipolar moment transversal to the layers has a zero component. When the electric field is applied, the positive charge of the hydrogen has to move to some extent in the direction of the Bias field. This produces a change in the dipolar moment of the mesogens that modifies the macroscopic polarization in the system. The variation in the polarity of the Bias field can produce the movement of the charge from one polar state (+) to the other (–) going through the original equilibrium state (0).

In mixtures with high monomer concentration, the observed macroscopic polarization must be correlated with the presence of well-oriented dipoles transverse to the smectic layers, as has been evidenced by Link et al. [4]. The existence of the hydrogen bonding together with the presence of an antiferroelectric-like phase should be responsible for this phenomenon. The influence of the electric field on the orientation of the liquid crystalline polymer/monomer mixtures with low monomer concentration is not yet clarified. Texture observations during electric field treatment have not been able to give any

evidence. Thus other experimental approaches, such as X-ray investigations in thin cells with and without field application must be considered in the future.

## Acknowledgements

Financial support from the Deutsche Forschungsgemeinschaft is acknowledged. E.A.S.B. and P.A.N.E. gratefully acknowledge financial support from Fundación Andes (Grants C-13222-2, C-13222-7); DID Universidad de Chile; CEPEDQ, Fac. de Cs. Químicas y Farm. U. de Chile, and Instec.

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