

Investigations on New Achiral Polymeric Liquid Crystalline Mixtures using a Pyroelectric Modulation Technique

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In this paper we report on the synthesis and characterization of new mixtures of achiral liquid crystalline side-chain polymers with their monomers. The samples have a basic structure similar to materials prepared earlier showing antiferroelectric behaviour. They are investigated to study the influence of peculiar differences in the molecular structure on their physical behaviour. A laser intensity modulation technique was used to investigate the pyroelectric activity of these compounds.

Keywords: achiral antiferroelectric liquid crystals; side chain liquid crystalline polymer; pyroelectric modulation technique

INTRODUCTION

Ferroelectric polymers have attracted much attention because of the possibility to achieve an electret with a durable polar order of dipolar molecules not at least in view of the potential of such polymers as versatile sensor materials using esp. piezoelectric and pyroelectric

properties. As one of the best known example of this class of materials one may mention polyvinylidene fluoride (PVDF)^[1]. Odd-numbered nylon derivatives and polyurea under special treatment also behave as ferroelectric polymers but with rather small piezo- and pyroelectric coefficients^[2]. Ferroelectric liquid crystalline polymers (FLCP) were realised after the discovery of ferroelectricity in low molar mass chiral tilted lamellar liquid crystals (LCs)^[3], transferring the concept successfully to polymeric LCs^[4]. In these materials the lateral dipole moments of the mesogenic moieties have a partial polar order due to the chirality of the molecules. Until recently, the presence of at least one chiral centre in the mesogenic molecules was considered as a basic requirement to achieve ferroelectricity in LC materials. This assumption was generally dismissed 1996 after the discovery that bilayer structures as present in bent-shaped or banana-shaped molecules make allowance for antiferroelectric properties^[5]. Similar behaviour was reported for dimeric molecules, where two rigid molecules are connected by a flexible hydrocarbon chain^[6]. In contrast to the chiral molecules, these materials establish a longitudinal polarisation.

However, already in 1995 another interesting system was reported, where the observed electrical behaviour was accounted to the formation of polar bilayer structures^[7]. These achiral materials consist of mixtures of 15% to 75% of monomer (M6R8) in the corresponding polymer (PM6R8); the molecular structures are shown in figure 1)^[8]. Pyroelectric measurements on mixtures in this concentration range showed the typical behaviour of antiferroelectric materials^[9].

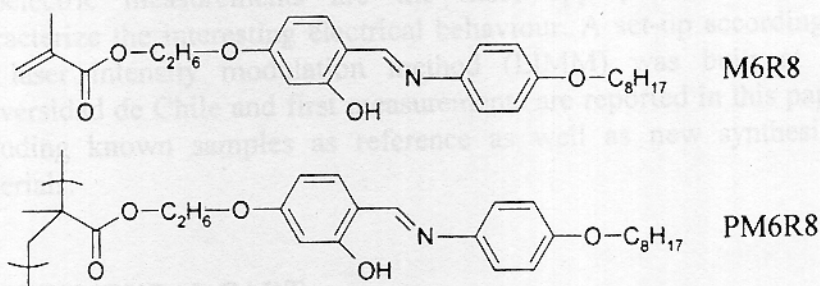


FIGURE 1 Molecular structure of achiral monomer/polymer mixtures with antiferroelectric properties

The mechanism involved in the appearance of antiferroelectricity seems to be related to the presence of a polar herringbone like structure

enabled due to the presence of the main chain. The assumption of the formation of polar bilayer structures with longitudinal polarisation was supported by the observation of related odd-even effects in thin free-standing films of mixtures with high monomer concentration^[10]. On the other hand some peculiarities of the chemical structure of the materials are important as well: Both polymer and monomer are chemically characterised by the presence of a salicylaldehyde group that obviously place a crucial role for the electrical properties (maybe due to the possibility of the formation of hydrogen bridges); materials without that group don't show antiferroelectric behaviour.

The antiferroelectric polymer/monomer mixtures are interesting materials not only from a fundamental point of view but also in respect to possible applications. Investigations on corona charged thin mesogenic films in the glassy state^[11] showed pyroelectric and piezoelectric coefficients as large as $\gamma = 3.3 \text{ nC/cm}^2\text{K}$ and $d_{33} \approx 9 \text{ pC/N}$, respectively, comparable to those observed in PVDF, and even higher.

To achieve a comprehensive understanding of the mechanism, which allows for the antiferroelectric behaviour, and especially of the influence of structural peculiarities one has to synthesize a large number of materials with more or less modified chemical structure and study their basic properties. In this paper we present the synthesis of new samples having alkyl chains (PM6R8n and PM6R14n) instead of oxyalkyl chains in their structure and compare their properties with the already studied samples PM6R8/M6R8. Since the relaxation time for the repolarisation process of the materials is typically about 10 s, pyroelectric measurements are the most appropriate method to characterize the interesting electrical behaviour. A set-up according to the laser intensity modulation method (LIMM) was built at the Universidad de Chile and first measurements are reported in this paper, including known samples as reference as well as new synthesized materials.

EXPERIMENTAL PART

Synthesis of the Materials

Commercial reactants such as p-octylaniline and p-tetradecylaniline as available from Aldrich were not submitted to further purification. Other reactants are available from Merck Co. The preparations of the samples

were carried out using a convergent synthetic pathway already described for M6R8 and PM6R8 in previous papers ^[12,13]. The synthesis of M6R8n, M6R14n and their corresponding polymers can be summarized as follows:

The resorcinic ester **1** can be condensed with the anilines **2** that posses aliphatic tails in para position thus allowing lateral chain length control (see figure 2). The condensation is carried out in refluxing ethanol in presence of hydroquinone. The monomers **3** just prepared are submitted to radical polymerisation over 24 hours at 60 °C using azo-isobutyronitrile (AIBN) as initiator and in a nitrogen atmosphere. The polymers are purified by precipitation with methanol from toluenic solution.

Preparation of the aldehyde **1** can be faced as follows: methacrylic acid is converted to their corresponding acid chloride by treating the acid with thionyl chloride or phosphorous trichloride. Then the methacryloyl chloride is esterified with 6-chloro-hexanol. The chlorine atom of the just prepared compound is exchanged with iodine using the Finkelstein reaction in order to increase the reactivity towards nucleophilic substitution by the 2-hydroxybenzaldehyde-4-phenoxy ion in a Williamson type reaction. The etherification takes place at 100 °C during 24 hours using dimethylethylurea (DMEU) as solvent and sodium bicarbonate as base. For a detailed description of the synthesis of aldehyde **1** see ^[13].

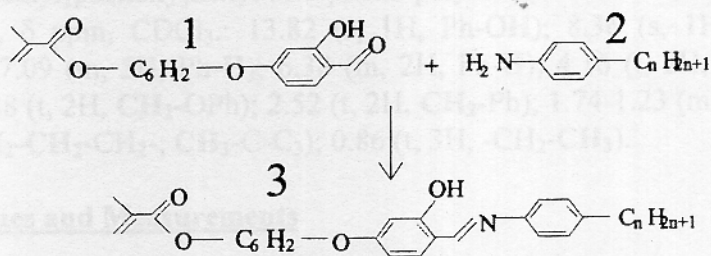


FIGURE 2 Synthesis of monomers M6R8n and M6R14.

2-methyl-2-propenoic acid-6-[3-hydroxy-4-[[[4-octyl]phenyl]imino]-methyl]phenoxy]hexyl ester (**M6R8n**)

¹H-NMR (CDCl₃) δ ppm: 13.94 (s, 1H, Arom.-OH); 8.48 (s, 1H, CH=N); 7.25 (m, 3H, Arom.-CH=N; Arom.-OC₈H₁₇); 6.52 (d, 2H, Arom.-OC₈H₁₇); 6.46 (m, 2H, Arom.-CH=N); 6.15 (s, 1H, trans

$\text{H}_2\text{C}=\text{C}$); 5.55 (s, 1H, *cis* $\text{H}_2\text{C}=\text{C}$); 4.28 (t, 2H, $\text{CO}_2\text{-CH}_2$); 4.05 (t, 2H, $\text{CH}_2\text{-O}$); 2.60 (t, 2H, Arom.- CH_2); 1.99 (s, 3H, $\text{H}_2\text{C}=\text{C-CH}_3$); 1.30-1.75 (m, 20H, $-\text{CH}_2-$); 0.89 (t, 3H, $-\text{CH}_2\text{-CH}_3$). $J_0 \phi\text{-OC}_8\text{H}_{17}$: 8.9 Hz

2-methyl-2-propenoic acid-6-[3-hydroxy-4-[[[4-octyl]phenyl]imino]-methyl]phenoxy]hexyl ester, homopolymer (**PM6R8n**)

$^1\text{H-NMR}$ (CDCl_3) δ ppm: 13.94 (s, 1H, Arom.- OH); 8.48 (s, 1H, $\text{CH}=\text{N}$); 7.25 (m, 3H, Arom.- $\text{CH}=\text{N}$; Arom.- OC_8H_{17}); 6.52 (d, 2H, Arom.- OC_8H_{17}); 6.46 (m, 2H, Arom.- $\text{CH}=\text{N}$); 6.15 (s, 1H, *trans* $\text{H}_2\text{C}=\text{C}$); 5.55 (s, 1H, *cis* $\text{H}_2\text{C}=\text{C}$); 4.28 (t, 2H, $\text{CO}_2\text{-CH}_2$); 4.05 (t, 2H, $\text{CH}_2\text{-O}$); 2.60 (t, 2H, Arom.- CH_2); 1.99 (s, 3H, $\text{H}_2\text{C}=\text{C-CH}_3$); 1.30-1.75 (m, 20H, $-\text{CH}_2-$); 0.89 (t, 3H, $-\text{CH}_2\text{-CH}_3$). $J_0 \phi\text{-OC}_8\text{H}_{17}$: 8.9 Hz

2-methyl-2-propenoic acid -6-[3-hydroxy-4-[[[4-tetradecyl]phenyl]imino]-methyl]phenoxy]hexyl ester (**M6R14n**)

$^1\text{H-NMR}$, δ ppm, CDCl_3 .: 13.92 (s, 1H, Ph- OH); 8.52 (s, 1H, Ph- $\text{CH}=\text{N}$); 7.22 (m, 5H, Ph- H); 6.48 (m, 2H, Ph- H); 6.10 (m, 1H, *trans* $\text{H-C}=\text{C-CH}_3$); 5.55 (m, 1H, *cis* $\text{H-C}=\text{C-CH}_3$); 4.16 (t, 2H, $\text{CH}_2\text{-O}_2\text{C}$); 4.00 (t, 2H, $\text{CH}_2\text{-OPh}$); 2.62 (t, 2H, $\text{CH}_2\text{-Ph}$); 1.95 (s, 3H, $\text{CH}_3\text{-C}=\text{C}$); 1.82-1.26 (m, 32H, $-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2-$); 0.88 (t, 3H, $-\text{CH}_2\text{-CH}_3$). J_0 : 6.6 Hz.

2-methyl-2-propenoic acid -6-[3-hydroxy-4-[[[4-tetradecyl]phenyl]imino]-methyl]phenoxy]hexyl ester, homopolymer (**PM6R14n**)

$^1\text{H-NMR}$, δ ppm, CDCl_3 .: 13.82 (s, 1H, Ph- OH); 8.36 (s, 1H, Ph- $\text{CH}=\text{N}$); 7.09 (m, 5H, Ph- H); 6.38 (m, 2H, Ph- H); 4.16 (t, 2H, $\text{CH}_2\text{-O}_2\text{C}$); 3.88 (t, 2H, $\text{CH}_2\text{-OPh}$); 2.52 (t, 2H, $\text{CH}_2\text{-Ph}$); 1.74-1.23 (m, 35H, $-\text{CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2-$; $\text{CH}_3\text{-C-C}_3$); 0.86 (t, 3H, $-\text{CH}_2\text{-CH}_3$).

Techniques and Measurements

Pyroelectric modulation technique

To measure the pyroelectric signal coming from the samples, the set-up as drafted in figure 3 was used. The samples were confined in commercial available liquid crystal cells (1, EHC) of 11.5 μm thickness at the isotropic phase by capillary force. The cells were placed inside a temperature controlled microscope heat stage (2, Instec MK1) controlled by a personal computer (4), allowing temperature scans at rates from 0.1 K/min up to 20 K/min in a temperature range from 0 $^\circ\text{C}$

until 200 °C. To achieve low temperatures, a temperature regulated external cooling system (3, Haake DC1-K15) was used to circulate a mixture of ethanol-water 2:1 at -15 ° C through the cooling jacket of the oven.

Temperature variation in the sample were obtained using modulated light from a semiconductor laser (5, $\lambda = 690\text{nm}$, $P = 27\text{ mW}$). The modulation frequency of 70 Hz was provided from the built-in generator of the lock-in amplifier (7, EG&G Model 5460). The pyroelectric response from poled samples was measured in the voltage mode of the lock-in amplifier. To make the poling process a DC voltage supply (9) was used. The pyroelectric signals were recorded with a second personal computer (8) which is connected to the lock-in amplifier and further processed by appropriate software. Due to two-channel technique the lock-in amplifier measures both the modulus of the pyroelectric response (usually in the millivolt range) and the phase in respect to the modulated laser light.

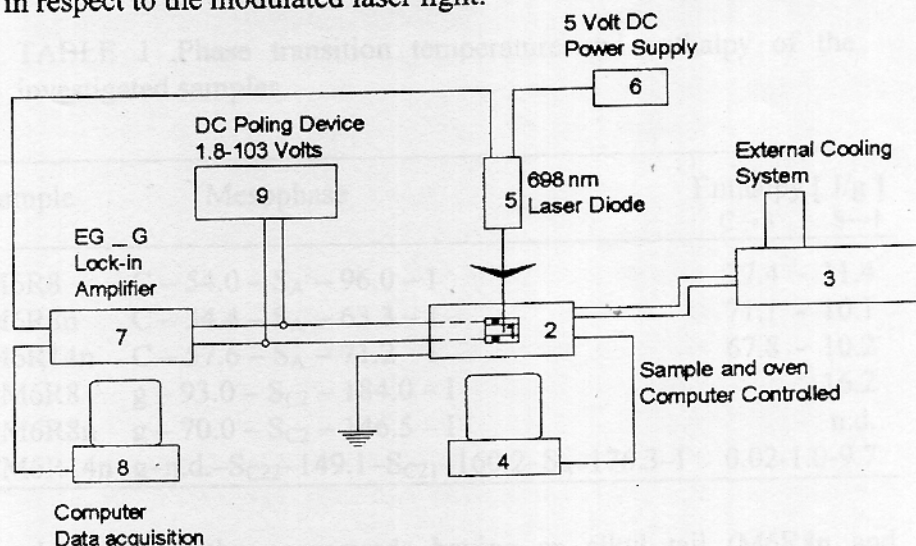


FIGURE 3 Pyroelectric modulation technique set-up.

Other methods

The phase transition temperatures for the investigated samples were determined using a differential scanning calorimeter (Perkin Elmer DSC-7). Mesomorphic textures were studied using a polarizing microscope (Leitz Orthoplan Pol) equipped with a hot stage (Mettler FP82) for the temperature control and a SVHS video recording system,

which allowed us to confirm the DSC data. X-ray experiments were carried out using a horizontal two-circle X-ray diffractometer (STOE STADI 2) with a linear position sensitive detector (STOE mini PSD) for the data collection.

RESULTS AND DISCUSSION

Structure Characterisation

Table 1 resumes the data obtained from DSC measurements for the investigated samples. All monomers and polymers show the existence of non-oriented lamellar phases. The X-ray characterization of PM6R8 and M6R8 has been already reported^[14]. A more detailed description of the structural characterisation for the other samples will be presented in a separate publication^[15].

TABLE 1 Phase transition temperature and enthalpy of the investigated samples.

Sample	Mesophase	Enthalpy [J/g]	
		C→S	S→I
M6R8	C - 54.0 - S _A - 96.0 - I	77.4	11.4
M6R8n	C - 34.4 - S _A - 63.3 - I	71.1	10.1
M6R14n	C - 57.6 - S _A - 71.2 - I	67.8	10.2
PM6R8	g - 93.0 - S _{C2} - 184.0 - I		16.2
PM6R8n	g - 70.0 - S _{C2} - 146.5 - I		n.d.
PM6R14n	g - n.d. - S _{C22} - 149.1 - S _{C21} - 160.2 - S _A - 176.3 - I	0.02-1.0-9.7	

In the case of the compounds having an alkyl tail (M6R8n and M6R14n) there is a decrease in the phase transition temperatures as compared with the alkoxy tailed compound (M6R8). The occurrence of the same kind of mesophases is observed in both cases, i.e. a smectic A phase for the monomers and a bilayered smectic C phase for the polymers. M6R8n shows a fan shaped texture typical for a smectic A phase. The existence of this phase was also confirmed by X-ray diffractometry. M6R14n shows on cooling at the transition from the liquid crystalline state to the solid state a DSC signal that is split into four different peaks. The temperature range for this splitting was 2.5 K

at around 44 °C. By polarising microscopy one observes at this temperature a phase transition from a smectic A to a smectic C phase.

For PM6R8n a nonlinear temperature dependence of the interlayer spacing d of the first order reflex at small angles in the mesophase and in the glassy state was observed. From these data one can postulated the existence of a tilted lamellar structure. For PM6R14n the temperature dependence of the interlayer spacing d of the first order reflex at small angles in the mesophase and in the glassy state is rather untypical, showing the existence of three different mesophases also confirmed by DSC analysis: a smectic A phase at high temperature and two similar smectic C2 phases on cooling^[15]. The behaviour may be attributed to the long chain tails that allows for the occurrence of the observed polymorphism.

Pyroelectric Measurements

Pyroelectric measurements were performed on previously poled samples. The poling was done applying a voltage of 103 V (i.e. $\approx 10\text{V}/\mu\text{m}$) to the sample cells during cooling the samples from the isotropic phase to room temperature. Samples from mixtures of 33% of monomer in their corresponding polymer - as proven to be the optimized mixture in earlier papers - were prepared for the measurements, denoted as PM6R8n-33 and PM6R14n-33 for mixtures PM6R8n/M6R8n and PM6R14n/M6R14n, respectively. PM6R8-33 (33% of M6R8 in PM6R8) was used as a comparative standard to calculate the pyroelectric coefficient γ for the new measurements. These values were obtained earlier using a pulse pyroelectric technique^[8,9]. The measured temperature dependence of the pyroelectric signals for the studied samples are shown in figure 4.

All the investigated mixtures show a remarkable high pyroelectric response in the glassy state as well as in the liquid crystalline phase. For PM6R8n-33, the pyroelectric signal is only half as high as in PM6R8-33. Also the temperature where the pyroelectric signal vanishes is significantly shifted to lower temperatures compared with PM6R8-33. The latter is in accordance with the observed phase behaviour where the absence of oxygen decreases strongly the phase transition temperatures (see table 1). Both, different phase and pyroelectric behaviour, may be attributed to the difference in length and flexibility of the terminal chain as well as in their polarity.

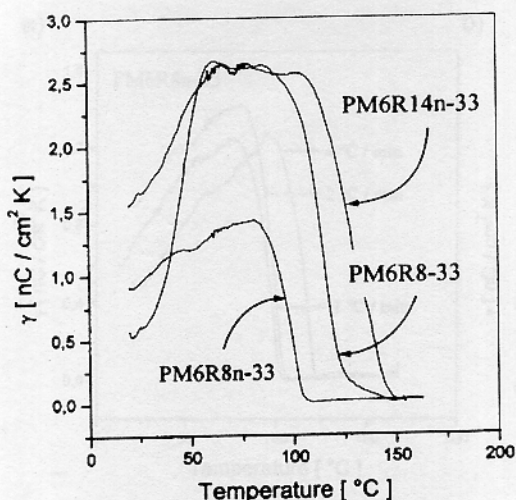


FIGURE 4
Pyroelectric response of
the samples PM6R8n-
33, PM6R14n-33
compared with PM6R8-
33 as standard.

The pyroelectric response of PM6R14n-33 is comparable with our standard mixture PM6R8-33. However, in case of PM6R14n-33 the ratio between the signal maximum and the initial signal in the glassy state is much higher, which may be due the occurrence of a higher order liquid crystalline phase in the polymer. The pyroelectric signal is - in contrast to what one may expect comparing the phase behaviour of PM6R8/M6R8 and PM6R14n/M6R14n - observable even at higher temperatures than in the case of PM6R8-33. However, this is - at least partially - a consequence of the dynamic behaviour of the system, which is not in thermal equilibrium during the measurements in a heating process.

This can be demonstrated considering the heating rate dependence of the pyroelectric response as depicted in figure 5. In case of PM6R8n-33 the lowest used heating rates of 1 and 2 K/min are close to equilibrium, whereas in case of PM6R14n-33 the curves are significantly different with a trend to decrease the temperature where the pyroelectric signal vanishes with lower heating rates.

At this point it is necessary to be rigorous and to have in mind that the antiferroelectric behaviour of the samples PM6R8n-33 and PM6R14n-33 has not yet been demonstrated. This is due to the lack of information about the corresponding voltage signal dependence of the pyroelectric effect (i.e. the antiferroelectric hysteresis loop), which couldn't be measured due to experimental difficulties. However, comparing the pyroelectric behaviour and especially its magnitude with PM6R8-33, it is possible to expect the same behaviour in these samples.

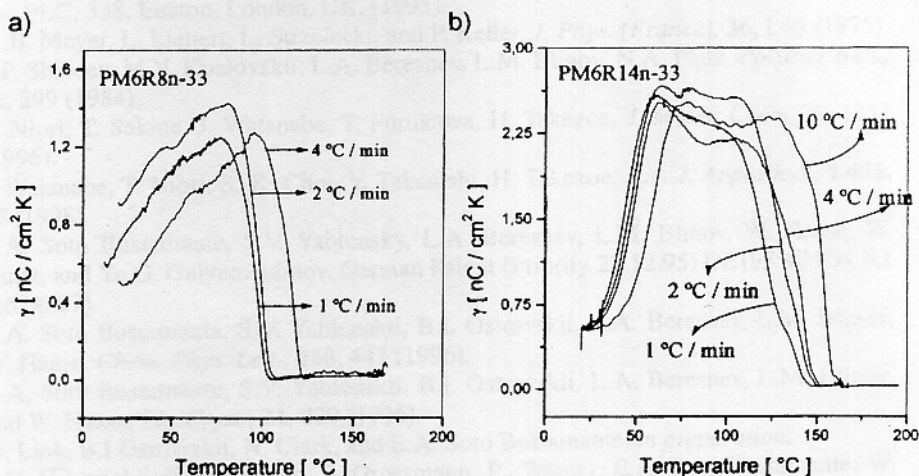


FIGURE 5 Heating rate dependence of the pyroelectric response of the samples PM6R8n-33 (a) and PM6R14n-33 (b).

CONCLUSION

A pyroelectric modulation technique has been implemented and was applied for the characterization of samples consisting of mixtures of achiral side chain liquid crystalline polymers with the corresponding monomer. Two derivatives of the previously investigated antiferroelectric system PM6R8/M6R8, with alkyl terminal chains instead of an alkoxy group were synthesized and their phase behaviour was characterized. Both systems showed interesting pyroelectric behaviour with signals in the same order of magnitude as PM6R8/M6R8. The heating rate dependence of the pyroelectric response demonstrated the kinetics of the behaviour. Good data reproducibility for the pyroelectric curves may be obtained for heating rate values of 1 K/min or less.

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