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On the way to polar achiral liquid crystals

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A brief review is presented of theoretical predictions and experimental observations concerning polar (pyroelectric, ferroelectric and antiferroelectric) achiral mesomorphic phases.

1. Introduction

Among the 32 crystallographic classes there are 10 that are polar. Polar crystals have at least one polar axis along which the spontaneous polarization, $\mathbf{P}_s$ [in $\mathrm{C\,m^{-2}}$ units] (a net dipole moment of a unit volume) arises. Polar crystals manifest pyroelectric properties, a linear electro-optical effect and optical second harmonic generation. Within a variety of polar crystals a narrower group of ferroelectrics exists in which the direction of the spontaneous polarization may be switched by an external electric field. Certain crystals may consist of two polar sublattices each possessing a finite polarization with opposite directions, $+P_1$ and $-P_2$. The spontaneous polarization of such a polar crystal is $\mathbf{P}_s = P_1 - P_2$. If an external electric field may reorient the polarization of one of the two sublattices, the field induced polarization is $\mathbf{P}_i = \pm(P_1 + P_2)$ and the crystal is a ferrielectric. In the particular case of $P_1 = -P_2 = P$, $\mathbf{P}_s = 0$, $\mathbf{P}_i = 2P$ and we deal with an antiferroelectric. Ferro-, ferri- and antiferro-electrics are of great interest for applications in electronics and optoelectronics (materials for capacitors, piezo-transducers, light modulators, light frequency converters, etc.) [1]. Even non-switchable polar crystals may be useful in piezoelectric and non-linear optical devices.

According to their symmetry all polar crystalline and mesomorphic phases are divided into two groups [2]. One of them comprises mirror-symmetric (achiral) phases with point symmetry groups from C_{2v} to $C_{\infty v}$. The other is composed of chiral molecules and has a point group symmetry ranging from C_1 to C_∞.

Since the beginning of this century achiral *crystalline* ferro-, ferri- 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 $\mathbf{P}_s$ is a secondary order parameter. Among proper ferroelectrics there have been found organic crystals (e.g. triglycine sulphate and thiourea) and crystalline polymers such as polyvinylidene fluoride (PVDF) and its copolymers [3]. The latter may be prepared in the form of ultrathin switchable Langmuir–Blodgett films [4]. It is worth noting that mesogenic compounds form polar crystals very rarely. One of the few examples is a crystal of 4-butyloxy-4′ cyanobiphenyl whose polar structure is well established by the X-ray technique [5]. This substance has a monotropic nematic phase and, on slow cooling from that phase, crystallizes in another solid modification which manifests ferroelectric switching [6]. A strongly polar crystalline state was also observed recently in a polyphilic compound (see below) by the second harmonic generation (SHG) technique [7].

On the other hand, chiral tilted mesophases (C*, F*, I*, etc.), including the polymeric phases, manifest both ferroelectric [8, 9] and antiferroelectric [10, 11] properties. The mechanism of ferroelectricity in these systems is quite specific: a tilt of the elongated chiral molecules, which is the order parameter of a tilted phase, results in a polar ordering of their short axes (and transverse dipole moments) perpendicular to the tilt plane. The $\mathbf{P}_s$ vector lies in the plane of the smectic layer perpendicularly to the tilt plane. Such materials also belong to 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. Below we shall review what has been done in this area up to now.

2. Theoretical approaches

In crystals (i.e. ionic), ferroelectricity arises as a result of the so-called polarization catastrophy when the ‘reduced’ sum of the electronic and ionic polarizabilities of an ion exceeds a certain value [12]. In a system consisting of molecules with dipole moments μ, a proper

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ferroelectric phase may form if, roughly speaking, the energy of the dipole–dipole interaction exceeds the thermal energy [13]:

$$\frac{\mu^2}{V_m} > kT . \qquad (1)$$

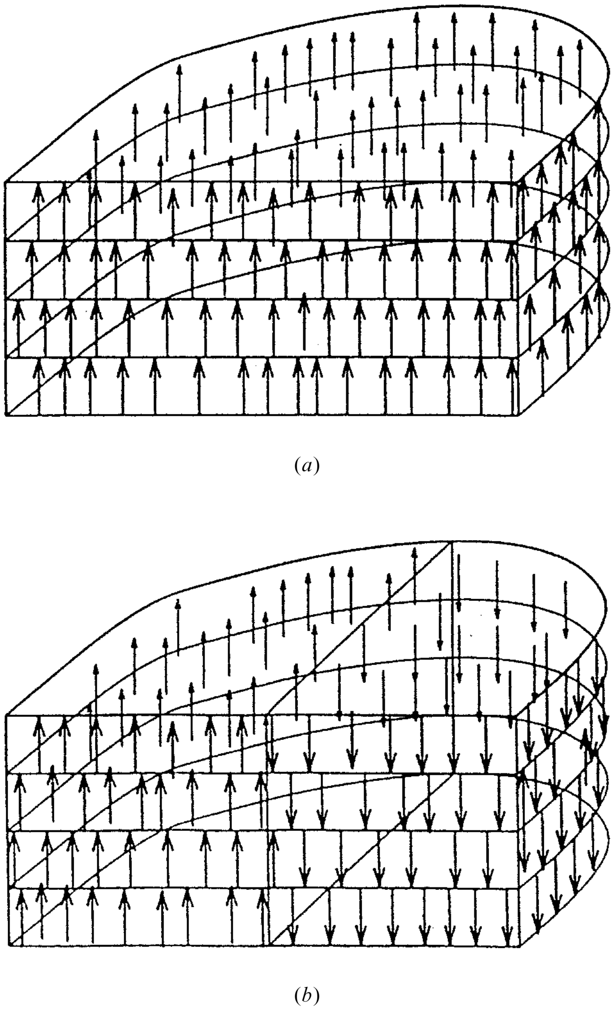
Here, V_m is the molecular volume and k is the Boltzmann constant. According to estimate (1), mesogenic molecules with typical dimensions $20 \times 5 \times 5 = 500\,\text{Å}^3$ should form a ferroelectric phase at room temperature if their dipole moments exceed a critical value $\mu_c = 5$ Debye, which is quite realistic a figure.

A precise criterion, however, depends on molecular shape and the role of other interactions (Van der Waals, steric, multipole electrical interactions, etc.). Model calculations are usually based on the assumption that a certain non-polar mesophase (nematic, smectic) already exists due to these other forces and the role of the dipole–dipole interactions in the formation of a polar state is investigated.

2.1. *Polar smectics*

Smectic phases were the first to be studied theoretically as candidates for achiral ferroelectrics. Prost and Barois [14] developed the Landau theory for a smectic A with two order parameters, one of which is the amplitude of the electron density wave and the other is the amplitude of the electric polarization wave; both wave vectors are in the direction of the smectic layer normal. The phase of the polarization wave may have discontinuities where a net electric charge forms (soliton-like defects). In such a defect system the macroscopic polarization may arise at the interfaces perpendicular to the normal to the smectic layers. Thus, for the first time, a 'longitudinal' proper mesomorphic ferroelectric was predicted.

Another approach was suggested by Petschek and Wiefling [15]. They considered polymer-like molecules consisting of a, b and c monomers which formed polar smectic layers of abc type. The overall multilayered structure is allowed to be ferroelectric abc.abc.abc.abc … or antiferroelectric abc.cba.abc.cba …. Monte Carlo computer simulations have been done for molecules of the type ababa where a and b are flexible and rigid molecular fragments [16]. For a certain critical value of μ, a phase transition (on cooling) from a non-polar smectic A to a polar smectic A_p has been predicted. Later, in their attempts to explain experiments with polyphilic compounds [17], Prost *et al.* [18] have presented a theoretical model that predicted a uniaxial ferroelectric $Sm(A_F)$ phase with lateral mesoscopic domains and quite unusual physical properties. Such a phase is shown schematically in figure 1 together with a uniform polar smectic A having $C_{\infty v}$ or $\infty\, mm$ point symmetry. The macroscopic polarization of such a phase


(*a*)

(*b*)

Figure 1. A uniform polar smectic A phase (*a*) and a uniaxial ferroelectric $Sm(A_F)$ phase (*b*) with lateral mesoscopic domains (stripe phase [18]).

is considerably less than the polarization of a single domain. It is of interest that a similar stripe domain 'antiphase' has been found by Monte Carlo simulations in a system of elongated ellipsoids with axial dipole moments shifted from the centres of the ellipsoids to their ends [19].

In the tilted smectic C phase of an achiral substance, the $\mathbf{P}_s$ vector must lie in the tilt plane. It might be at a certain angle to the layer planes [17] or lie in the layer plane as was discussed theoretically by Brand and co-workers [20, 21].

2.2. *Polar nematics*

A possibility of formation of a polar nematic phase from asymmetric molecules with steric dipoles follows from computer simulation [22]. A particular molecular form was not specified, but the interaction potential included a polar term. If the molecules are assumed to possess longitudinal dipole moments, the phase should be ferroelectric [22]. For dipolar molecules with spherical shape (both 'soft' [23] and 'hard' [24] spheres in terms of the interaction potential chosen) a polar nematic phase has been predicted for a certain dipolar strength. For hard spheres with diameter D, e.g. at

$$\mu^* = \left(\frac{\mu^2}{D^3 kT} \right)^{1/2} = 3 \qquad (2)$$

the polar nematic phase arises with quadrupolar and polar order parameters equal to $S=0{\cdot}65$ and $P=0{\cdot}85$, respectively [24]. No polar phase has been found for elongated spherocylinders with logitudinal dipoles, but a polar state is possible for spherocylinders with transverse dipoles [25].

The problem was also discussed from the standpoint of phase transition theory and the result was different. A numerical analysis has been carried out by Lee and Lee [26] for a system of hard dipolar spherocylinders (length L, diameter D, dipole moment μ). A hard core repulsion and dipolar interaction were taken into account. A phase diagram including the isotropic, non-polar nematic ($D_{\infty h}$ point symmetry) and polar nematic phases ($C_{\infty v}$ symmetry; figure 2) has been predicted. Figure 3 shows an appearance of the polar order parameter P_1 as a function of the dipolar strength of the form (2) with parameter L^2D instead of D^3. With increasing μ at fixed temperature, the polar nematic phase arises when μ^* reaches a critical value of 0·33. The nematic order parameter P_2 slightly increases with dipolar strength near the non-polar nematic–polar nematic transition (figure 3).

In solid ferroelectrics, a uniformly polarized state is unstable and the ferroelectric is usually broken into domains. The polar nematic phase is also unstable and, in order to reduce the electrostatic energy it acquires a helical structure [27]—i.e. a polar nematic that is, in fact, a cholesteric [figure 2(*c*)]. The pitch of such a cholesteric depends on the spontaneous polarization $\mathbf{P}_s$ and the geometrical shape of the sample:

$$h = 2\pi \left(\frac{4K_{22}}{\mathbf{P}_s^2} \right)^{1/3} R^{1/3}. \qquad (3)$$

Here K_{22} is the twist elastic modulus and R is the radius of a cylindrical sample with the cylindrical axis coinciding with the initial director.

2.3. *Polar discotics*

Lin [28] suggested the formation of polar columns from bowl-like molecules with dipole moments directed as shown in figure 4(*a*). Such columns may form either ferroelectric or antiferroelectric phases [figure 4(*b*) and (*c*)]. Quantitatively the problem has been considered analytically and by computer simulation. From a mean field model Palffy–Muhoray *et al.* predicted the formation of a polar nematic phase by oblate (disc-like) molecules [29]. Weis *et al.* [24], by Monte Carlo simulations of a system consisting of cut spheres, showed a transition from non-polar columns to polar columns with neighbouring columns packed antiparallel to each other (antiferroelectric structure). Generally speaking, a disc-like shape is preferable for formation of polar phases to a calamitic shape, if, in both cases, the molecular dipole moments are parallel to the rotation axis.

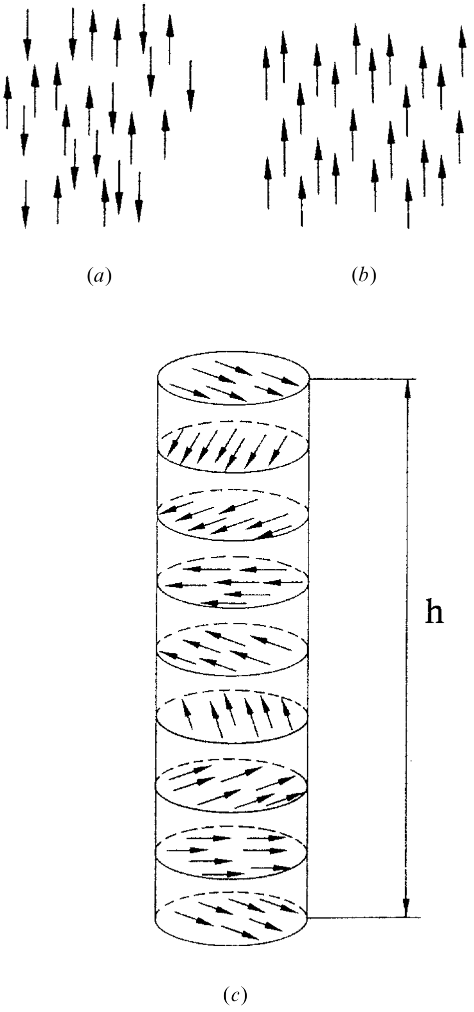


Figure 2. Conventional non-polar nematic (*a*), polar nematic (*b*) and polar cholesteric (*c*).

3. Experimental observations

Few recent experiments seem to be in accordance with theoretical predictions. Below we shall briefly discuss the main structural features and physical properties of achiral polar mesophases.

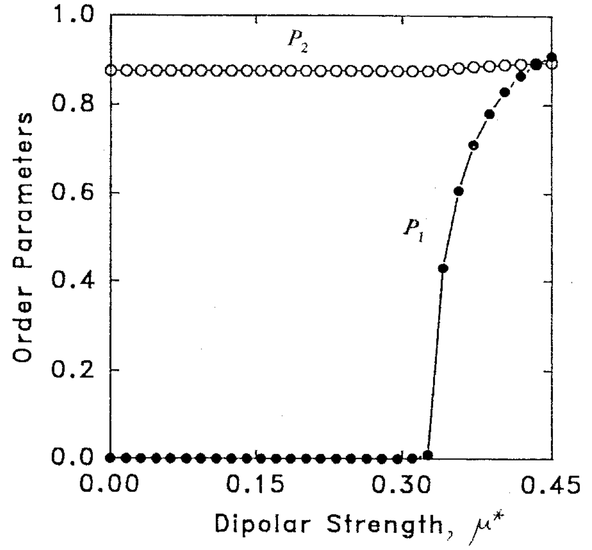


Figure 3. The polar P_1 and quadrupolar (orientational) P_2 order parameters of the nematic phase as a function of dipolar strength μ^* [26].

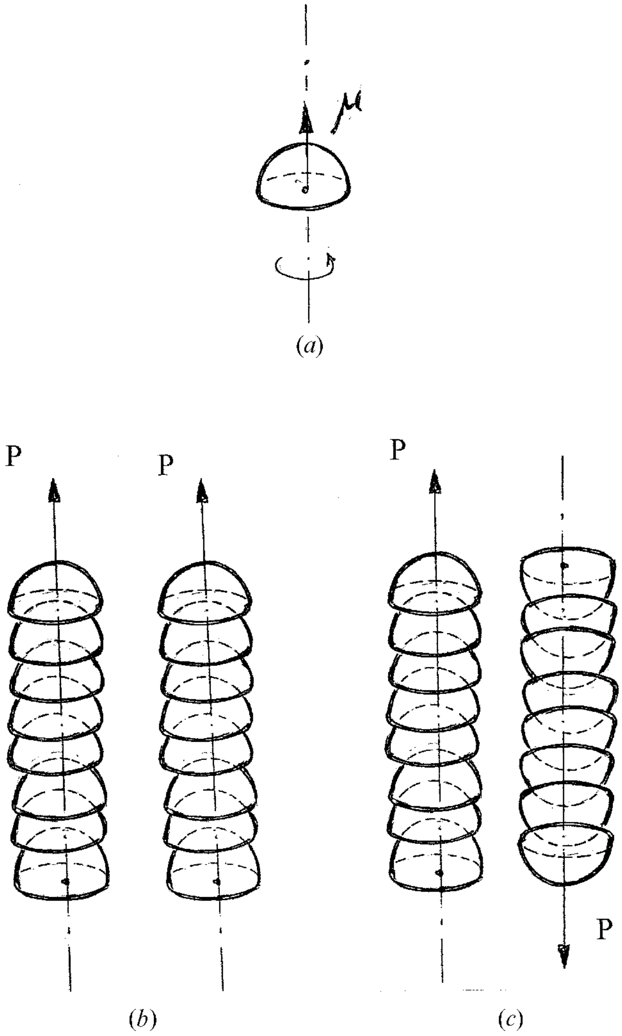
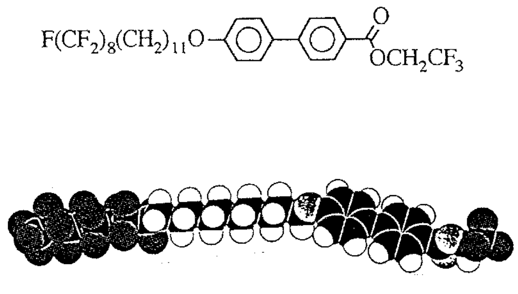


Figure 4. A bowl-like molecule (*a*), a ferroelectric (*b*) and an antiferroelectric (*c*) ordering of polar columns.



$F(CF_2)_8(CH_2)_{11}O-C_6H_4-C_6H_4-C(=O)OCH_2CF_3$

Figure 5. Polyphilic compound PC1; chemical formula and a computer model.

3.1. *Highly ordered polar smectic formed by polyphilic compounds*

For the first time, weak ferroelectric properties have been observed in an achiral lamellar mesophase formed by a polyphilic compound PC1 [17]. A chemical approach to construct new polar materials has been suggested by Tournilhac *et al.* [30]. The basic idea was to use a so-called polyphilic effect to form the 'building elements' of a polar phase. According to this concept, chemically different moieties of a molecule tend to segregate to form polar aggregates, lamellae or smectic layers; the latter can form a polar phase as was discussed in [15, 16].

Compound PC1 is made up of three distinct parts: perfluoroalkyl and alkyl side chains and a biphenyl rigid core (figure 5). X-ray structure investigations of PC1 showed the following phase sequences: on heating—crystal 98°C smectic A 115°C isotropic; on cooling—isotropic 115°C smectic A 82°C smectic X. The latter was stable down to room temperature, but crystallized on the next heating cycle. Ferroelectricity of the X phase was demonstrated by measurements of the pyroelectric effect and hysteresis in the acoustically induced piezoelectric response [17, 31]. Figure 6 shows the pyroelectric voltage and the field induced polarization of PC1 as functions of temperature. The pyro-effect is observed only in the X and crystalline phases. The X phase manifests rather a small $\mathbf{P}_S$ value, of the order of $4\,\mathrm{nC\,cm^{-2}}$; the latter is consistent with its strongly disordered structure [32]. The phase consists of mesoscopic domains, as shown in figure 7 and discussed theoretically in [18]. High spontaneous polarization does exist within each of those domains, but almost averages out for a macroscopic sample. The same is true for the second harmonic intensity: it is strong in monocrystalline areas in the crystal phase, but dramatically reduces in the smectic X phase [7].

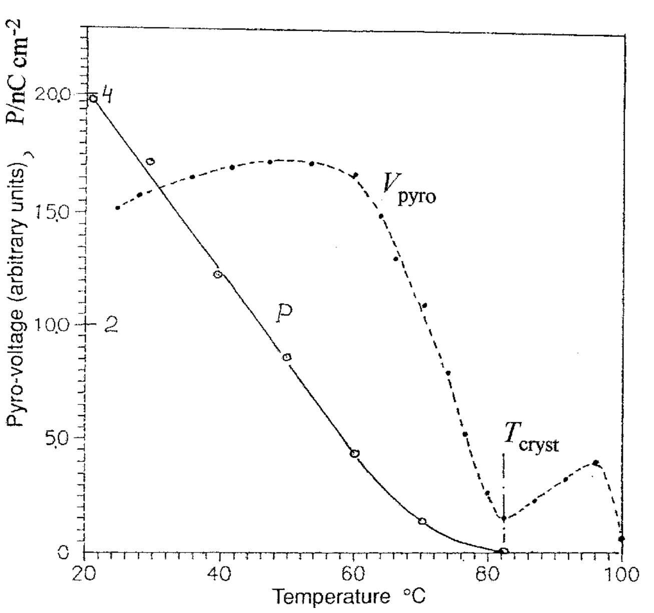


Figure 6. Pyroelectric voltage (full points) and the field induced polarization (open circles) of PC1 as functions of temperature (poling d.c. voltage +30 V, cell thickness 11 mm).

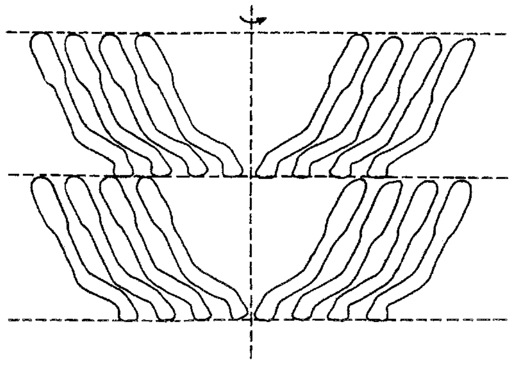
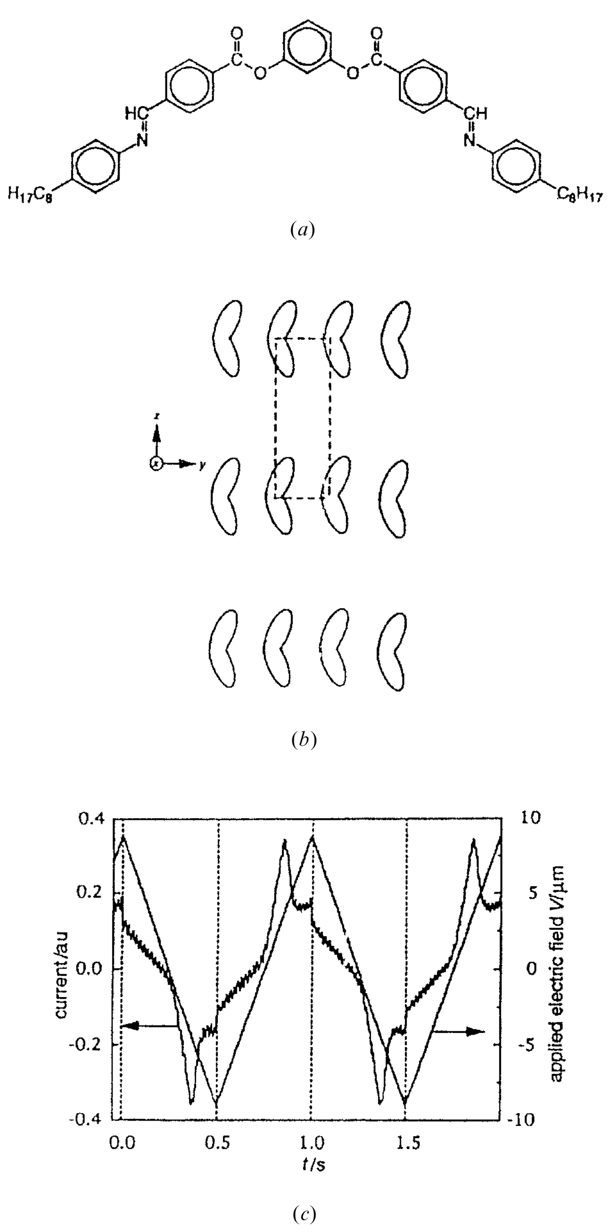


Figure 7. Polar structure with azimuthal disorder formed by polyphilic molecules.



(a)

(b)

(c)

Figure 8. Banana-shaped molecule B8 (a), a possible structure of a biaxial smectic A (b) and repolarization current oscillograms (c) [33].

3.2. *Biaxial smectic A formed by banana-shape molecules*

Niori *et al.* [33] have synthesized an achiral mesogenic compound B8 whose molecules are banana-like [figure 8 (*a*)]. On heating, the compound shows the following phases: crystal −97·7°C–S_2–156·4°C–S_1–161·4°C–isotropic. The most interesting is the S_1 phase: the X-ray diffraction study and optical observations show that it is a biaxial smectic A phase (symmetry C_{2v}), with a structure shown schematically in figure 8 (*b*). In the figure the smectic layer normal coincides with the z-axis; the spontaneous polarization is allowed along the y-axis. An external electric field may switch the direction of the banana dipoles (i.e. $\mathbf{P}_s$) from, say, $-y$ to $+y$, and the repolarization current can be measured by a conventional technique using a triangular wave voltage [figure 8 (*c*)]. The $\mathbf{P}_s$ value estimated is fairly high, 50 nC cm^{-2}. The polar nature of the S_1 phase is also confirmed by dielectric permittivity measurements.

3.3. *Antiferroelectric smectics C formed by achiral polymer–monomer mixtures*

The first example of the antiferroelectric behaviour of mesomorphic mixtures composed of an achiral side group polymer and its monomer was demonstrated by

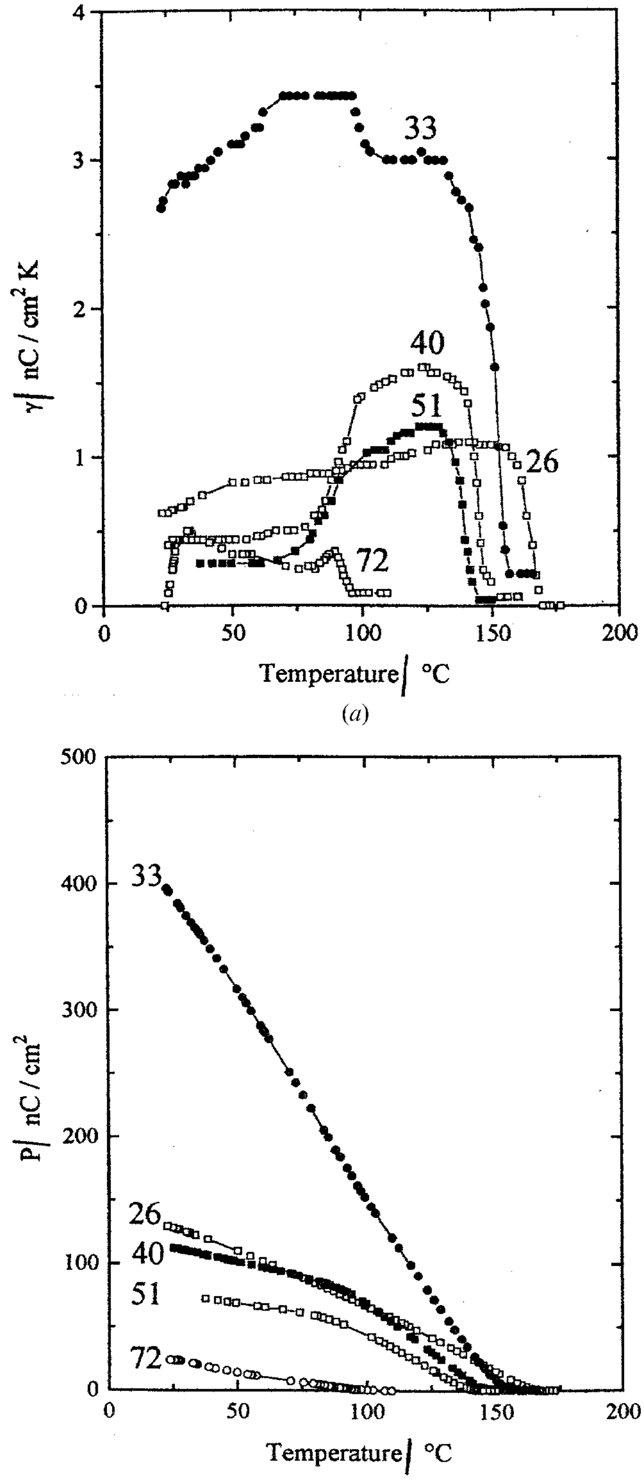
Soto Bustamante *et al.* [34, 35]. Of particular interest is the fact that none of the two counterparts alone manifests this behaviour. Extremely unusual electrical properties were observed for mixtures of an achiral side group methacrylate polymer PM6R8 with its monomer M6R8. Figure 9 shows the pyroelectric coefficient (*a*) and macroscopic polarization (*b*) as functions of temperature for these mixtures at various concentration (in wt%) of the monomer. All the measurements were carried out on cooling 10-μm-thick cells under a d.c. bias field $E=12\,\mathrm{V\,\mu m^{-1}}$. At zero field no pyroelectric response is observed on cooling from the isotropic phase to room temperature. With the bias field applied, the field induced pyro-response (and polarization) in the isotropic phase ($T>170$°C) is still negligible for all of the mixtures. On transition to the bilayer smectic C phase, a sharp increase in the signal, in some cases by more than an order of magnitude, is easily seen. Field dependence of the pyroelectric response has the form of the double-loop hysteresis curve typical of antiferroelectrics. On further cooling with a bias electric field applied, a strongly polar glass is formed which, after field removal, shows a pyro-effect and second harmonic generation [36], the intensities of both being much stronger than those anticipated for polymer electrets.

The magnitude of the pyro-response and macroscopic polarization manifests a very sharp maximum as a function of monomer concentration. At optimum concentration of the monomer about 30% of the pyroelectric coefficient in the smectic phase reaches a value of $4\,\mathrm{nC\,cm^{-2}\,K}$, exceeding that observed in ferroelectric crystalline PVDF-TrFE copolymers. In the glassy state, even in the field-off regime, a slightly lower pyroelectric coefficient may be kept stable for longer than one year. The macroscopic polarization measured in the mesophase reaches values of about $400\,\mathrm{nC\,cm^{-2}}$, requiring a dipole moment projection onto the smectic plane of about 1 Debye per mesogenic unit. The $\mathbf{P}_s$ vector is supposed to be located in the tilt plane, the case observed in chiral antiferrolelectrics [37].

Figure 10 displays the chemical formulae of the monomer and polymer molecules and the structure of the smectic C phase with alternating molecular tilt. Such an antiferroelectric structure is compatible with the X-ray data (bilayered smectic C with liquid-like layers and a very pronounced second order reflection) and unusual electric properties discussed in references [20, 21] and observed in the polymer–monomer mixtures. The monomer additive is assumed to be provoking the alternating tilt structure in a side group polymer which, in its pure state, has only the conventional smectic C phase.

3.4. *Polar polymer nematic*

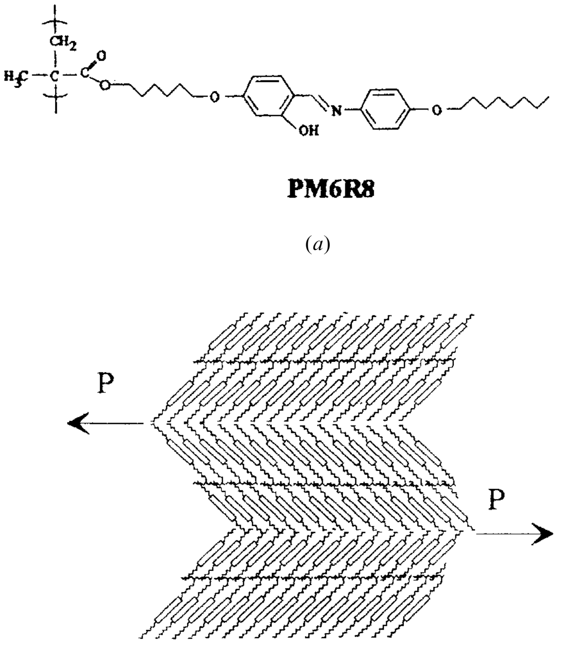
The only example, to the author's knowledge, of a nematic liquid crystal with spontaneous polar ordering



(*a*)

(*b*)

Figure 9. Pyroelectric coefficient (*a*) and macroscopic polarization (*b*) as functions of temperature for PM6R8–M6R8 mixtures at various concentrations (in wt%) of the monomer (10-μm-thick cells under DC bias field $E=12\,\mathrm{V\,\mu m^{-1}}$).



(*a*)

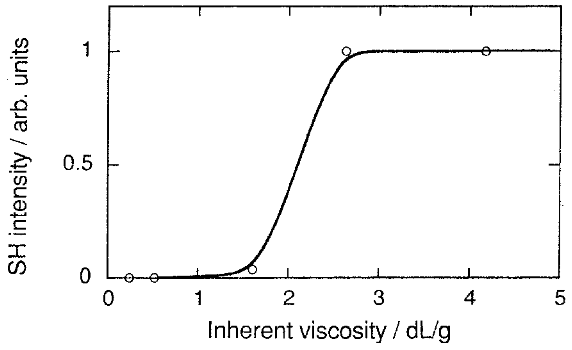
(*b*)

Figure 10. Chemical structures of monomer M6R8 and polymer PM6R8 (*a*) and a possible packing of the mesogenic groups of a side group polymer in the bilayer smectic C phase with alternating tilt (*b*).

is a main chain aromatic polyester [38] that consists of 4-hydroxybenzoic acid fragments linked to 6-hydroxy-2-naphthoic acid in a 73/27 molar ratio [figure 11 (*a*)]. Each of the mesogenic units has a dipole moment about 2 D directed along the polymer chain in one direction and the longer the chain the higher is the magnitude of the dipole moment (e.g. according to calculations, a tetramer should have $\mu \approx 8$ D). Thus, with increasing degree of polymerization, a critical magnitude of the dipolar strength μ^* predicted theoretically [equation (2)] must be reached and the nematic becomes polar.

Indeed, with increasing viscosity of the material, that is with increasing molecular mass of the polymer, the intensity of the second harmonic light generation behaves as expected [figure 11 (*b*)]. For short polymer chains the SHG intensity is negligible. However, at a certain critical length the intensity grows almost step-like, and this fact is attributed to the appearance of the polar state. More detailed SHG investigation [39] showed, however, that the direction of the polar axis does not coincide precisely with the nematic director, but instead there is some distribution of the mirror planes (and therefore polar axes which are obliged to be in the mirror planes) around the nematic director.

(*a*)



(*b*)

Figure 11. (*a*) A main chain aromatic polyester that consists of 4-hydroxybenzoic acid fragments linked to 6-hydroxy-2-naphthoic acid moieties; (*b*) variation of the SHG intensity with viscosity of the copolymer [38].

3.5. *Polar columnar phase consisting of bowl-like molecules*

Ferroelectric properties of a columnar phase consisting of bowl-like molecules were observed by Swager *et al.* [40] on vanadyl complexes **7** with propylene bridging groups, [figure 12 (*a*)] [41]. Such complexes form a kind of linear chain along the column axis. Triangular wave polarization measurements revealed characteristic bumps in the transient current in a more ordered columnar phase at 140°C [figure 12 (*b*) (above)], but not in the less ordered phase at 167°C [see the same figure (lower part)]. The $\mathbf{P}_S$ magnitude estimated for the more ordered phase from the current peaks is rather high, of the order of 100 nC cm^{-2}.

4. Concluding remarks

The whole set of recent experimental results shows promise of development of new materials which, being achiral, combine ferroelectric and liquid crystalline properties. Such materials may be of great interest for piezoelectric, pyroelectric, electro-optical and non-linear optical applications.

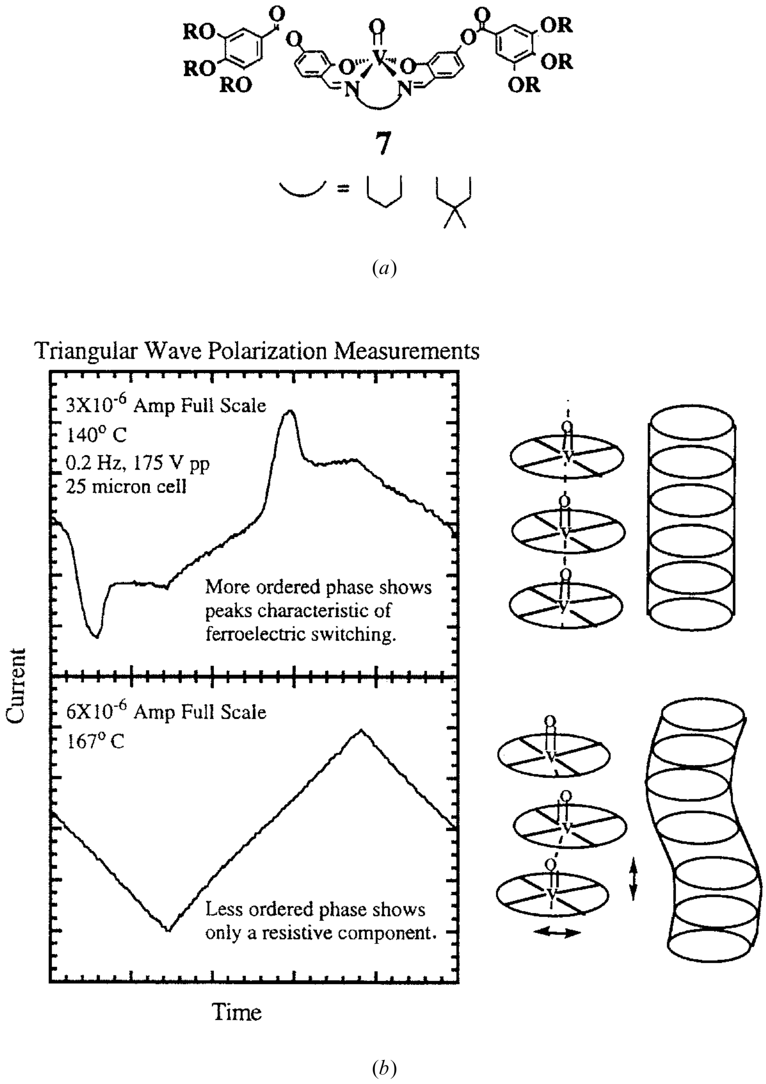


Figure 12. (*a*) The chemical structure of the vanadyl complexes and (*b*) repolarization currents observed on electric field switching of the more ordered (above) and less ordered (below) columnar phases [41].

A search for polar (or, more specifically, ferroelectric) materials is not easy. It is well known that ferroelectric materials show repolarization currents caused by electric field induced switching of the spontaneous polarization, and non-switchable polar materials manifest such specific properties as the pyro-effect, the linear electro-optical effect and optical second harmonic generation. Of course, this is true but, in fact, it is true only in the first approximation. Let us present some misleading examples of observing the same properties in non-polar materials.

Typical hysteresis loops expressed in the coordinates 'bias field–electric current' have been observed in non-polar *p*-azoxyanisole [42, 43] and interpreted as a manifestation of ferroelectricity, although they originated from non-linear ion conductivity in the samples. In this respect, the observation of loops in the coordinates 'bias field–pyroresponse' seems to be more reliable. Transient ionic currents may be of the same shape as current peaks due to polarization switching as has been shown by Vaxiviere *et al.* for chiral ferroelectric liquid crystals [44].

Pyroelectric effect measurements in the field-off regime are very reliable, but require stable monodomain samples. When a d.c. electric field is used for sample monodomain formation, the field induced polarization contributes to the total pyro-response and must be filtered out, e.g. by removal of the linear part from the pyro-response—bias voltage dependence. Even in the field-off regime, there is danger from a built-in polarization which may originate from a previous electric poling or from interface effects. In the latter case, especially important for thin layers, a surface or false pyroelectric effect is observed [45].

Also, SHG alone cannot be a decisive factor in the determination of a polar structure. It is known that in centrosymmetric systems, SHG is forbidden only in the so-called electric dipole approximation. When magnetic dipoles or electric quadrupoles are taken into consideration, SHG is allowed even in non-polar systems. An example is a phase matched SHG with very specific polarization properties observed in conventional (non-polar) nematics [46] and accounted for by the quadrupolar mechanism.

Therefore, only careful investigations of a potential candidate by a variety of techniques may enable one to refer it to a class of achiral polar liquid crystals, and the discovery of novel polar phases is still a challenge for us.

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