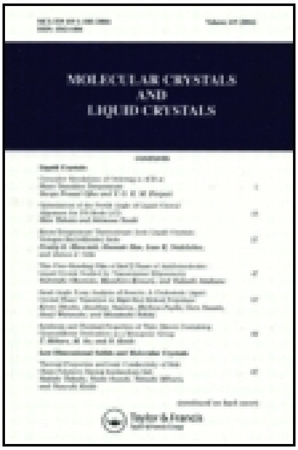

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Polar Liquid Crystals Formed from Polar Rigid-Rod Polyester Based on Hydroxy Benzoic Acid and Hydroxy Naphthoic Acid

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Polar Liquid Crystals Formed from Polar Rigid-Rod Polyester Based on Hydroxy Benzoic Acid and Hydroxy Naphthoic Acid

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We describe a distinct nematic liquid crystal with ferroelectric ordering which is formed from the polar rod-like aromatic polyester. The nematic liquid crystal is biaxial and the polarity appears along both axes as determined by measurements of the second harmonic generation. The strong dipole-dipole interaction between polar rod-like molecules may be ascribed to the origin of the polarity.

Keywords: polyester; nematic liquid crystal; polar ordering; second harmonic generation; rigid-rod polymer

1. Introduction

Ferroelectric liquid crystals are of considerable theoretical and technological interest.[1] It has been recognized that a tilted smectic phase made up of chiral molecules can be ferroelectric.[2] The chirality of molecules and their tilted association into the smectic layer, reducing the overall symmetry of the liquid crystal, are essential for conventional ferroelectric liquid crystals.[3]

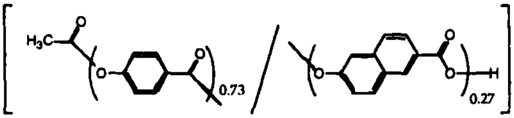
The great attention has been directed to the non-chiral ferroelectric system. Tournilhac et al.[4] found that polyphilic molecules comprising three or more chemically different subunits can form a ferroelectric smectic liquid crystal as a result of the segregation of the units into homogeneous microdomains. Watanabe et al.[5] reported that the ferroelectric smectic phase with C_{2v} symmetry can be formed from main-chain liquid crystal polymers if two different odd-numbered aliphatic spacers are incorporated into the backbone in a regularly alternate fashion and are segregated into different microdomains. Watanabe et al.[6-9] further found that the banana-shaped molecules and twin dimers can form the ferroelectric smectic liquid crystals.

Recently, the results of computer simulation have demonstrated that ferroelectricity could appear even in the nematic phase if the constituent rod-like molecules have a strong dipole moment.[10-12] By considering the dipole-dipole interaction and hard-core repulsion using a simple mean field model within the Onsager formalism, Lee and Lee[12] showed that the rod-like molecules exhibit conventional isotropic-nematic, nematic-ferroelectric nematic, and direct isotropic-ferroelectric nematic transitions as a function of temperature or pressure. On the other hand, Coulter et al.[13] showed by X-ray analysis that polar rod-like aromatic polyesters based on hydroxy benzoic acid are packed with a net chain directionality in the crystalline phase. The existence of polar crystalline phases in related polyesters has also been confirmed by second-harmonic generation (SHG) measurements by Stuetz[14] and Asada.[15] These studies suggest that the polar rod-like polymers tend to organize with polar ordering.

Here, we describe a distinct nematic liquid crystal with polar ordering which is formed from a polar rod-like aromatic polyester. The polarity in the nematic phase appears along the nematic director which is determined by SHG measurements. The strong dipole-dipole interaction between polar rod-like molecules may be the origin of the polarity.

2. Experimental

The materials used are aromatic copolyesters which comprise 4-hydroxy benzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA) in a molar ratio of 73/27.



Copolyester A

Several specimens with different inherent viscosities were prepared by controlling the reaction time of melt condensation. Samples were abbreviated here as P-n where the number, n, following to P indicates the inherent viscosity (see Table I). This type of polymer has a rod-like structure[16,17] and is known to form the nematic phase.[18] The crystal-to-nematic transition temperatures are 283°C for P-14 with the highest molecular weight and 190°C for the lowest molecular weight P-1. No nematic-to-isotropic transition was observed in any of the polymers up to the decomposition temperature of around 350 °C. Oriented films were prepared by hot-pressing the nematic liquid crystals and drawing then uniaxially. The film thickness was about 3mm. The order parameter of the resultant films determined by X-ray diffraction was around 0.95.

Table I. Inherent viscosity, melting temperature and relative SHG intensity of copolymers A

Polyester	Inherent viscosity (dL/g)	Tm (°C)	SHG intensity (a.u.)
P-1	0.11	190	0
P-2	0.25	210	0
P-3	0.30	225	0
P-4	0.52	230	0
P-5	0.92	250	0.01
P-6	1.38	265	0.19
P-7	1.61	274	0.04
P-8	1.62	274	0.25
P-9	2.22	275	0.33
P-10	2.63	277	1.00
P-11	2.79	277	0.60
P-12	3.10	278	1.10
P-13	3.15	279	1.00
P-14	4.17	283	1.00

SHG was used as a probe to monitor the spontaneous polarization in the medium. Q-switched Nd: YAG laser light (1064 nm) was illuminated perpendicular to the films (illumination area; 0.1mm in diameter) and the SHG signal was detected using a photomultiplier tube after passing through a monochromator with a boxcar averager.

3. Results and discussion

Figure 1 shows the intensity of SH from the film P-14 with the highest molecular weight as a function of input polarization angle. Here, the polarization of the analyzer was fixed parallel to the drawing axis of the film and the SHG signal was plotted against the angle between the input polarization and orientation axis (polymer chain axis) of the film. Highly efficient SHG with marked anisotropy can be observed without poling. There are maxima at around 0° and 180° and minima at around 90° and 270°, showing that the spontaneous polarization is parallel to the orientation (polymer chain) direction. The nonlinear optical coefficient along the orientation axis was evaluated as approximately 5 pm/V using the Maker fringe method.

P-14 polymer shows a crystal-to-nematic transition at about 280°C. The typical nematic phase was identified by optical microscopy and X-ray diffraction. On heating to the nematic phase, SHG activity was still observed as in the crystalline phase. Anisotropy of SHG, as shown in Fig. 1, was also observed in the oriented nematic phase. These features of the nematic phase were not altered at all even after annealing for over 2h at 290 °C. We conclude that the nematic phase is polar.

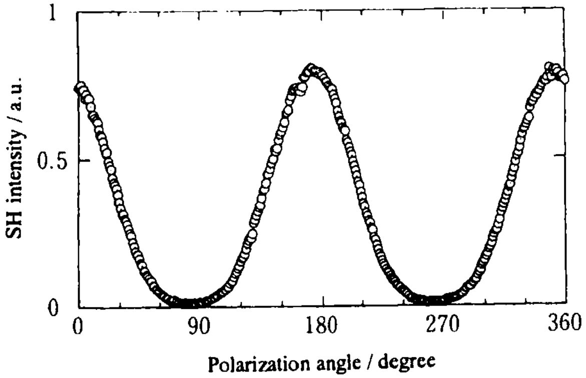


Figure 1. Dependence of the SH intensity on the polarization angle for the film P-14.

The origin of SHG activity along the nematic director can be shown to be composed of two stages. First, the constituent polymer possesses a rigid conformation and a polarity along the polymer chain direction. The dipole moment roughly corresponds to 2 x Dp(degree of polymerization) Debye. Second, the polar molecules in the nematic phase are packed such that there is no chance of their polarity being canceled. At this stage, it is interesting to refer to the result calculated by Lee and Lee[12] that the ferroelectric nematic phase appears if the rod-like molecules have a large dipole moment. The transformation of conventional nematic to ferroelectric nematic phase is predicted to take place when the dipole strength, given by

$$d^* \propto \sqrt{\frac{d^2}{V}}\ , \qquad (1)$$

exceeds the critical value of $d_C^* = 0.362$ due to an increase of molar dipole moment, d, or a decrease of molar volume, V. This mechanism of producing the ferroelectric ordering seems practical in the present polymeric system based on the following consideration. In the present polymer, the dipole moment may increase proportionally with the degree of polymerization, n, as mentioned above. The molar volume is also proportional to n and so, eq. (1) can be rewritten as

$$d^* \propto \sqrt{\frac{(nd_1)^2}{nv_1}} = \sqrt{n}\sqrt{\frac{d_1^2}{v_1}}\,, \qquad (2)$$

where d_1 and v_1 are the dipole moment and volume of the repeating unit, respectively. The dipole strength, d*, thus increases proportionally with the square root of the molecular weight, making it possible for the present polymer P-14 to attain a considerably large value of d* which may exceed the critical value d_c*.

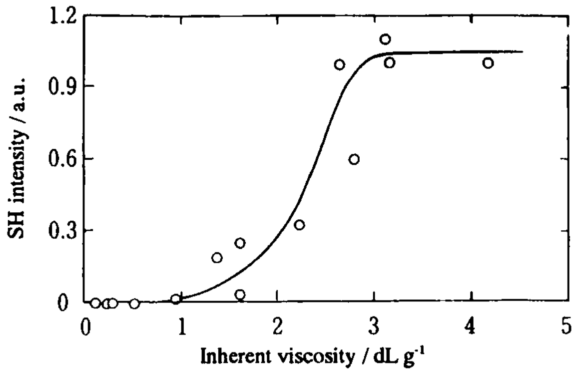


Figure 2. Variation of SH intensity with the inherent viscosity of copolyesters A.

These considerations encouraged us to study the dependence of the SH intensity on the molecular weight of the polymer. Figure 2 shows the relative SH intensities of the samples P-1 to P-13 measured with respect to that of sample P-14 which had the highest molecular weight. We found that the SHG active nematic phase appears beyond a critical molecular weight such that only the higher molecular weight samples with inherent viscosities above 2.5 dL/g show efficient SHG (see Table I). Unfortunately, the molecular weight of the polymer cannot be precisely determined because of the limited solubility in conventional solvent, but this tendency is in qualitative agreement with the theoretical prediction.

In order to investigate the more detailed structure and symmetry of the system, SHG intensities were measured for the oriented film under various polarization conditions. Figures 3(a) displays SHG profiles, I(ϕp, 0°), I(ϕp, 90°) and I(0°, ϕa), at about 290°C (nematic phase). Here, ϕp and ϕa shows the polarization angles of polarizer and analyzer against the polymer chain axis, respectively. The patterns essentially do not change when the observation is made from the reverse side of the film. I(90°, ϕa) was too weak to detect reasonable signal. Two following observations should be stated.

(1) I(ϕp, 0°) shows the maxima at angles slightly different from zero.

(2) I(ϕp, 90°) shows the two-leaves pattern.

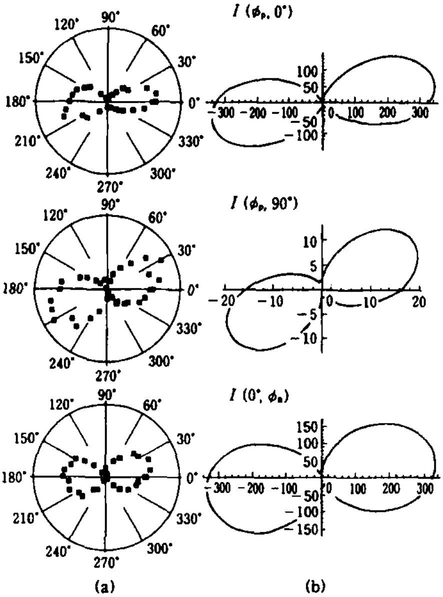


Figure 3. SHG profiles of P-14, I(ϕp, 0°), I(ϕp, 90°) and I(0°, ϕa), (a) at room temperature (crystalline phase), (b) at 290°C (nematic phase), and (c) the simulated results in C_S symmetry. The mutual comparison of the scales of the signal intensities is effective.

Because of these facts, the symmetry should not be $C_{\infty v}$. Hence, we examined C_S symmetry. The χ tensor in C_S symmetry has six nonzero elements,

$$\begin{pmatrix} \chi_{xxx} & \chi_{xyy} & \chi_{xzz} & 0 & \chi_{zxx} & 0 \\ 0 & 0 & 0 & \chi_{zyy} & 0 & \chi_{xyy} \\ \chi_{zxx} & \chi_{zyy} & \chi_{zzz} & 0 & \chi_{xzz} & 0 \end{pmatrix} \qquad (3)$$

with a xz mirror plane. When the mirror plane normal makes an angle θ with respect to the light propagation direction, the SH intensity under the projection model is given by

$$\begin{aligned} I(\phi_p, \phi_a) = |(&\chi_{xxx}\sin^2\phi_p \cos^3\theta + \chi_{xyy}\sin^2\phi_p \sin^2\theta \cos\theta \\ &+ \chi_{xzz}\cos^2\phi_p \cos\theta + \chi_{zxx}\sin2\phi_p \cos^2\theta \\ &+ \chi_{zyy}\sin2\phi_p \sin^2\theta + \chi_{xyy}\sin^2\phi_p \sin 2\theta \sin \theta) \sin\phi_a \\ &+ (\chi_{zxx}\sin^2\phi_p \cos^2\theta + \chi_{zyy}\sin^2\phi_p \sin^2\theta \\ &+ \chi_{zzz}\cos^2\phi_p + \chi_{xzz}\sin2\phi_p \cos \theta) \cos\phi_a|^2 \end{aligned} \tag{4}$$

The data were collected from the fiber specimen so that the simulation was performed under the random orientation about θ. The simulated results are shown in Fig. 3(c), where the parameters used are $\chi_{xxx} = -0.07$, $\chi_{xyy} = -0.11$, $\chi_{xzz} = -0.36$, $\chi_{zxx} = 0.08$, $\chi_{zyy} = 0.10$ and $\chi_{zzz} = 1$. The agreement is very good. Thus, we can reach the distinct conclusion that the basic structure of nematic has C_s symmetry. In other words, the nematic liquid crystal is biaxial and the polarity appears along both axes. One of the satisfactory structures can be illustrated in Figure 4. This structure is very specific since it requires not only the specific polar packing of polymers but also the specific conformation for each polymer in which the C=O groups are sticking out of the chain to the similar direction to results in non-zero component of dipole moment perpendicular to the chain axis.

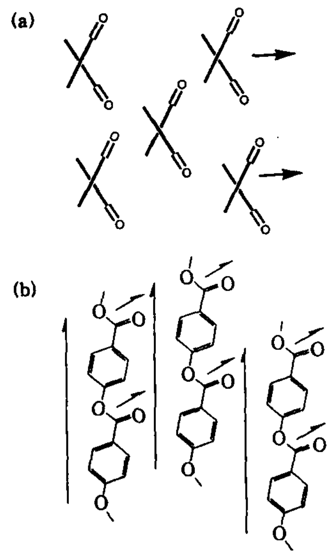


Figure 4. One plausible structure of polar nematic liquid crystal satisfying the SHG data of Fig.3. (a) and (b) show the structures projected on the planes parallel and perpendicular to the chain axis, respectively.

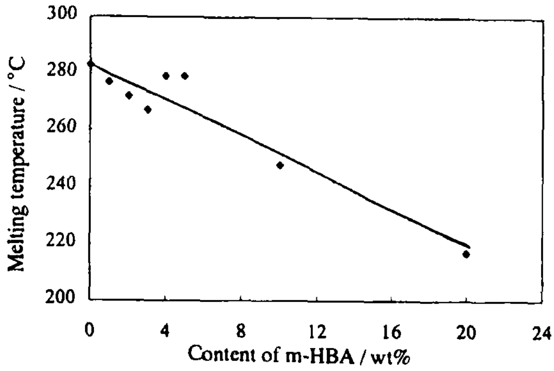
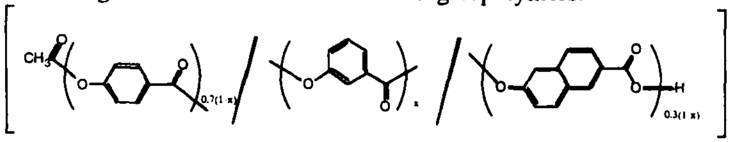


Figure 5. Dependence of crystal-nematic transition temperature on the component of m-HBA in copolyester B.

To show that this conclusion is not artificial, we refer to another interesting result observed in the following copolymers.



Copolyester B

Here, we used meta-hydroxy benzoic acid (m-HBA) as a third comonomer unit to introduce the kink structure. As expected, the crystal to nematic transition temperature decreases with the increase of m-HBA component (see Figure 5). The steady decrease indicates that m-HBA component is randomly introduced. The SHG measurement was performed for the fiber with 5% of m-HBA component. The results are shown in Figure 6. In a comparison with Figure 3, one can find some essential difference; for example, two leaves pattern of I(ϕp, 90°) profile is altered to the four leaves. The calculation by the equation (4) leads to the conclusion that symmetry may be a C_{2v} or $C_{\infty v}$. This is reasonable since the polarity perpendicular to the chain is forced to be canceled when the polymers assume the conformation with a smaller bent angle which conforms the nematic field[19].

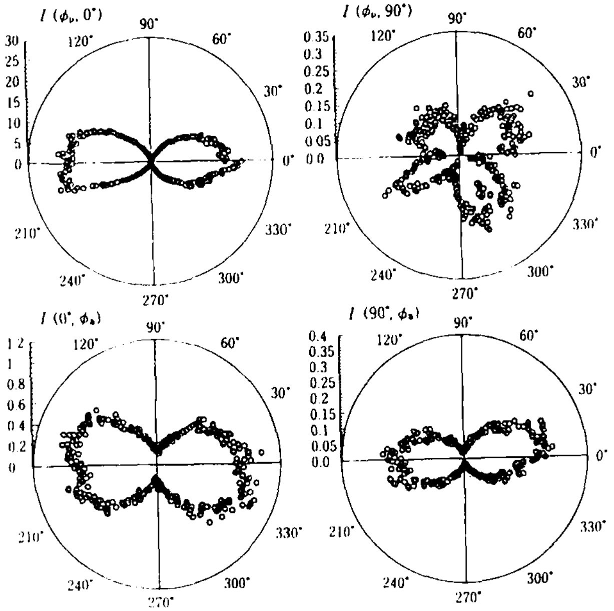


Figure 6. SHG profiles, I(ϕ_p, 0°), I(ϕ_p, 90°), I(0°, ϕ_a) and I(90°, ϕ_a) observed for the oriented film of polymer (B) with the m-HBA component of 5 wt%.

We can thus conclude that the aromatic polyester based on HBA and HNA forms a novel nematic liquid crystal with polar ordering along the nematic director. The SH profiles as a function of incident or SH polarizations are well simulated under the model of C_S symmetry with a mirror plane rotationally disordered about the molecular long axis. The film consists of such polar domains and the polarization aligns along the same direction but with a random sense. This is the first example of a material that shows polarity in the nematic phase.[20] The strong dipole-dipole interaction may produce long-range polar ordering. The polar nematic phase should be ferroelectric due to its fluidity, but switching behaviour induced by an external field has not been observed to date, probably because of the high viscosity.

Finally, it should be noted that another typical material with polarity, α-helical polypeptide, can also form the polar structure in their thermotropic and lyotropic cholesteric liquid crystals. More details of this will be presented in the literatures.[21,22]

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