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SHG-ACTIVE FILMS FORMED FROM UNIAXIAL AND BIAXIAL NEMATIC LIQUID CRYSTALS WITH POLAR ORDERING

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Abstract We found aromatic copolymers comprising 4'-hydroxy 4-biphenyl carboxylic acid and 6-hydroxy 2-naphthoic acid with high second-harmonic-generation (SHG) activity. The polarization dependence of SHG in the solid film formed from the nematic phase reveals uniaxial and biaxial polar orderings.

INTRODUCTION

Recently we found nematic liquid crystals with polar ordering in aromatic copolymer comprising 4-hydroxybenzoic acid and 6-hydroxy 2-naphthoic acid.[1] It was found that the SHG activity appears in compounds with a high degree of polymerization. Because of this fact, we suggested the important role of the strong dipole-dipole interaction between polar rod-like molecules for the origin of the appearance of the polar ordering.[1,2] The polarization dependence of the SH intensity was able to be simulated using the model structure consisting of biaxial domains with their mirror planes parallel to the director direction.[3]

In this paper, we used 4'-hydroxy 4-biphenyl carboxylic acid instead of 4-hydroxybenzoic acid, so that the biaxial nature tends to change to the uniaxial nature. We actually confirmed in the crystalline phase that the symmetry changes from biaxial to uniaxial by changing the molar ratio of 4'-hydroxy 4-biphenyl carboxylic acid with respect to 6-hydroxy 2-naphthoic acid.

EXPERIMENTAL

The materials used were aromatic copolymer comprising 4'-hydroxy 4-biphenyl carboxylic acid (HBPCA) and 6-hydroxy 2-naphthoic acid (HNA), as illustrated in Fig.1. We prepared the copolymers with two different molar ratios. The copolymer used in our previous work, 4-hydroxybenzoic acid (HBA) and HNA, is also shown for comparison.

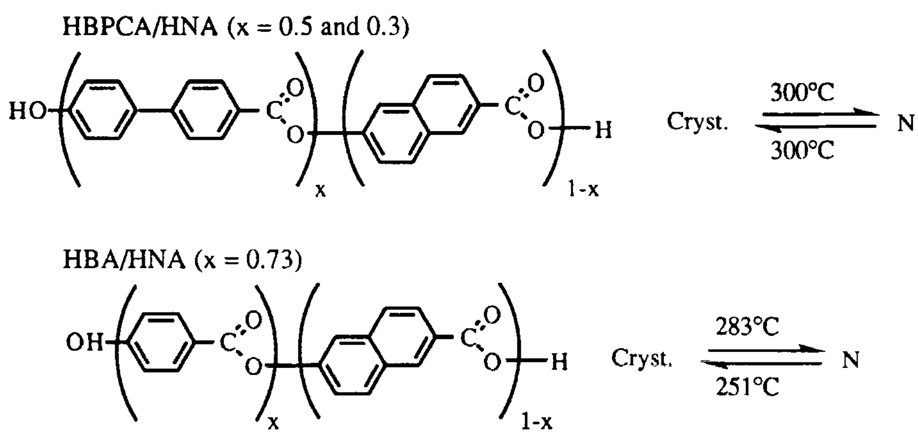

FIGURE 1 Molecular structures of HBPCA/HNA used and HBA/HNA for comparison.

In the present experiment, we only used a solid film, since the temperature range of the nematic phase is fairly high. We can expect that the symmetry and the SHG activity retain in the nematic phase, according to the previous work using an HBA/HNA system. The sample film was prepared by shearing the nematic uniaxially.

The SHG experiments were carried out as follows. A Q-switched Nd:YAG laser light (B. M. Industries, 501-D/NS 4/100, 1.06 μm, 6 ns pulse duration and 100 Hz repetition) was cast upon the film along the film normal direction and the SH light was detected from the transmitted direction. The angular dependence of the SH light was measured by rotating either a polarizer or an analyzer. Three polarization conditions employed were $I(\phi_p, 0°)$, $I(\phi_p, 90°)$ and $I(0°, \phi_a)$, where ϕ_p and ϕ_a are the angles of polarization of the polarizer and the analyzer, respectively, and 0° and 90° are the stretched and the perpendicular directions, respectively.

RESULTS AND DISCUSSION

Figure 2 shows the polarization dependence of the SH intensity in films of (a) HBPCA/HNA=50/50 and (b) HBPCA/HNA=30/70. The most important difference to be noted is in the geometry of I(ϕ_p, 90°). In HBPCA/HNA=50/50, the four-leaves pattern is observed, while the two-leaves pattern in HBPCA/HNA=30/70.

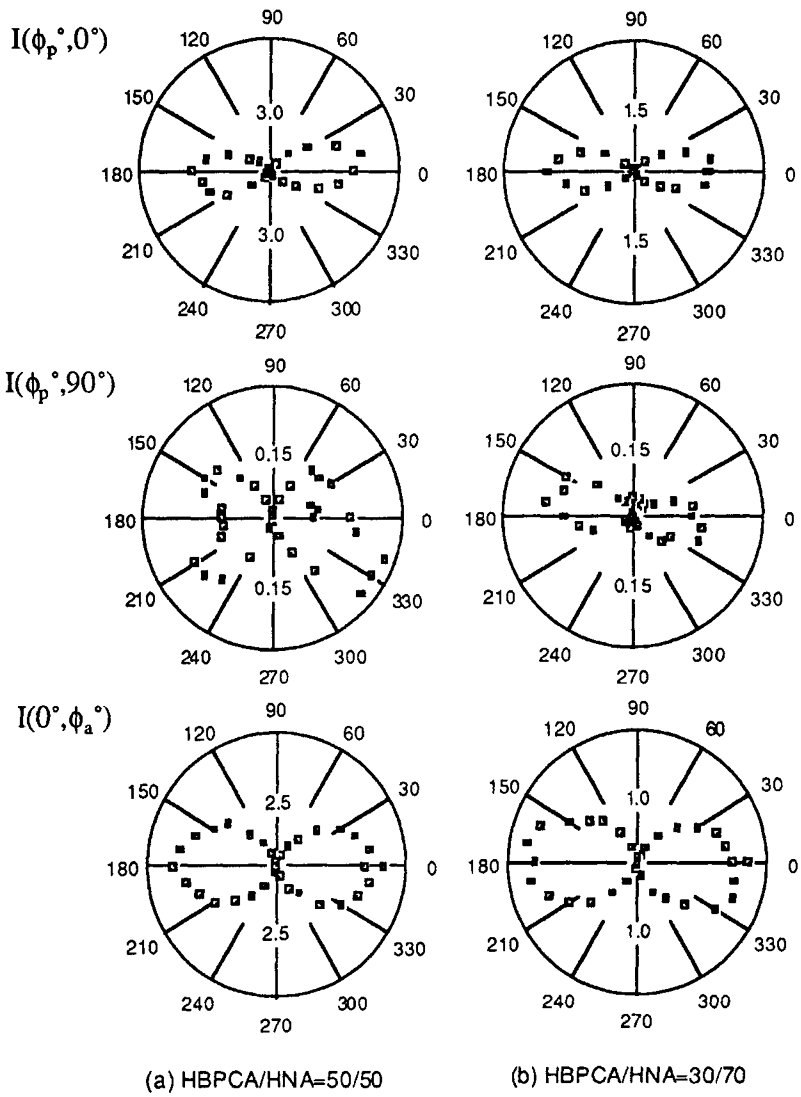

FIGURE 2 The polarization dependence of SH intensity in films with (a) HBPCA/HNA = 50/50 and (b) HBPCA/HNA = 30/70.

In order to understand the SH pattern displayed in Fig. 2, we simulate the pattern under the assumption of $C_{\infty v}$ and C_S symmetries. The χ tensor in C_S symmetry has six nonzero elements,

$$\begin{pmatrix} \chi_{xxx} & \chi_{xyy} & \chi_{xzz} & 0 & \chi_{zxx} & 0 \\ 0 & 0 & 0 & \chi_{zyy} & 0 & \chi_{xyy} \\ \chi_{zxx} & \chi_{zyy} & \chi_{zzz} & 0 & \chi_{xzz} & 0 \end{pmatrix} \tag{1}$$

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

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

On the other hands, the χ tensor in $C_{\infty v}$ symmetry has two nonzero elements, χ_{zzz} and χ_{zxx} $(=\chi_{zyy})$

$$\begin{pmatrix} 0 & 0 & 0 & 0 & \chi_{zxx} & 0 \\ 0 & 0 & 0 & \chi_{zyy} & 0 & 0 \\ \chi_{zxx} & \chi_{zyy} & \chi_{zzz} & 0 & 0 & 0 \end{pmatrix} \tag{3}$$

with a C_∞ rotation axis along z axis. For an incident light parallel to the y axis, the SH intensity under the projection model is given by

$$I(\phi_p, \phi_a) = \big|\chi_{zxx}(\sin^2\phi_p\cos\phi_a + \sin2\phi_p\sin\phi_a) + \chi_{zzz}\cos^2\phi_p\cos\phi_a\big|^2 \tag{4}$$

The simulated results are shown in Fig. 3, where the parameters used are χ_{zzz}/χ_{zxx} = 3.64 for Fig. 3(a) and χ_{xxx} = -0.07, χ_{xyy} = -0.11, χ_{xzz} = +0.36, χ_{zxx} = -0.08, χ_{zyy} = 0.10 and χ_{zzz} = 1 for Fig. 3(b). In Fig. 3(b), the random orientation about θ were assumed. The simulated results are very similar to the experimental results shown in Figs. 2(a) and 2(b). Thus, we can conclude that the films with HBPCA/HNA = 50/50 and 30/70 have $C_{\infty v}$ (uniaxial) and C_S (biaxial) symmetries, respectively. It should be noted that the film with HBA/HNA = 73/27 exhibits C_S (biaxial) symmetry. By replacing HBA by HBPCA, an uniaxial nature increases and an uniaxial phase is realized. Actually, if the molar ratio of HBPCA decreases, biaxiality appears, as shown in Fig. 2.

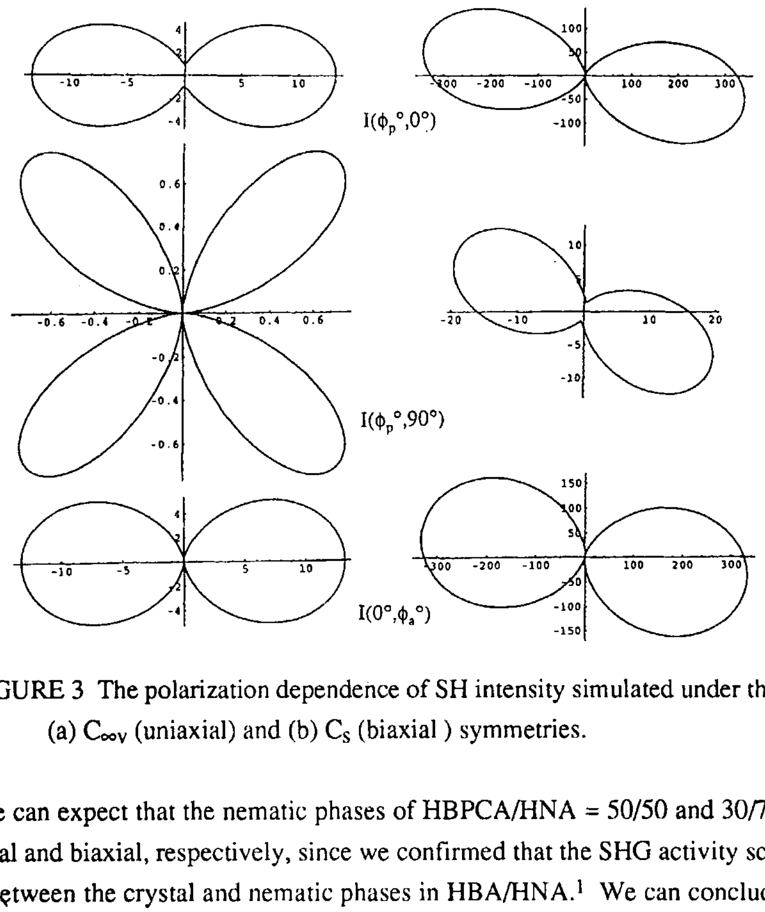

FIGURE 3 The polarization dependence of SH intensity simulated under the (a) $C_{\infty v}$ (uniaxial) and (b) C_S (biaxial) symmetries.

We can expect that the nematic phases of HBPCA/HNA = 50/50 and 30/70 also are uniaxial and biaxial, respectively, since we confirmed that the SHG activity scarcely changes between the crystal and nematic phases in HBA/HNA.[1] We can conclude that the uniaxial and biaxial nematic phases with polar ordering are realized in the systems with HBPCA/HNA = 50/50 and 30/70, respectively.

REFERENCES

1. T. Watanabe, S. Miyata, T. Furukawa, H. Takezoe, T. Nishi, M. Sone, A. Migita and J. Watanabe, Jpn. J. Appl. Phys., **35**, L505 (1996).
2. J. Lee and S.-D. Lee, Mol. Cryst. Liq. Cryst., **254**, 395 (1994).
3. T. Furukawa, K. Ishikawa, H. Takezoe, A. Fukuda, T. Watanabe, S. Miyata, T. Nishi, M. Sone and J. Watanabe, Mol. Cryst. Liq. Cryst., **15**, 167 (1996).