Polar Structure in Polypeptide Cholesteric Liquid Crystals Evidenced from Observation of Second-Harmonic Generation Due To the Helicoidal Cavity Effect

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Recently, interesting theoretical predictions[1,2] have been reported with respect to the ferroelectricity in liquid crystals which are composed of polar polymers. Terentjev et al.[1] predicted that an isotropic liquid composed of polar molecules undergoes a transition into a ferroelectric phase with symmetry $C_{\infty v}$. Ferroelectric ordering is more likely to occur in the nematic phase of polymers with directed polar segments rather than in low molecular weight nematic phases of polar molecules. Theory also shows that the transition temperature for ferroelectric instability mainly depends on the order parameter, the dipole moment, and the axial ratio of the molecule. Another interesting theory was reported by Lee and Lee.[2] By considering the dipole−dipole interaction and hard-core repulsion using a simple mean field model within the Onsager formalism, they showed that rodlike molecules possessing large dipole moments exhibit nematic−ferroelectric nematic and isotropic−ferroelectric nematic transitions in addition to the conventional isotropic−nematic transition, as a function of temperature or pressure.

There are two classes of liquid crystalline poymers with large dipole moments accumulated along their chain axes. One of them is the aromatic copolyester consisting of 4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid which has a dipole moment of 2.5 D × Dp (degree of polymerization).[3] Watanabe et al.[3] and Furukawa et al.[4] actually demonstrated that a distinct nematic liquid crystal with polar ordering is formed from this aromatic polyester, through the observation of second harmonic generation (SHG) for uniaxially oriented samples. The polar structure depends strongly on the molecular weight so that the polar ordering appears in the nematic phase of polymers with the relatively higher molecular weights.[3] This phenomenon is also in qualitative agreement with the theoretical prediction given by Lee and Lee.[2]

More recently, we have treated another representative polymer, namely the α-helical polypeptide which has roughly a dipole moment of 3.4 D × Dp.[5] It is interesting that its lyotropic cholesteric phase also shows significant SHG under the application of an electric field.[6] Using a SHG interferometry technique, the phase of the SHG was reversed by reversing the electric field. Furthermore, by applying a triangular wave voltage, a switching current peak was observed. These results show the switching of the polarization, which is expected for a ferroelectric cholesteric liquid crystal that is illustrated in Figure 1.[7] In this case, however, one cannot rule out the possibility that the SHG activity (or polar structure) has been induced by the electric field which was applied to unwind the helical structure. Thus, we have to give direct evidence that there is a polar arrangement of the molecules in the undisturbed helicoidal structure.

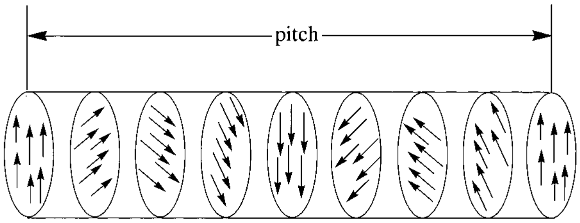

Figure 1. Helical structure of the polar cholesteric liquid crystal. The arrows show the direction of polarity in α-helical polypeptides.

At this aspect, several research groups have reported the interesting phenomenon in which the harmonic generation is enhanced due to the helicoidal distributed-feedback (DFB) cavity effect. The first report was made by Shelton and Shen.[8] They observed that the inhomogeneous phase matching of the harmonic generation could be explained in cholesteric liquid crystals by taking account of the Umklapp process[9] in the helical structure. Belyakov and Shipov[10] predicted theoretically that the harmonic generation could be enhanced in cholesteric liquid crystals when the harmonic frequency is near the selective reflection band. In these cholesteric systems, of course, the enhancement takes place only for the third harmonic (TH) light, but not for the second harmonic (SH) light. On the other hand, Kajikawa et al.[11] and Furukawa et al.[12] showed that SH light is generated inside the helicoid of the ferroelectric chiral S_C phase when the propagation direction of light could be confined to a direction parallel to the helicoidal axis. Not only the transmitted but also the reflected SH intensities markedly increase when the wavelength of the SH light coincides with the optical pitch of the helicoid.[13] This helicoid SHG cavity effect is due to the existence of polarity in a direction perpendicular to the helical axis. Thus, by measuring the SHG due to helicoidal DFB cavity effect, we can safely clarify whether in the polypeptide cholesteric liquid crystal there is a polar arrangement of molecules or not.

In this study, we examined the SHG cavity effect by using a solid cholesteric film of poly(γ-benzyl L-glutamate) (PBLG) which retains the cholesteric helical structure of the lyotropic solution. PBLG was synthesized by the NCA method with an initiator of triethylamine. The molecular weight was estimated as 1.2 × 10^5 from the viscosity measurement in dichloroacetic acid at 25 °C. We know that cholesteric films of PBLG with visible colors can be prepared by casting cholesteric solutions in benzyl alcohol at 60∼80 °C. Since a cholesteric film with a relatively larger pitch can be produced by casting at a higher temperature,[14] for convenience, we prepared the cholesteric films with a wide distribution of pitches by using a temperature gradient on casting. In the film

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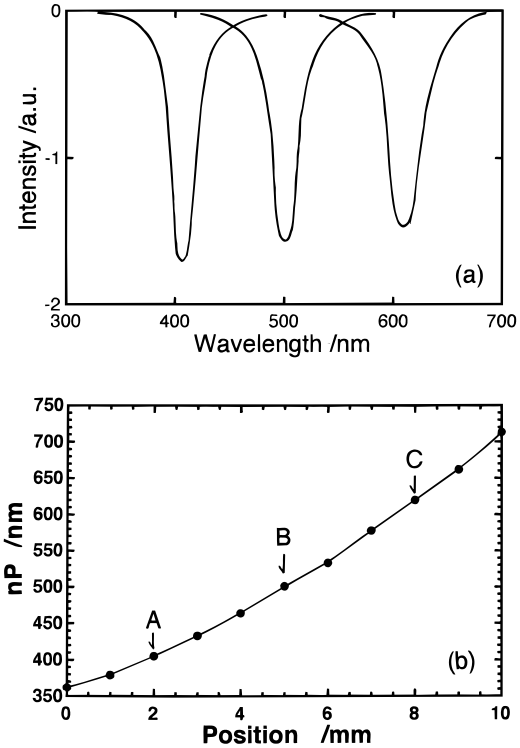

Figure 2. (a) Circular dichroic spectra observed at different positions of the cholesteric film with a forcused beam of 0.5 mm diameter. In part b, the optical pitches determined from the CD spectra are plotted as a function of the film position. The three spectra in part a were observed at the positions A, B, and C, given here.

used here, the pitches vary from 300 to 700 nm in a span of 10 mm so that the helicoidal DFB cavity effect can be examined by measuring the SHG as a function of position. Here, the position was defined as the distance from the confined position. The film thickness was around 50 μm.

The optical pitches (nP) were determined from the circular dichroism (CD) of the reflected light. Here the light was irradiated perpendicularly to the film surface with a focused beam of 0.5 mm diameter by using a JASCO Model J-20. As found in Figure 2a, the CD spectra measured at different positions are very sharp and peak widths are around 20−30 nm, showing that a well-ordered cholesteric helical structure had formed with a helicoid axis lying perpendicular to the film surface.[15] In Figure 2b, the optical pitches collected are plotted as a function of the film position.

The SHG was measured for the same sample, and its intensity (full circle) was plotted as a function of the position in Figure 3. Here, the fundamental beam of a Nd:YAG laser (1064 nm) was irradiated in a direction normal to the film surface so that it propagated along the helical axis, and the transmitted SHG signal was detected using a photomultiplier tube after passing through a monochromator with a boxcar averager. For the same sample, light with a wavelength of 532 nm was irradiated in order to ensure the position where the optical pitch corresponded to the SH light wavelength. Its transmitted intensity (open circle) is also plotted in Figure 3. The position with the lowest intensity, i.e., with the highest reflection coincides with that detected from the CD measurement (see Figure 2b) and the SH intensity resonantly exhibits a sharp peak at this position. Otherwise, the SH intensity is negligibly weak. This resonance effect was observed not only for the transmitted SH light, but also for the reflected light. This is a helicoidal cavity effect which has been observed for the chiral S_C phase.[11,12]

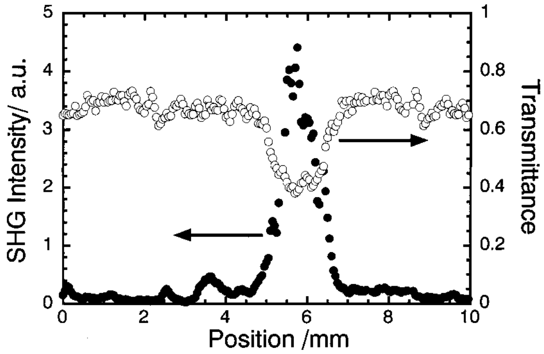

Figure 3. SH intensities (full circles) determined as a function of the film position. The transmitted intensities of the light with a wavelength of 532 nm corresponding to SH light are also plotted as open circles as a function of the film position.

Two possibilities were considered as the origin of SHG activity due to the helicoidal DFB cavity effects. The first was a dipole polarization which is observed in the medium with a noncentrosymmetric structure, and second was an electric quadrupole or magnetic dipole contribution. These quadrupole effects appear even in the centrosymmetric structure.[16] In general, the quadrupole polarization of organic molecules is very weak compared with the dipolar polarization and furthermore it has been observed only in specific material systems, for example, in C_{60} and phthalocyanine having highly symmetric structures.[17,18] Large two-dimensional and three-dimensional π-conjugated systems are required to exhibit large quadrupole or magnetic dipoles.[19] On the other hand, PBLG shows only a one-dimensional dipolar character, and the quadrupole effects are negligible in this system.

We thus reach the conclusion that the cholesteric liquid crystal formed by α-helical polypeptide is not a conventional cholesteric liquid crystal, but the polar cholesteric liquid crystal shown in Figure 1. The polarity appears in a plane perpendicular to the helical axis as in the ferroelectric chiral S_C phase. This result coincides with the previous conclusion in which cholesteric solutions exhibited a ferroelectric response under an applied electric field.[6] We believe that the polarity in this polypeptide system, as well as in the aromatic polyesters,[3,4] may result from the dipole−dipole interaction predicted by the theories.[1,2]

References and Notes

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