

Photoinduced circular anisotropy in a photochromic W-shaped-molecule-doped polymeric liquid crystal film

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Photoinduced circular anisotropy has been demonstrated in thin films of a main-chain polymeric liquid crystal (PLC) system doped with photochromic W-shaped molecules containing two azobenzene groups by irradiating with circularly polarized light (CPL). Reversible photoinduced circular dichroism (CD) was observed with sign relevant to the handedness of the CPL. The experimentally observed CD spectra were analyzed using the DeVoe polarizability model associated with the coupled oscillator method. We also propose a mechanism for the photoinduced circular anisotropy in our system; nucleating the W-shaped molecules with preferential twisted conformation by CPL irradiation, and triggering the local formation of a chiral structure in the W-shaped-molecule-doped main-chain PLC medium.

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I. INTRODUCTION

Organic materials containing photochromic chromophores have attracted much attention because of the ability to change the macroscopic material properties through the photoinduced isomerization cycles of photochromic bonds [1,2]. In particular, the studies of photoinduced changes in glassy polymers containing photochromic chromophores showed their potential for optical image recording in the form of bulk refractive index gratings [3] and surface relief gratings [4] as well as for integrated optics and nonlinear optics [5].

A different approach emerged recently; Nikolova *et al.* reported the appearance of a significant photoinduced optical activity in films of liquid crystalline polyesters with azobenzene mesogens in the side chain and in films of prealigned amorphous side-chain azobenzene polymers [6,7]. More recently, Natansohn *et al.* investigated photoinduced circular dichroism (CD) and chiro-optical switching in thin films of an achiral (donor-acceptor) liquid crystalline polymer with azobenzene mesogens in the side chain [8–10]. These studies have successfully demonstrated that CD and optical activity were induced in thin films of achiral glassy polymers with azobenzene chromophores in their side chains by circularly polarized light (CPL) exposure.

In this paper, we present photoinduced circular anisotropy properties in thin films of a main-chain polymeric liquid crystal system doped with photochromic W-shaped azobenzene molecules as a chiral trigger. The experimentally observed CD spectra were analyzed using the DeVoe polarizability model associated with the coupled oscillator method [11,12]. We also propose a possible mechanism to induce the circular anisotropy in our system.

II. EXPERIMENTAL PROCEDURES

The main-chain polymeric liquid crystal system doped with photochromic molecules used for this study is a mixture of about 80 wt % of a commercialized main-chain polymeric liquid crystal (PLC) material (Nippon Oil Corp., $T_g = 105^\circ\text{C}$) and about 20 wt % of low-molecular-weight photochromic molecules. The commercial PLC material for the host matrix is an aromatic main-chain nematic polyester containing three units shown in Fig. 1(a), with the following phase sequences: isotropic-(250 °C)-nematic-(105 °C)-glass. The photochromic molecule used for a chiral trigger contains two azobenzene groups, *N,N'*-bis [2-hydroxy-5-(4'-*n*-tetradecylphenylazo)benzylidene]-4-nitro-1,3-phenylenediamine shown in Fig. 1(b). We hereafter refer to this molecule as a W-shaped azobenzene molecule. The detailed synthesis and properties of W-shaped azobenzene molecules were described elsewhere [13]. The phase sequence of the mixed system with W-shaped molecules is found to be isotropic-(232 °C)-nematic-(90 °C)-glass.

These W-shaped azobenzene molecules were so designed to have high azobenzene content per single molecule and unique bent-core shape with a twisted molecular chirality. The W-shaped azobenzene molecules themselves spontane-

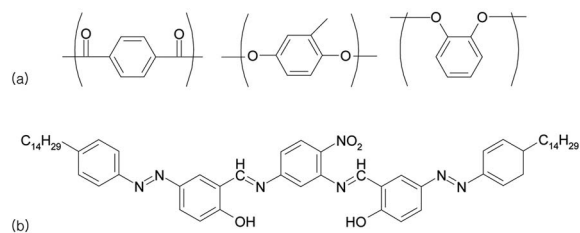


FIG. 1. Chemical structure of (a) constituent elements in the host PLC and (b) photochromic molecules used in this study.

ously segregate into two chiral domains in the liquid crystal and/or crystal phase [13,14]. If one of the crossed polarizers is slightly rotated clockwise, then one domain becomes dark and the other domain becomes bright. If we rotate the polarizer counterclockwise, the bright and dark regions are interchanged. This optical property has been also observed in several bent-core materials [15,16] which have molecular chirality. Thus, the bent-core molecules are regarded as racemic mixtures rather than an achiral system because of the spontaneous segregation into two chiral domains [17]. The unique shape of the molecules can play a key role in inducing chirality in this case. In a previous report [15], Thisayukta *et al.* described that this chirality should originate from the nature of the individual molecules and molecular chirality is produced by the twisted conformation.

These films were prepared by spin-coating a solution of the polymer and dopant (trigger) in tetrachloroethane onto fused quartz slides without surface treatment such as rubbing. The film thickness prepared for this study was less than $0.8 \mu\text{m}$. Before irradiation, the samples were heated up to the nematic phase (160°C) in order to remove residual solvent and then cooled quickly to room temperature to intentionally yield a polydomain phase. From a polarized microscope observation, we confirmed that the multidomain glassy phase with no preferred orientation of the director was formed at room temperature after such an annealing procedure. Polydomain samples are needed to prepare the film without any initial linear anisotropy and to avoid the birefringence effect on CD measurements. Although the domains prepared here were multidomains, the film is transparent due to smaller domain size than visible light wavelength. Thus, the light scattering (the stray light) could be disregarded.

Irradiation was performed at room temperature with a mercury lamp (365 nm) after passing through a Fresnel rhomb to obtain CPL. The intensity of the irradiation light was $30 \text{ mW}/\text{cm}^2$ and the light was incident on the film directly. uv-visible absorption spectra were recorded with a Hitachi U-3410. As an evaluation tool of the photoinduced circular anisotropy, CD was measured from 200 to 800 nm with a Jasco J-720WI spectropolarimeter at room temperature.

III. EXPERIMENTAL RESULTS

For the first step, we examined the ability of photoinduced circular anisotropy for the main-chain PLC films with and without *W*-shaped azobenzene molecules (*W*-doped film and host film, respectively). Figure 2(a) shows uv-visible absorption spectra of the *W*-doped film and the host film. As shown in the figure, the absorption centered at 350 nm for the *W*-doped film is assigned to an azobenzene chromophore, whereas the absorption peaks located at 250 and 290 nm are due to the strong electronic absorption of functional groups in the host main-chain liquid crystalline material.

The induction of circular anisotropy was examined by measuring CD spectra after irradiation for 120 min with right- or left-circularly polarized light (RCPL or LCPL) for both the pure host and *W*-doped films at room temperature. First, we confirmed that there exists no induction of distinct

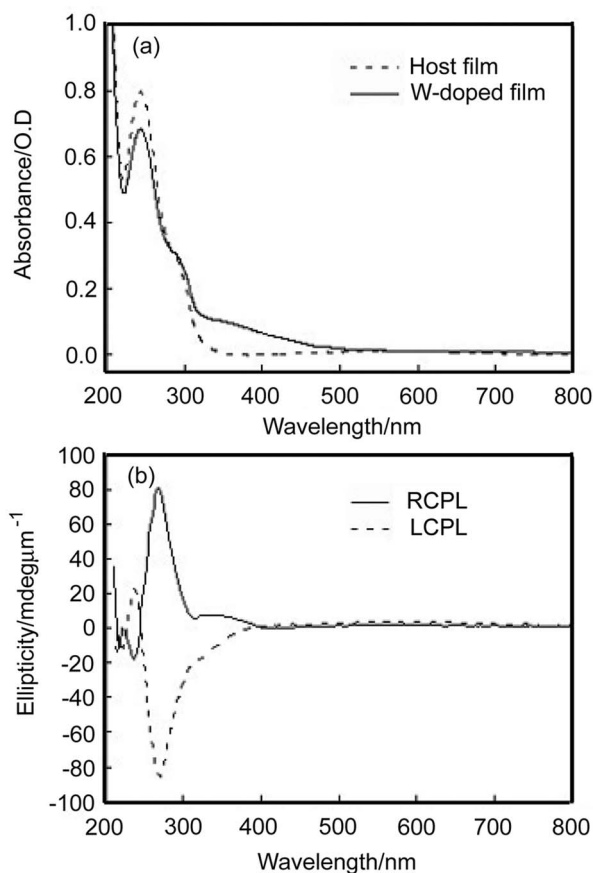


FIG. 2. Absorption and CD spectra of the thin films. (a) Absorption spectra of the main-chain polymeric LC film and *W*-molecule-doped polymeric LC film, and (b) CD spectra of *W*-molecule-doped polymeric LC films after irradiation with right and left CPL.

circular anisotropy in the pure host film. In contrast, a fairly large CD was clearly observed in the *W*-doped film after irradiation of CPL, as shown in Fig. 2(b). It is noted that the observed CD does not come from birefringent effect but from pure circular anisotropy effect by CD observation. Actually, we confirmed that the CD spectrum essentially does not change by azimuthally rotating the sample film. Thus, the initially achiral films became chiral by doping the host PLC with the *W*-shaped azobenzene molecules and by CPL irradiation, as observed by the CD spectroscopy. As shown in Fig. 2(b), two CD bands of opposite sign (Cotton effect) are observed at about 265 and 235 nm with a crossover point at about 250 nm in addition to a small and broad CD band (uncompleted Cotton effect) at 300 nm–400 nm. We also performed the similar evaluation after irradiation for 120 min with RCPL or LCPL for *W*-doped films in liquid crystalline state at a higher temperature. According to our preliminary experiment, the CD signal obtained was much higher than those obtained at room temperature. The details will be reported in a separate paper.

The observed feature of these CD spectra indicates that the photoinduced circular anisotropy was induced not only for the *W*-shaped azobenzene chromophores but also for the host mesogens; namely, the photoinduced changes of the

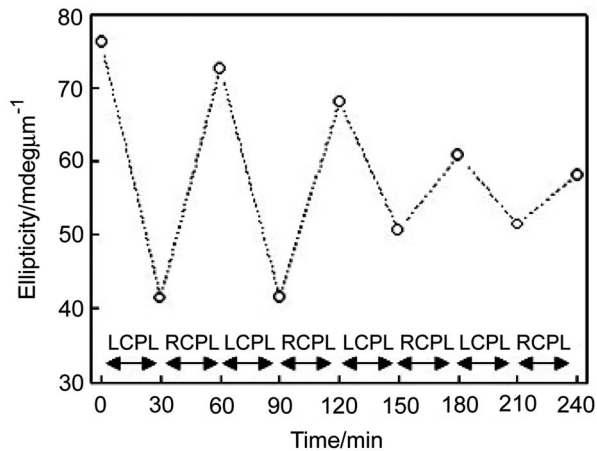


FIG. 3. Optical switching of CD at 265 nm for the intrinsic inert mesogens by alternating irradiation with right and left CPL.

W-shaped molecules seems to promote the reorientation of the PLC matrix. This cooperative motion effect is similar to that observed in an achiral side-chain polymer liquid crystal system [10]. The other notable feature is that the CD signals induced by opposite CPL are perfect mirror images, indicating that enantiomeric chiral structures were produced by CPL of opposite handedness. Moreover, it is also notable that the photoinduced chirality of this main-chain system can be maintained constant at least for several months at room temperature, unless the films are heated up above the glass transition temperature ($T_g=90^\circ\text{C}$) of the polymer.

For the next step, we examined the photomodulation of this phenomenon for W-doped film on alternating CPL irradiation at room temperature. Figure 3 shows the changes of the CD signal at 265 nm for the W-doped film by alternating irradiation with RCPL and LCPL at room temperature. The first data point (0 min) was taken after irradiating a virgin sample with RCPL for 120 min. The following points were taken after the alternating irradiation with LCPL and RCPL for 30 min. In this way, a repeatable circular anisotropy change was found to be possible by alternating irradiation with RCPL and LCPL. Although the film prepared here consisted of multiple domains, the repeatable photomodulation was also observed at different spots on the same films. Thus, the photomodulation does not depend on the specific domains on the film. We also confirmed the CD sign change with the LCPL irradiation of 150 min at room temperature. There are several examples for photomodulation in multidomain phase. Recently, Rochon *et al.* have also reported the optical switch based on the change of chirality in prochiral multidomain polymer film using CPL [8,10]. This photomodulation of chiroptical properties of materials can lead to the development of materials for reversible optical storage. Unfortunately, the CD signal gradually decreases with an increase of irradiation cycles and irradiation times. Since original performance is recovered back by thermal treatment above T_g of W-doped film, no decomposition of molecules takes place. We can suspect that azobenzene chromophores become less active due to partial reorientation along the light propagation direction, as already reported [10], resulting in

the decrease of the amplitude of the CD variation.

We presented photoinduced circular anisotropy properties in thin films of a main-chain polymeric liquid crystal system doped with photochromic W-shaped azobenzene molecules as a chiral trigger. It was found that the levels of photoinduced chirality of our main chain system are comparable to that of side-chain liquid crystalline systems [10]. It is also notable that when we use another kind of rodlike azobenzene molecules such as disperse red 1 (DR1), the induced chirality was quite low at the same irradiation condition, indicating W-shaped azobenzene molecules with molecular chirality is one of good candidates for photoinduced chirality.

IV. DISCUSSION

A. Analysis of the observed CD spectra

Circular dichroism spectroscopy measures differences in the absorption of left-handed polarized light versus right-handed polarized light. Thus, if there are chiral structures, the CD spectrum can be observed at the absorption band. So, by absorption spectrum analysis, the observed CD can be predicted. To explain and confirm the origin of the observed photoinduced circular anisotropy, we analyzed the observed CD spectrum of the W-doped film using the coupled oscillator method; the DeVoe polarizability model for optical activity [11,12]. The DeVoe polarizability model is particularly useful to carry out quantitative calculations of the intensity of Cotton effects due to electrically allowed transition. In the DeVoe model, the W-doped PLC system is considered to be composed of a set of subsystems, the chromophores, which are polarized by the external electromagnetic radiation and are coupled to each other by their own dipolar oscillating fields. The optical properties (such as absorption, refraction, optical rotatory dispersion, CD, etc.) of the molecules can be calculated by taking into account the interaction of the subsystems. Each subsystem is represented in terms of one (or more) oscillator(s): each oscillator brings about an electric dipole allowed transition, defined by the polarization direction e_i and the complex polarizabilities $\alpha_i(\lambda)=R_i(\lambda)+iI_i(\lambda)$, where $R_i(\lambda)$ and $I_i(\lambda)$ are, respectively, the real and imaginary parts of the i th complex polarizability relevant to the electric absorption of each subsystem at a wavelength λ . $I_i(\lambda)$ is obtainable from the absorption band of the W-doped PLC system and $R_i(\lambda)$ can be also calculated from $I_i(\lambda)$ by means of the Kramers-Kronig transformation.

The simplified formulation of CD as a wavelength-dependent function is given by

$$\Delta\varepsilon(\lambda) \approx \frac{96}{3298} \pi^2 \vec{\gamma}_{12} \cdot (\vec{e}_1 \times \vec{e}_2) G_{12} \lambda^2 I(\lambda) R(\lambda), \quad (1)$$

where e_1 is a unit vector representing oscillator 1, e_2 is the same for the oscillator 2, γ_{12} is a vector representing the distance vector between the locations of the oscillator 2 and the oscillator 1, G_{12} is the point-dipole-point-dipole interaction energy. Calculation of $\Delta\varepsilon(\lambda)$ requires calculation of the geometrical factor $(e_1 \times e_2) \cdot \gamma_{12}$, G_{12} , and the values $I(\lambda)$ and $R(\lambda)$. The detailed analysis method is described in Ref. [12].

In our case, to make analysis simpler, we considered only values $I_i(\lambda)$ and $R_i(\lambda)$ from the absorption spectrum of the

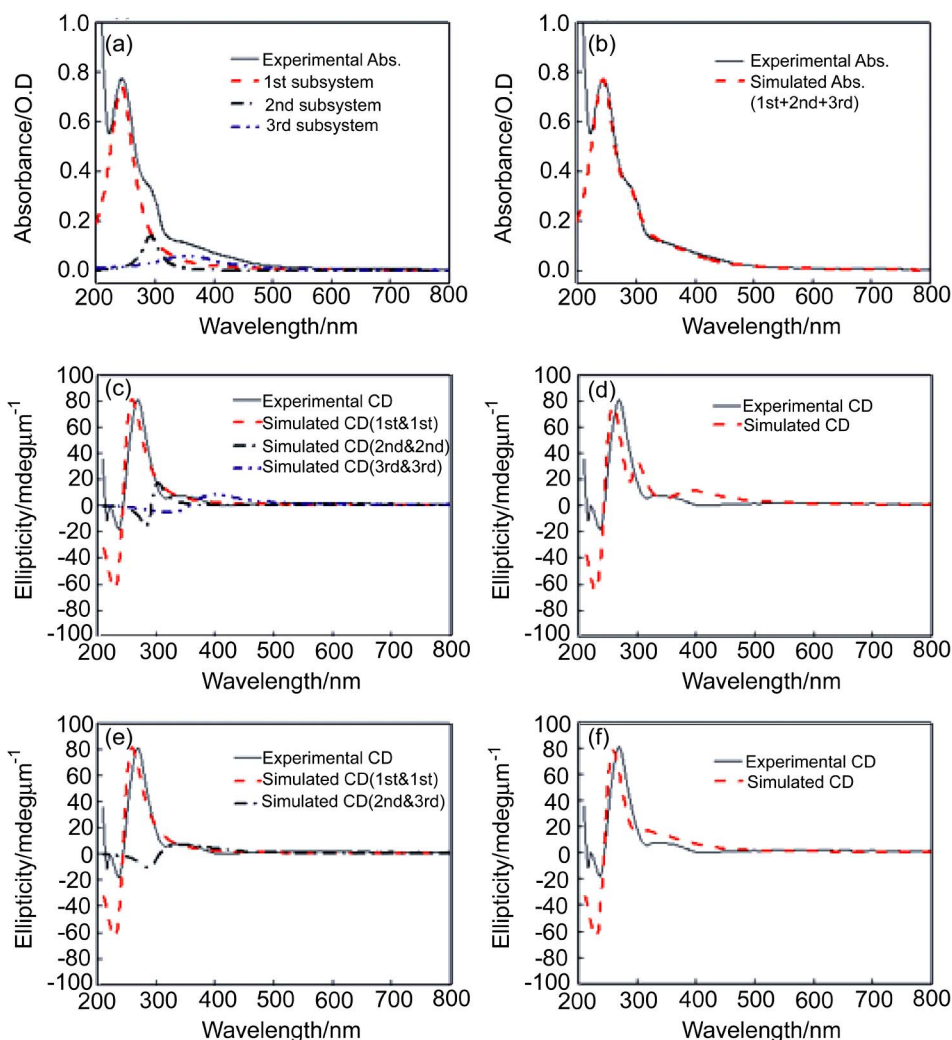


FIG. 4. (Color online) (a) The absorption spectrum of the main-chain polymeric liquid crystal film doped with W-shaped molecules. The spectrum is decomposed into three bands, two of which (first and second) are assigned to the transition in the host PLC matrix, and the other to that in the W-shaped molecule. (b) Comparison between the absorption spectrum by summing up the decomposed ones and the experimental one. (c) CD spectra simulated by considering coupled oscillators within the subsystems corresponding to each first (red dashed line), second (black dash-dotted line), and third (blue dash-dot-dotted line) peaks. (d) Comparison between the experimental and simulated CD spectra. (e) CD spectra simulated by considering a coupled oscillator within the subsystem corresponding to the first peak (red dashed line) and a coupled oscillator between subsystems corresponding to the second and third peaks (black dash-dotted line). (f) Comparison between the experimental and simulated CD spectra, successfully displaying the large Cotton band at around 250 nm and the small and broad CD band at 300–400 nm with uncompleted Cotton effect. The agreement is satisfactory.

film, and geometrical factors were assumed to be constants. In Fig. 4(a), we decomposed the absorption spectrum of the W-doped PLC film into three absorption bands (subsystems) assuming a Lorentzian shape, which are referred to as the first, second, and third subsystems. As shown in Fig. 4(b), the decomposition is successfully achieved except for the fundamental absorption band in the uv region. Comparing the absorption spectrum of the pure PLC film with that of the W-doped PLC film, the first and second subsystems are assigned to the transition in the host PLC matrix, and the third subsystem is that in the W-shaped molecule.

First, from the oscillators within the first subsystem, we obtained a theoretically calculated CD curve, which agrees well with the experimentally observed major CD peak after the irradiation with RCPL, as shown by the dashed (red) line

in Fig. 4(c), although the signal in the shorter wavelength region deviates from the simulation because of the influence of the fundamental absorption. It strongly indicates that the large Cotton effect (two CD bands of opposite sign are located at about 265 and 235 nm with a crossover point at about 250 nm) originates from the coupling between the oscillators within the subsystem corresponding to the first absorption band.

Next, we applied the same procedure to calculate the CD spectra for the second and third absorption peaks [Fig. 4(c)]. However, the obtained overall CD spectrum is significantly different from the experimental one, as shown in Fig. 4(d). Then, we considered the *intercoupling* between second and third subsystems. For the simulation, we used $I_2(\lambda)R_3(\lambda) + I_3(\lambda)R_2(\lambda)$ instead of $I(\lambda)R(\lambda)$ in Eq. (1), where the sub-

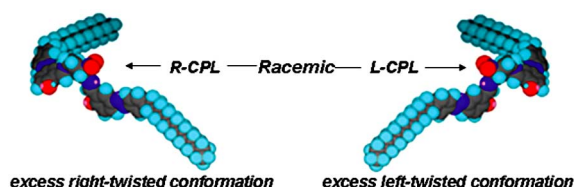


FIG. 5. (Color online) The most stable conformation calculated by MOPAC of the *W*-shaped azobenzene molecule is the twisted conformation. In a certain domain, the net excess of one population over that with the opposite enantiomer in the *W*-doped film is negligibly small, i.e., the mixture is racemic in the initial state. With increasing CPL irradiation, the statistical population with an enantiomeric excess of the *W*-shaped molecules is increasing.

scripts second and third respectively refer to the second and third subsystems. The calculated CD spectrum exhibits a small and broad CD band at 300–400 nm, as shown by the dash-dotted (black) curve in Fig. 4(e). The agreement between the obtained overall CD spectrum and the experimental one is satisfactory, as shown in Fig. 4(f), indicating that the host (second subsystem) and the *W*-shaped molecule (third subsystem) cooperatively interact with each other after CPL irradiation. According to the theoretical analysis described above, the observed CD spectra in the *W*-doped PLC film is due to a coupling between the oscillators between subsystems (between the second and third subsystems) as well as within a subsystem (within the first subsystem).

B. Mechanism of photoinduced circular anisotropy

The mechanism of the induced chirality in our system is not fully understood until now, but possible explanations can be made; i.e., (1) induced enantiomeric excess with imbalance in two enantiomers of the *W*-shaped molecule by CPL irradiation in a *W*-doped film, and (2) transfer of molecular chirality of the *W*-shaped molecule to a host main-chain PLC.

For the first step, we need to take a look at the conformational twisted structure of the *W*-shaped molecule in the *W*-doped film. The distinct fact that bent-core molecules with a twisted conformation enhance the twisting power in the chiral nematic phase was reported by Thisayukta *et al.* [15]. The twisted conformation in the *W*-shaped molecule is also strongly supported by MOPAC calculation as the most stable one, as shown in Fig. 5. Actually, it is known that the *W*-shaped molecules spontaneously resolve into two chiral domains as reported previously [13,14]. The chirality with opposite handedness can be obtained by the opposite preferential twisted conformation of the *W*-shaped molecules.

In a certain domain, if the net excess of one population over that with the opposite enantiomer in the *W*-doped film is negligibly small, this system can be regarded as racemic. Next, with increasing RCPL irradiation, the electric field direction rotates right along the beam, which transfers angular momentum from the RCPL to the *W*-shaped molecules, and then the net population with the right-twisted conformation of the *W*-shaped molecules increase, namely, macroscopic (+)-handedness chirality is induced in our prepared films. It

is well known that, when a CP photon is absorbed, transfer of angular momentum from the CPL to the medium induces precession of the chromophores with a sense of rotation consistent with the sense of the CPL [18–20]. Therefore, in the case of LCPL irradiation, the net population with the left-twisted conformation of the *W*-shaped molecules increases, namely, macroscopic (–)-handedness chirality is induced. These asymmetric photoreactions by CPL irradiations can be regarded as a kind of photoresolution reaction [21].

Now the next question is how the induced preferential chirality of *W*-shaped molecules induces a reorientation of the main-chain PLC; i.e., is the induced chirality of *W*-shaped molecules transferred to a host main-chain PLC? First, the *trans-cis* isomerization of the *W*-shaped molecules can nucleate free volumes and perturb the initial polymer backbone ordering of *W*-doped PLC film during the CPL irradiation. Next, under the condition of induced free volumes and the induced perturbation state, the transfer of angular momentum from the CPL triggers the statistical population of the preferential ordering of *W*-shaped molecules, forcing the polymer backbone to reorient with a massive displacement of the polymer material. Finally, according to this realignment of the polymer backbone, locally formed exciton coupling with a preferential sense would generate the ellipticity in the region of corresponding electrically allowed transition of the *W*-doped PLC film as observed experimentally. Actually the photoinduced chirality is observed only in systems containing photochromic bonds such as azobenzene bonds. In particular, the *W*-shaped molecules containing two azobenzene groups are more apt to nucleate the free volume between the polymer backbone, in which the *W*-shaped molecules easily change their conformation and/or orientation, transforming themselves to a preferential twisted conformation by CPL irradiation.

Here, it is necessary that significant change develops even in the glassy phase of the main-chain PLC with nematic alignment. Such a reorientation is possible when the effective T_g could be substantially lowered. Actually the T_g of polymer surfaces is known to be remarkably lower than that of the bulk [22]. It is true that the effective surface is nucleated by the induced free volume due to the photoisomerization mentioned above. Not only the lowering of T_g but also local heating induced by photoabsorption may be also responsible for the assisting photoinduced reorientation, as is reported by Tripathy *et al.* [23]. In this way, with increasing CPL exposure, the change of the statistical population of the twisted conformation with a preferential twist of the *W*-shaped molecule can lead to reorientation of the main-chain PLC, resulting in induced circular anisotropy in our system.

Rochon *et al.* [8,9] suggested that this process induces a chiral structure of azobenzene chromophores in the side-chain polymer film similar to that present in cholesteric liquid crystals with a large pitch, namely, a macroscopic helix may be induced in their system. However, in our *W*-doped film, the formation of a macroscopic helix was not recognized. Our alternative origin for this induced chirality is locally formed exciton coupling with a preferential sense. The nucleation of coupled oscillators with a preferential twist by the irradiation of CPL is attributed to a transfer of the angular

momentum from the CPL to the medium and the preferential twisted conformation of the *W*-shaped molecule itself, forcing the host polymer backbone to reorient with a massive displacement. Our model is free from the unrealistic cartoon that main-chain polymers form macroscopic helix structures. Furthermore, the local exciton coupling model may even provide an alternative model for the systems of Rochon *et al.*

V. CONCLUSIONS

We have demonstrated that a CPL-induced circular anisotropy can be achieved in photochromic *W*-shaped-azobenzene-molecule-doped main-chain PLC systems. By doping the *W*-shaped azobenzene molecules, the thin film of an intrinsically inert main-chain PLC matrix becomes photoresponsive on irradiation with CPL. A photomodulation by alternating irradiation with CPL of opposite handedness was

demonstrated. The experimentally observed CD spectra were analyzed using the DeVoe polarizability model associated with the coupled oscillator method. The theoretically calculated circular dichroism agreed well with the experimentally observed CD spectra. We also proposed a mechanism for the photoinduced chirality; nucleating the *W*-shaped molecules with preferential twisted conformation by CPL irradiation, and triggering the local formation of a chiral structure in the *W*-shaped-molecule-doped main-chain PLC medium.

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- [1] B. L. Feringa, R. A. van Delden, N. Koumura, and E. M. Geertsema, *Chem. Rev. (Washington, D.C.)* **100**, 1789 (2000).
- [2] A. Natansohn and P. Rochon, *Adv. Mater. (Weinheim, Ger.)* **11**, 1387 (1999).
- [3] C. Barrett, B. Choudhury, A. Natansohn, and P. Rochon, *Macromolecules* **31**, 4845 (1998).
- [4] J. Kumar, L. Li, X. L. Jiang, D. Y. Kim, T. S. Lee, and S. Tripathy, *Appl. Phys. Lett.* **72**, 2096 (1998).
- [5] S. Balasubramanian, X. G. Wang, H. C. Wang, K. Yang, J. Kumar, S. Tripathy, and L. Li, *Chem. Mater.* **10**, 1554 (1998).
- [6] L. Nikolova, T. Todorov, M. Ivanove, F. Andruzzi, S. Hvilsted, and P. S. Ramanujam, *Opt. Mater.* **8**, 255 (1997).
- [7] L. Nikolova, L. Nedelchev, T. Todorov, Tz. Petrova, N. Tomova, V. Dragostinova, P. S. Ramanujam, and S. Hvilsted, *Appl. Phys. Lett.* **77**, 657 (2000).
- [8] G. Iftime, F. L. Labarthe, A. Natansohn, and P. Rochon, *J. Am. Chem. Soc.* **122**, 12646 (2000).
- [9] D. Hore, Y. Wu, A. Natansohn, and P. Rochon, *J. Appl. Phys.* **94**, 2162 (2003).
- [10] Y. Wu, A. Natansohn, and P. Rochon, *Macromolecules* **37**, 6801 (2004).
- [11] H. DeVoe, *J. Phys. Chem.* **75**, 1509 (1971).
- [12] S. Superchi, E. Giorgio, and C. Rocini, *Chirality* **16**, 422 (2004).
- [13] N. V. S. Rao, M. K. Paul, I. Miyake, Y. Takanishi, K. Ishikawa, and H. Takezoe, *J. Mater. Chem.* **13**, 2880 (2003).
- [14] I. Miyake, Y. Takanishi, N. V. S. Rao, M. K. Paul, K. Ishikawa, and H. Takezoe, *J. Mater. Chem.* **15**, 4688 (2005).
- [15] J. Thisayukta, H. Niwano, H. Takezoe, and J. Watanabe, *J. Am. Chem. Soc.* **124**, 3354 (2002).
- [16] D. J. Earl, M. A. Osipov, H. Takezoe, Y. Takanishi, and M. R. Wilson, *Phys. Rev. E* **71**, 021706 (2005).
- [17] K. Shiromo, D. A. Sahade, T. Oda, T. Nihira, Y. Takanishi, K. Ishikawa, and H. Takezoe, *Angew. Chem., Int. Ed.* **44**, 1948 (2005).
- [18] I. Naydenova, L. Nikolova, P. S. Ramanujam, and S. Hvilsted, *J. Opt. A, Pure Appl. Opt.* **1**, 438 (1999).
- [19] L. Angiolini, R. Bozio, L. Giorgini, D. Pedron, G. Turco, and A. Dauri, *Chem.-Eur. J.* **8**, 4241 (2002).
- [20] M. E. J. Friese, T. A. Nieminen, N. R. Heckenberg, and H. Rubinsztein-Dunlop, *Nature (London)* **394**, 348 (1998).
- [21] B. L. Feringa and R. A. van Delden, *Angew. Chem., Int. Ed.* **38**, 3419 (1999).
- [22] T. Kajiyama, K. Tanaka, N. Satomi, and A. Takahara, *Sci. Technol. Adv. Mater.* **1**, 31 (2000).
- [23] D. Y. Kim, L. Li, X. L. Jiang, V. Shivshankar, J. Kumar, and S. Tripathy, *Macromolecules* **28**, 8835 (1995).