Photorefractive Properties of the Isotropic Phase of Cyanobiphenyl Side-chain Liquid Crystalline Polymers

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(Received November 15, 2001; CL-011153)

The photorefractive properties of side-chain liquid crystalline polymers possessing cyanobiphenyl chromophores were investigated. The diffraction efficiencies were found to be strongly dependent on temperature. It was found that the refractive index grating persisted after the writing beams were blocked. The persistence of the grating was strongly affected by the length of the alkyl spacer chain that connects the mesogen with the polymer main chain.

The photorefractive effect in organic polymers has been extensively studied since it was first reported in 1991.[1] Organic photorefractive materials are comprised of three components; a nonlinear optical chromophore, a photoconductive compound, and an electron trap reagent.[2] When two laser beams interfere in a photorefractive material, a refractive index grating is created. The mechanism of the creation of this refractive index grating consists of two processes; the generation of a space-charge field (internal electric field) due to charge separation between the bright and dark areas of the interference, and a subsequent change in the refractive index via an electrooptic effect (Pockels effect). The photorefractivity of organic materials is greater than that of inorganic materials because organic materials have larger Pockels constants. Furthermore the internal electric field induces a reorientation of the component chromophores, which adds to the photorefractivity.[2–11] Recently, we have reported the photorefractive properties of the isotropic phase of liquid crystalline (LC) polymers.[12] The diffraction efficiency was found to be enhanced in the isotropic phase of LC polymers compared to amorphous polymers with almost identical molecular structures. In this study, the temperature dependence of the diffraction efficiencies of the isotropic phase of cyanobiphenyl liquid crystalline polymers was measured by four-wave mixing experiments. The persistence of the index grating after the writing beams were cut off was also investigated. The memory effect of the photorefractive grating is of interest for its application in holographic memories.[13,14] However, there have been no report on the investigation of the memory effect of the photorefractivity of polymer materials.

The structures of the compounds used in this study are shown in Figure 1. Cyanobiphenyl side-chain polymers (CBn) with three different spacer lengths ($n = 6, 11, 12$) were used as host polymers. The molecular weights and the phase transition temperatures of the CBn polymers are listed in Table 1. CDH (45 wt%) was incorporated as a photoconductive compound, and TNF (1 wt%) was used as a sensitizer/electron trap reagent. The concentrations of the photoconductive compounds were set such that the host polymers did not exhibit the liquid crystal phase. The mixture of CDH/TNF/CBn was sandwiched between two pieces of ITO glass and the film thickness was adjusted to be 100 μm. The samples were optically isotropic and transparent. The four-wave mixing experiments were performed using two s-polarized writing beams (beam 1 and 2) and a p-polarized probe beam (beam 3), counter-propagating to one of the writing beams (see Figure 3 inset). An external electric field of 40 V/μm was applied to the sample. A He–Ne laser (Mellesgriot, 633 nm, 6 mW output) was used as a light source. Beam 1 and beam 2 interfered inside the sample film, and the intensity of the diffraction of beam 3 (beam 4) was measured by a photodiode (E-O TECH ET2010, response < 1 ns) and recorded by a storage-oscilloscope. The angle between the two writing beams was 7.7 ° inside the film, the refractive index of the samples was 1.65, and the grating period was 2.8 μm. The diffraction efficiency is defined as $\Delta I/I_0$, where I_0 represents the transmitted intensity of beam 3 through the sample without beams 1 and 2, and ΔI represents the intensity of the diffracted beam.

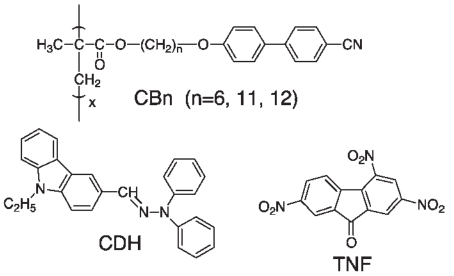

Figure 1. Structures of compounds.

The temperature dependences of the diffraction efficiencies of CDH/TNF/CBn are shown in Figure 2. The glass transition temperatures (Tg) of CDH/TNF/CBn mixtures that could not be detected in DSC measurements must be lower than those of pure polymers, however, a large change in diffraction efficiency was observed around the Tg of the pure polymer. The diffraction efficiencies of CBn are very small at lower temperatures. The diffraction efficiency becomes larger as the temperature rises above the polymer's Tg. At higher temperatures, the film is

Table 1. Properties of polymers

	Mn	Mw	Mw/Mn	Phase transition temperature[a]/°C				
CB6	16000	20000	1.2	g	60	N	114	I
CB11	26000	61000	2.3	g	38	Sm	119	I
CB12	36000	55000	1.5	g	34	Sm	123	I

[a] g, glassy state; Sm, smectic phase; N, nematic phase; I, isotropic phase.

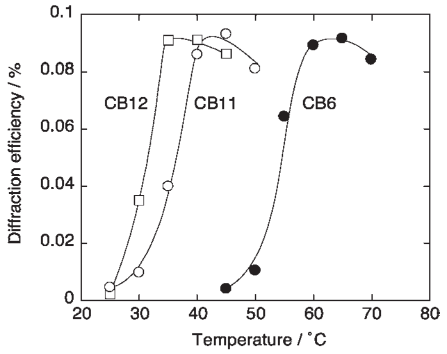

Figure 2. Temperature dependences of diffraction efficiencies of CBn/CDH/TNF mixtures.

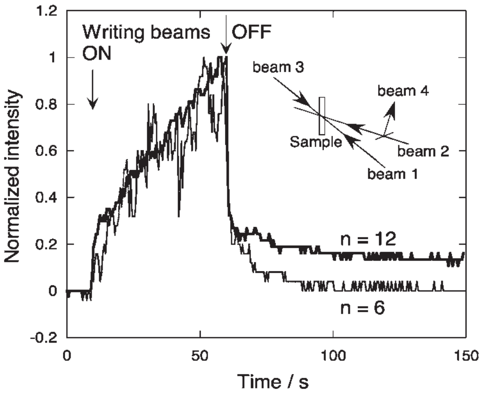

Figure 3. Diffraction signals of CB12 and CB6 mixed with 40% of CDH and 1 wt% of TNF measured at 30 °C.

softened and can be polarized readily by the external electric field and a larger electrooptic effect can be induced. In addition, the mesogens become more mobile and hence the orientational photorefractive effect can be induced more effectively by the photoinduced internal electric field. Figure 3 shows the diffraction signals observed in the CB6 and CB12 samples. When the irradiation of the sample by the writing beams was stopped, the intensity of the diffraction signal dropped sharply, but did not drop completely to zero immediately. A weak signal could still be observed after both writing beams were cut off. This persisting diffraction signal was observed in polymers with spacer chains longer than n = 11. A memory effect in the index grating in low-molecular-weight LC/polymer composites has been reported elsewhere.[15] This memory effect of the diffraction in LC/polymer composites arises from the persistence of the orientational grating and its origin has not been identified. However, it is thought that the orientational grating of the mesogens is stabilized by the presence of the polymer. Considering that the persistence of the index grating was observed only in CBn with longer spacer chain ($n > 11$), the mobility of mesogens plays an important role in the memory effect of the photorefractivity. The persistence of the diffraction in CBn is not observed when the temperature is raised above 45 °C. It is inferred that the orientational grating is disturbed by the thermal motions of the cyanobiphenyl chromophores. The intensity of the persisting signal was larger at lower CDH concentrations. At higher CDH concentrations, Tg decreases as the orientational grating cannot be sustained because of thermal motions of the mesogens. In addition, the interaction between the chromophores and the alkyl chains are reduced by the presence of the dopant. Thus, the persistence of the orientational grating is enhanced in polymers with longer spacer chains and lower CDH concentrations.

References

1 S. Ducharme, J. C. Scott, R. J. Twieg, and W. E. Moerner, *Phys. Rev. Lett.*, **66**, 1846 (1991).
2 W. E. Moerner and S. M. Silence, *Chem. Rev.*, **94**, 127 (1994).
3 K. Meerholz, B. L. Volodin, B. Kippelen, and N. Peyghambarian, *Nature*, **371**, 497 (1994).
4 W. K. Chan, Y. Chen, Z. Peng, and L. Yu, *J. Am. Chem. Soc.*, **115**, 11735 (1993).
5 Z. Peng, Z. Bao, and L. Yu, *J. Am. Chem. Soc.*, **116**, 6003 (1994).
6 Z. Peng, A. R. Gharavi, and L. Yu, *J. Am. Chem. Soc.*, **119**, 4622 (1997).
7 Y. Cui, B. Swedek, N. Cheng, K. S. Kim, and P. N. Prasad, *J. Phys. Chem. B*, **101**, 3530 (1997).
8 A. Grunnet-Jepsen, C. L. Thompson, and W. E. Moerner, *Science*, **277**, 549 (1997).
9 B. Kippelen, S. R. Marder, E. Hendrickx, J. L. Maldonado, G. Guillemet, B. L. Volodin, D. D. Steele, Y. Enami, Sandalphon; Y. J. Yao, J. F. Wang, H. Röckel, L. Erskine, and N. Peyghambarianl., *Science*, **279**, 54 (1998).
10 K. Meerholz, Y. D. Nardin, R. Bittner, R. Wortmann, and F. Wurthner, *Appl. Phys. Lett.*, **73**, 4 (1998).
11 E. Hendrickx, J. F. Wang, J. L. Maldonado, B. L. Volodin, E. A. Mash, A. Persoons, B. Kippelen, and N. Peyghambarian, *Macromolecules*, **31**, 734 (1998).
12 T. Sasaki, M. Goto, Y. Ishikawa, and T. Yoshimi, *J. Phys. Chem. B*, **103**, 1925 (1999).
13 L. Solymar, J. D. Webb, and A. Grunnet-Jepsen, "*The Physics and Applications of Photorefractive Materials*," Oxford, New York (1996).
14 P. Yeh, "*Introduction to Photorefractive Nonlinear Optics*," Wiley, New York (1993).
15 H. Ono and N. Kawatsuki, *Jpn. J. Appl. Phys.*, **36**, 6444 (1997).