Photorefractivity in polymer dissolved liquid crystal composites composed of low-molecular-weight nematic liquid crystals and copolymer comprising mesogenic side groups

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Abstract

This paper describes the photorefractive effect of the liquid crystalline composite materials comprising low-molecular-weight nematic liquid crystals (L-LC), copolymer with mesogenic side groups and a small amount of photosensitizer. Copolymers with four kinds of mesogenic side groups were investigated with respect to the compatibility between the L-LC and the copolymer and the photorefractivity of the composites. Two of them could be miscible with L-LC and the composite exhibited LC phase even though the copolymer itself did not show a LC phase. High gain coefficients ($>200$ cm$^{-1}$) under the low applied dc electric field ($<1$ V/μm) was observed when the composites showed a mesophase without any macroscopic phase separation.

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1. Introduction

Photorefractive (PR) effect is a light-induced change in refractive index of an electrooptical material, and many applications such as real-time optical holography, optical image amplification, phase conjugate mirrors, etc. are proposed by the use of PR materials [1]. Since Moerner et al. investigated the PR effect in organic polymers in 1991 [2], several types of organic PR materials have emerged because of their high PR performance, variety of material design, and lower cost than inorganic crystals. Many kinds of compositional PR materials containing photoconductive polymers with nonlinear optical (NLO) chromophore have been investigated although such a material requires high operation electric field to obtain a photorefractivity [2–8]. A large PR effect was also found by the use of orientational PR effect of a low-molecular-weight liquid crystal (L-LC) system [9]. Khoo et al. showed high PR gain coefficient of the L-LC system by doping with fullerene to give photoconductivity [9,10]. The advantage of the LC system is that PR gratings can be written at a low electric field and that no NLO chromophore is necessary to induce the photorefractivity. However, such a good PR performance in the L-LC systems is only observed in the Raman-Nath region, which is not suitable for high-resolution applications. Therefore, several efforts have been carried out to improve the resolution by combining the L-LC with a polymer.

The first approach was carried out by the use of polymer dispersed LCs (PDLCs) with doping a photosensitizer [11,12]. The high-resolution PR grating could be observed, but this system is not transparent against a slantwise incident light beam because of its phase-separated structure. Polymer-stabilized LC using a small amount of polymer was also applied to the PR material although its two-beam-coupled gain-coefficient in the Bragg region was very small around 10 cm$^{-1}$ [13,14]. For the high-performance PR materials, we proposed 'polymer dissolved LC composites (PDLCCs)', in which the polymer was dissolved in L-LC...
and the composite showed no phase separation [15–19]. When a polymer exhibits liquid crystallinity, it can be dissolved in L-LC with a small amount of fullerene [15]. A transparent PR sample is easily fabricated by aligning the entire mesogenic groups homeotropically. This type of PDLCC exhibited a gain coefficient of 200 cm K$^{-1}$ or more at 0.2 V/mm dc electric field [15–17]. Furthermore, it is not necessary for the polymer to exhibit liquid crystallinity if the polymer/L-LC mixture for itself showed a LC phase without phase separation [18–21]. We found that a methacrylate copolymer with a mesogenic 4-cyanophenylbenzoate side group and an N-ethylcarbazoyl side group, which was an amorphous polymer, can be dissolved in L-LC and the composite exhibited a liquid crystalline phase when the composition of the copolymer was less than 40 wt-% in the mixture. This type of PDLCC also exhibited good PR performances [18–21].

However, all the (co)polymers in our PDLCC system so far have been studied only by the use of a 4-cyanophenylbenzoate as a mesogenic side group. In this paper, to study an influence of the chemical structure of the mesogenic side group in the polymer unit, copolymers with four kinds of mesogenic side groups and N-ethylcarbazoyl side group were synthesized and the synthesized copolymers were applied to the PDLCC (Fig. 1). The copolymers were mixed with L-LC doped with a small amount (<0.3 wt-%) of 2,4,7-trinitro-9-fruorenone (TNF) as a photosensitizer [18]. The miscibility among the materials was investigated by a differential scanning calorimetry (DSC) and a polarization optical microscopy observation, and the photorefractivity of the PDLCC was evaluated by a two beam coupling method. Furthermore, effect of the amount of TNF in the PDLCC on the photorefractivity and the PR response was explored.

2. Experimental

2.1. Materials

The nematic liquid crystal mixture of E7 (BDH-Merck Japan) was used as L-LC. The chemical structure and composition of E7 is shown in Fig. 2. TNF was obtained from Tokyo Kasei Chemicals and recrystallized from chloroform prior to use. The E7 was doped with 0.02–0.3 wt-% of TNF prior to use. 6-(4-Cyanophenylbenzoate-4-yloxy)hexyl methacrylate, 6-(4-methoxyphenylbenzoate-4-yloxy)hexyl methacrylate, 6-(4-nitrophenylbenzoate-4-yloxy)hexyl and 6-(4-dicyanovinylphenyl)benzoate-4-yloxy)hexyl methacrylate were synthesized according to the literature and a similar method in the literature [20]. N-(2-methacryloxyethyl)carbazoyl was obtained from OS-Tekuno. The (co)polymers were synthesized by a free radical (co)polymerization of corresponding methacrylate in THF solution with AIBN as an initiator. After the polymerization, a homogeneous solution was poured into excess diethyl ether to precipitate a polymer. The polymer was purified by reprecipitations for two times from chloroform solution and diethyl ether.

2.2. Characterization

The copolymer composition was determined by 1H-NMR spectroscopy with Bruker DRX-500. The number-average of molecular weight was measured by a gel permeation chromatography (GPC, Tosho-GPC system with TSK-GHM column) using chloroform as eluent. The transition temperatures were determined by DSC (Seiko-I, DSC-220) with a heating rate of 10 K/min. The miscibility of various compositions of the polymer and the L-LC was evaluated by the DSC and polarization optical microscope of Olympus BH-2P attached with a temperature-controlled stage of Linkam TH600PM. Photoconductivity was measured by a picoammeter of Keithley model 485 at a wavelength of 512 nm.

2.3. Sample preparation

The sample was prepared by mixing a copolymer (2 series) and E7 at 140 °C, and by stirring until the mixture became transparent. After cooling to room temperature, the mixture was used for thermal measurements of DSC and polarization optical microscopy. For the measurement of PR performances, the sample was prepared by mixing a copolymer (2 series) and L-LC (E7 doped with 0.02–0.3 wt/wt-% of TNF) at 140 °C (copolymer/L-LC = 20/80 wt/wt-%). This homogeneous solution was sandwiched between two indium-tin-oxide (ITO)-coated glass substrates with a 50 μm-thick polyimide film as a spacer. Once the mixture was cooled to room temperature, it
became opaque showing the mesogenic phase. In the case of copolymers 2a and 2b, since the copolymer was dissolved in L-LC, transparent film was obtained after application of dc-electric field of 0.6 V/\(\mu m\). Such a transparent film kept its homeotropic alignment state without the dc field. However, films from copolymers 2c and 2d did not exhibit a homeotropic alignment of the mesogenic groups due to a phase separation of the mixture. Detailed results will be discussed hereafter.

2.4. Measurement of PR performances

To investigate PR properties of the PDLCC, we performed two-beam coupling experiment in the tilted geometry as shown in Fig. 3. A linearly polarized beam from a He-Ne laser at 632.8 nm was divided into two beams (5.6 and 5.8 mW) and the polarization direction of both beams was controlled to the \(p\)-polarized direction. The sample was tilted at an angle \(q = 45^\circ\) relative to the bisector of the two incident beams, and the angle between the two beams was 16\(^\circ\).

3. Results and discussion

3.1. Polymer synthesis

All (co)polymers were synthesized by a radical solution polymerization in THF. Table 1 summarizes copolymer composition, molecular weight and thermal properties of the polymers. Homopolymers except 1d showed nematic liquid crystalline phase, while all copolymers 2a–2d showed no liquid crystallinity and showed one glass transition around 75–94 °C. These temperatures are higher than the clearing point \(T_i\) of E7 (60 °C). The loss of the liquid crystallinity for 2a—2c is because that copolymers contain large amount (\(\sim 50\%\)) of \(N\)-ethylcarbazoyl group in the side chain. Since copolymers 2a—2d contain \(N\)-ethylcarbazoyl group, the photoconductivity of the mixture is easily achieved by adding a small amount of TNF [18].

3.2. Miscibility of copolymer and L-LC

To investigate the compatibility among the materials, we first measured the DSC of mixtures of copolymer and E7. Parts a-d of Fig. 4 show DSC heating curves of each copolymer/E7 mixtures with various compositions. For copolymers 2a and 2b, the endothermic peak of \(T_i\) of E7 at 60 °C decreased and became broad when the copolymer was mixed with E7, and the peak became unclear when the composition of the copolymer was 40 wt-% and more, as shown in Fig. 4(a) and (b). For copolymers 2c and 2d, when the composition of the copolymer was 10 and 20 wt-%, the endothermic peak was broad and the \(T_i\) of E7 can be seen as shown in Fig. 4(c) and (d). When the composition of the copolymer was 40 wt-% and more, DSC curves became broad as was the case of copolymers 2a and 2b. In addition, the glass transition \(T_g\) of the copolymer disappeared when E7 was mixed with the copolymer for all cases. The decrease of \(T_i\) of E7 by mixing with 10–30 wt-% of copolymers 2a or 2b suggests that these copolymers could be dissolved in E7 and the mixture exhibits LC phase.

| Composition, molecular weight and thermal property of synthesized copolymers |
|---|---|---|---|
| R | Composition \(^a\) | \(X\) | \(M_w \times 10^4\) | \(M_w/M_n\) | Thermal property \(^c\) (°C) |
| 1a | CN | 0 | 1.98 | 1.61 | G 47 N 117 I |
| 1b | OCH\(_3\) | 0 | 3.06 | 2.30 | G 33 N 108 I |
| 1c | NO\(_2\) | 0 | 1.02 | 1.32 | G 35 N 98 I |
| 1d | C=2(CN)\(_2\) | 0 | 1.60 | 1.57 | G 59 I |
| 2a | CN | 50 | 5.35 | 2.41 | G 83 I |
| 2b | OCH\(_3\) | 50 | 7.08 | 2.27 | G 75 I |
| 2c | NO\(_2\) | 48 | 9.63 | 3.21 | G 86 I |
| 2d | C=2(CN)\(_2\) | 45 | 5.88 | 3.10 | G 94 I |

\(^a\) Determined by \(^1\)H-NMR.
\(^b\) Determined by GPC, polystyrene standards.
\(^c\) Determined by DSC.
The miscibility of copolymer/E7 was further observed by the polarization optical microscopy. When copolymers 2a or 2b was mixed with E7 (20/80 wt/wt-%), the mixture displayed a homogeneous LC texture at room temperature, suggesting that the copolymer be dissolved in E7. When the sample was heated again from this state, the mixture became isotropic around 55—59 °C for both polymer mixtures. This result is consistent with the DSC data as described above. Other compositions of 10 or 30 wt-% of the copolymer in E7 displayed similar textures. In addition, when a dc voltage of 0.6 V/μm was applied to these samples at 30 °C, the opaque sample film became transparent completely. For example, Fig. 5 shows conoscopic picture of the PDLCC film of 2b/E7 (20/80 wt/wt-%), indicating a homeotropic alignment of the mesogenic groups. This state was memorized under no dc-electric field and stable more than one year at room temperature. However, no-LC phase was observed and the mixture was transparent at room temperature when the composition of the copolymer was 60 wt-% or more. This is a consequence that the LC acts as a plasticizer in an amorphous polymer mixture. In this case, the homeotropic alignment could not be obtained under the dc-electric field because of no-liquid crystallinity of the sample.

In contrast, phase-separated structures were observed for copolymers 2c or 2d when it was mixed with E7 (10—30 wt% of the copolymer in the mixture). When the sample was heated, one phase became clear gradually around 52—60 °C, while another phase became clear at 60.5 °C, indicating that this phase consisted of E7. This result is also consistent with the DSC data. In addition, no-homeotropically-aligned film was obtained for the opaque sample using copolymers 2c or 2d.

It is known that a phase separation occurs when a polymer, such as PMMA which exhibits no-LC phase, is mixed with nematic liquid crystals [22,23]. In the case of copolymers 2a and 2b, E7 was compatible with the copolymer although it showed no-LC phase. The E7 may partially be dissolved in the copolymer 2c and 2d since both separated-phases exhibit mesogenic textures. It seems that the miscibility of the copolymer and E7 is dependent on
the chemical structure of the mesogenic side groups. Since the homopolymers 1a and 1b exhibited LC phase and the E7 contained both cyano- and alkoxy-groups, the miscibility of the mesogenic groups in 2a and 2b with E7 will be superior to that in 2c and 2d. It should be noted that the homopolymers 1a—1c are compatible with E7 and the homeotropic alignment is feasible regardless of the composition of the mixture because these homopolymers exhibit LC phase. If the copolymer exhibited no-LC phase, the nitro-group may not be suitable for the compatibility with E7. Therefore, both liquid crystallinity of the homopolymer and chemical structure of the side groups are important for the miscibility of the mixtures.

3.3. Photorefractivity of PDLCC films

Photorefractivity arises from the effect of simultaneous photoconductivity and electro-optic response in a material. The electro-optic response in the photorefractive PDLCC originates from reorientation of LC molecules. When a dc voltage of 0.2 V/µm was applied to the PDLCC film of 2a/E7/TNF (= 20/79.6/0.4 wt/wt/wt-%), a current under the dark state was 17.1 nA. Once the sample was irradiated by a frequency doubled Nd-YAG laser (wavelength, \( \lambda = 512 \) nm), the current increased to 17.6 nA. Other PDLCC samples exhibited similar change in current under the light irradiation.

To investigate PR properties of the PDLCCs, we performed two-beam coupling experiment in the tilted geometry as shown in Fig. 3. In this paper, transparent homeotropically-aligned PDLCC samples with copolymers 2a or 2b were used for the PR measurement, and the samples with copolymers 2c or 2d were not available since they showed a phase separation and no-homeotropic alignment of the film was obtained under the dc-electric filed. The gain coefficient (\( G \)) of the PDLCC film was calculated from Eq. (1).

\[
G = \frac{1}{d} \left[ \ln \frac{I_{12}}{I_1} - \ln \left( \frac{\xi + 1}{\xi + 1 + \frac{I_{12}}{I_1}} \right) \right] - \alpha, \tag{1}
\]

where \( \alpha \) is the sample absorbance, \( d \) is the thickness of the grating, \( \xi \) is \( I_1/I_2 \), \( I_1 \) is the intensity of beam 1 in the absence of beam 2, and \( I_{12} \) is the intensity of beam 1 with beam 2 applied. In this geometry, the grating pitch is 3.2 µm and the Q-value was around 18, indicating that the Bragg grating can be realized. In addition, the transparency of the sample is important to obtain a good PR performance since the scattering and the absorption of the incident light beam reduces the net gain coefficient. In our case, the absorption of the film was less than 10\(^{-2}\) at 632.8 nm and the film was completely transparent, resulting in \( \alpha < 2 \) cm\(^{-1}\). For example, Fig. 6 shows an asymmetric energy transfer signals in the two-beam coupling experiments using a sample of 2b/E7/TNF (20/79.92/0.08 wt/wt/wt-%). It shows that one beam gained the optical energy and another beam lost optical energy due to the two-beam coupling.

Fig. 7 plots the gain coefficient of the PDLCC film (copolymer/E7/TNF = 20/79.96/0.04 wt/wt/wt-%) as a function of an applied dc-electric field. 3.4. Effect of the TNF composition

To examine the effect of TNF composition on the PR performance of PDLCC films, the photorefractivity of
the sample with various composition of TNF was investigated. Fig. 8 plots the gain coefficient of the PDLCC film using copolymers 2a and 2b as a function of the TNF composition. The applied dc-electric field was 0.6 V/μm and the ratio of the copolymer/E7 doped with TNF was 20/80 wt/wt-% for all cases. It exhibits that the gain coefficient increases with increasing the TNF composition and it becomes a saturated value when the composition of TNF is 0.16 wt-% and more. The increase of the photorefractivity will be because that the photoconductivity is larger when the composition of TNF is increased as shown in Fig. 9. The reorientation of the L-LC could be more effective under the larger photocurrent because larger space charge field is expected to be generated in the heavier doping with TNF. In addition, since there was little difference in the influence of the TNF composition between copolymers 2a and 2b, the effect of the end group of the mesogenic side chain of the copolymer on the behavior of the PDLCC will also be small.

Finally, switching response of the PDLCC films was investigated. Fig. 10 plots the switching time (τ) of the sample film under 0.6 V/μm as a function of the TNF composition. The experimental conditions were the same as in Fig. 8. The τ was determined by measuring the increase of the intensity of the beam from 10 to 90% of its steady state after opening the another beam. The switching time τ was in the range between 195 and 374 ms for copolymer 2a, and between 143 and 292 ms for copolymer 2b, and became faster when the TNF composition was increased for both cases. The faster response in the larger TNF composition is caused by an increase of the space charge field in the PDLCC film. However, the switching response should be affected by the molecular weight of the polymers due to the viscosity of the materials as well as the mobility of photo-generated charges in the PDLCC system. Further study should be required to clarify these influences on the PR performance in the PDLCC system.

4. Conclusions

Methacrylate copolymers with different mesogenic side groups were synthesized, and the compatibility between the copolymer and L-LC was investigated for the application to PDLCC. The copolymer can be dissolved in L-LC and exhibited nematic LC phase when the copolymer composition was 30 wt-% or less for the copolymer 2a and 2b. On the other hand, a phase separation occurred for the copolymer 2c and 2d. The homeotropic alignment of the film was obtained under a dc-electric field if the mixture exhibited liquid crystallinity without phase separation, and these samples can be applied to the PR experiments. For all PDLCC films, high gain coefficients (> 200 cm⁻¹) under the
low applied dc-electric field (\(< 1 \text{ V/\mu m}\)) were obtained, and the gain coefficient increased and the response became faster when the composition of TNF in the PDLCC was increased regardless of the mesogenic side group in the copolymer. It is clear that further basic study of the relationship among the composition of the materials in the PDLCC, the type of the mesogenic side groups and their photorefractive properties is needed in order to improve the PR performance.

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References

[1] P. Günter, J.P. Huignard, Photorefractive Materials and their Applications, vols. 1 and 2, Springer, Berlin, 1988.
[2] S. Ducharme, J.C. Scott, R.J. Twieg, W.E. Moerner, Observation of the photorefractive effect in a polymer, Phys. Rev. Lett. 66 (1991) 1846–1849.
[3] W.E. Moerner, S.M. Silence, Polymeric photorefractive materials, Chem. Rev. 94 (1994) 127–155.
[4] M.E. Orczyk, B. Swedek, J. Aieba, P.N. Prasad, Enhanced photorefractive performance in a photorefractive polymeric composite, J. Appl. Phys. 76 (1994) 4995–4998.
[5] K. Ogino, T. Nomura, T. Shichi, S. Park, H. Sato, T. Aoyama, T. Wada, Synthesis of polymers having tetraphenyldiaminobiphenyl units for a host polymer of photorefractive composite, Chem. Mater. 9 (1997) 2768–2775.
[6] D. Wright, M.A. Diaz-Garcia, J.D. Casperson, M. DeClaue, W.E. Moerner, R.J. Tweig, High-speed photorefractive polymer composites, Appl. Phys. Lett. 73 (1998) 1490–1492.
[7] M.A. Diaz-Garcia, D. Wright, J.D. Casperson, B. Smith, E. Glazer, W.E. Moerner, L.I. Sukhominova, R.J. Tweig, Photorefractive properties of poly(N-vinyl carbazole)-based composites for high-speed applications, Chem. Mater. 11 (1999) 1784–1791.
[8] K. Meerholz, B.L. Volodin Sandalphon, B. Kippelen, N. Peyghambarian, A photorefractive polymer with high gain and diffraction efficiency near 100%, Nature 371 (1994) 497–500.
[9] I.C. Khoo, H. Li, Y. Liang, Observation of orientational photorefractive effects in nematic liquid crystals, Opt. Lett. 19 (1994) 1723–1725.
[10] I.C. Khoo, Holographic grating formation in dye- and fullerene C60-doped nematic liquid-crystal film, Opt. Lett. 20 (1995) 2137–2139.
[11] H. Ono, N. Kawatsuki, Orientational photorefractive effects observed in polymer-dispersed liquid crystals, Opt. Lett. 22 (1997) 1144–1146.
[12] A. Golemm, B.L. Volodin, B. Kippelen, N. Peyghambarian, Photorefractive polymer-dispersed liquid crystals, Opt. Lett. 22 (1997) 1226–1228.
[13] G.P. Wiederrecht, B.A. Yoon, M.R. Wasielewski, High photorefractive gain in nematic liquid crystals doped with electron donor and acceptor molecules, Science 270 (1995) 1794–1797.
[14] G.P. Wiederrecht, B.A. Yoon, W.A. Svec, M.R. Wasielewski, Photorefractivity in nematic liquid crystals containing electron donor–acceptor molecules that undergo intramolecular charge separation, J. Am. Chem. Soc. 119 (1997) 3358–3364.
[15] H. Ono, I. Saito, N. Kawatsuki, Photorefractive Bragg diffraction in high- and low-molar-mass liquid crystal mixtures, Appl. Phys. Lett. 72 (1998) 1942–1944.
[16] H. Ono, N. Kawatsuki, Response characteristics of high-performance photorefractive liquid crystals, Jpn. J. Appl. Phys. 38 (1999) 737–740.
[17] H. Ono, N. Kawatsuki, High-performance photorefractivity in high- and low-molar-mass liquid crystal mixtures, J. Appl. Phys. 85 (1999) 2482–2487.
[18] H. Ono, A. Hanazawa, T. Kawamura, H. Norigasa, N. Kawatsuki, Response characteristics of high-performance photorefractive mesogenic composites, J. Appl. Phys. 86 (1999) 1785–1790.
[19] H. Ono, T. Kawamura, N.M. Frias, K. Kitamura, N. Kawatsuki, H. Norigasa, Photorefractive mesogenic composites, Adv. Mater. 12 (2000) 143–146.
[20] H. Ono, K. Kitamura, N. Kawatsuki, Optical phase conjugation from phase-shifted gratings in photorefractive mesogenic composites, Liq. Cryst. 29 (2001) 1339–1345.
[21] H. Ono, H. Shimokawa, A. Emoto, N. Kawatsuki, Photorefractive liquid crystal-polymer dispersion with different morphology, J. Appl. Phys. 94 (2003) 23–30.
[22] T. Kajiyama, H. Kikuchi, A. Takahara, Polymer/(liquid crystal) composite systems for novel electro-optical effects, Proc. SPIE 1665 (1992) 20–31.
[23] H. Ono, N. Kawatsuki, Effects of molecular weight on morphology and electrooptical properties of poly(methylmethacrylate)/liquid crystal composites fabricated by a solvent-induced phase separation method, Polym. Bull. 35 (1995) 365–370.