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Preparation of Highly Efficient Polymeric Photorefractive Composite Containing an Isophorone-Based NLO Chromophore

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We synthesized 2-{3-[(*E*)-2-(dibutylamino)-1-ethenyl]-5,5-dimethyl-2-cyclohexenylidene}-malononitrile as a noval nonlinear optical (NLO) chromophore for photorefractive materials. The photorefractive polymeric composite composed of photoconducting carbazole-substituted polysiloxane, NLO chromophore, and 2,4,7-trinitro-9-fluorenone exhibited excellent photorefractive properties. The gain coefficient of the composite containing 30 wt % of chromophore was as high as 390 cm^{-1} at the electric field of 100 V/μm, which is one of the largest values obtained so far in the field of polymeric photorefractive materials. And the composite with a thickness of 60 μm showed the maximum diffraction efficiency of 56% at 30 V/μm.

Introduction

Photorefractive effect refers to the spatial modulation of the refractive index of materials due to the light-induced redistribution of charge.[1,2] To possess photorefractive properties, the material is required to possess photoconductivity and optical nonlinearity simultaneously. When nonuniform light, formed by the interference of two coherent laser beams, is illuminated on material, the photocharges are generated preferentially in the bright region. The generated photocharges are transported via diffusion or drift under the applied external field and are finally trapped in the dark region. The light-induced redistribution of the charge inside the material results in an internal electric field, according to Poisson's equation ($\mathrm{d}E/\mathrm{d}x = 4\pi\rho/\epsilon$, where ρ is space-charge density and ϵ is dielectric constant of material). After a spatially modulated space-charge field is formed, the refractive index of materials with optical nonlinearity is modulated through an electrooptic effect.

The photorefractive effect was first discovered in 1966 in a ferroelectric inorganic crystal, $LiNbO_3$.[3] During the nonlinear optical experiment, Ashkin et al. found the deformation of the wave front of the laser beam due to the optical modulation of the refractive index of the $LiNbO_3$ crystal, which was one year later recognized as a new optical phenomenon referred to as the photorefractive effect.[4] In the case of a polymeric system, the photorefractive effect was first found in 1991.[5] IBM researchers found the formation of photorefractive grating in polymeric material based on the nonlinear epoxy polymer bisphenol A diglycidyl diether 4-nitro-1,2-phenylenediamine (bisA-NPDA) doped with the hole-transporting agent (diethylamino)benzaldehyde diphenylhydrazone. The performance of the first polymeric photorefractive material was so poor as to exhibit a diffraction efficiency (η) of 5×10^{-5} % and the gain coefficient (Γ) of 0.33 cm^{-1}. Since the first discovery, however, significant improvement in the performance of the polymeric material was accomplished within a short research period. Only three years after the first discovery, the performance of a polymeric composite was reported to exceed its inorganic counterpart. In 1994, the poly-*N*-vinylcarbazole (PVK) composite doped with 2,5-dimethyl-(4-*p*-nitrophenylazo)anisole (DMNPAA, 50 wt %) chromophore, ethylcarbazole (ECZ, 16 wt %) as a plasticizer and 2,4,7-trinitro-9-fluorenone (TNF, 1 wt %) as a charge sensitizer, showed a large gain coefficient of 220 cm^{-1} and a diffraction efficiency of nearly 100% at the applied electric field of 90 V/μm.[6] Recently, the much improved polymer composite doped with 2,2-*N*,*N*-dihexylamino-7-dicyanomethylidenyl-3,4,5,6,10-pentahydronaphthalene (DHADC-MPN) chromophore[7] was reported, being compared with the previous polymeric materials. Due to the improved figure-of-merit of the DHADC-MPN chromophore, PVK:DHADC-MPN:ECZ:TNF composite in the weight % ratio of 39:40:19:2 showed an index modulation (Δn) of 4.4×10^{-3} at 40 V/μm and a maximum diffraction efficiency ($\eta_{\max} = 10\%$) even at 30 V/μm, which is one of the greatest performances reported so far. And significant improvement in the response speed was also accomplished in a polymeric composite with low glass transition temper-

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ature.[8] PVK composite doped with 2-[4-bis(2-methoxyethyl)amino]benzylidene]maloni-trile chromophore (AODCST, 35 wt %), butyl benzyl phthalate (BBP, 15 wt %) as a liquid plasticizer and C_{60} (0.5 wt %) as a charge generator, exhibited the fast response time of 5 ms as well as the large gain coefficient of 230 cm^{-1} at the light intensity of 1 W/cm^2 and the applied electric field of 100 V/μm, which shows the possibility of applying polymeric material to video-rate optical processing.

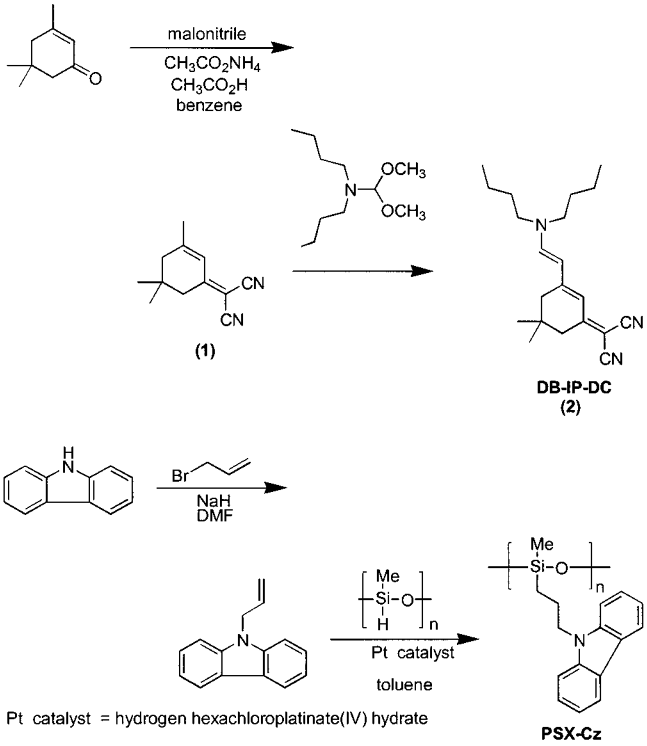
However, despite the rapid progresses accomplished for polymeric photorefractive materials,[6-8] polymeric systems have suffered from the usage of the high applied voltages required for obtaining the high photorefractive properties and the phase-separation due to the high dopant concentration, which are serious obstacles to the application of polymeric composites to the various optical applications. Consequently, to prepare photorefractive composite that is able to be used for practical optical devices, the effort to improve the photorefractive performance is still strongly required.

Therefore, in this work, we attempted to prepare a highly efficient photorefractive composite with long term phase stability. In the case of the photorefractive composite system consisting of photoconducting polymer and NLO chromophore, the magnitude of refractive index modulation and the phase stability are largely governed by the properties of the chromophore embedded in the photoconductive medium. Thus, we put an emphasis on the preparation of a novel chromophore with improved electrooptical property and compatibility with matrix polymer, and the photorefractive properties of a composite containing a new chromophore are discussed.

Experimental Section

Materials. Photoconducting poly[methyl-3-(9-carbazolyl)-propylsiloxane] (PSX-Cz) and 2-{[4-(dibutylamino)phenyl]-methylene}malononitrile (DB-Bz-DC) chromophore were synthesized by the previously described method.[9,10] 2,4,7-Trinitro-9-fluorenone (TNF), purchased from Kanto Chem. Co. Inc., was used after purification. A novel nonlinear optical chromophore, 2-{3-[(*E*)-2-(dibutylamino)-1-ethenyl]-5,5-dimethyl-2-cyclohexenylidene}malonitrile (DB-IP-DC) was synthesized using the reaction scheme, as shown in Figure 1. All reagents were purchased from Aldrich Chem. Co.

Synthesis of 2-(3,5,5-Trimethyl-2-cyclohexenylidene)-malonitrile (1). A three-necked flask equipped with a nitrogen inlet, a Dean–Stark trap, and a condenser was charged with isophorenone (10 *g*, 72.4 mmol), malonitrile (4.779 *g*, 72.4 mmol), ammonium acetate (14.5 mmol), acetic acid (1.5 mL), and benzene (40 mL). The mixture was stirred at 100 °C for 12 h under a stream of nitrogen. After the benzene was removed, the reaction mixture was neutralized with 1 M of aqueous sodium bicarbonate solution. Then, the organic layer was extracted with ethyl acetate and dried over $MgSO_4$. After ethyl acetate was removed under reduced pressure, the reaction product was obtained. The crude product was purified by using silica gel column chromatography (ethyl acetate: hexane = 10: 90 by volume % as a mixed eluent solvent) followed by recrystallization from hexane. Yield: 94%. Mp: 70 °C. FT-IR (KBr pellet, cm^{-1}): 2202 (C≡N). ^{1}H NMR ($CDCl_3$, δ from TMS): 1.00 (s, 2×CH_3), 2.02 (s, CH_3), 2.08 (s, CH_2), 2.52 (s, CH_2), 6.61 (s, ═CH).



Pt catalyst = hydrogen hexachloroplatinate(IV) hydrate

Figure 1. Reaction schemes for chromophore and photoconducting polymer.

Synthesis of 2-{3-[(*E*)-2-(Dibutylamino)-1-ethenyl]-5,5-dimethyl-2-cyclohexenylidene}malononitrile (DB-IP-DC) (2). 2-(3,5,5-Trimethyl-2-cyclohexenylidene)malonitrile (1) (10 g, 0.0536 mol) was dissolved in *N*,*N*-dibutylformamide dimethyl acetal (20 mL).[11] The mixture was stirred at ambient temperature for 30 min and then 110 °C for 3 h under nitrogen atmosphere. After the reaction mixture was cooled to room temperature, the volatile components were removed using a rotary evaporator, and the dark-red residue was obtained. The reaction product was dissolved in a mixed solvent of methylene chloride (10 mL) and methanol (150 mL). After the solution was concentrated and then cooled to 5 °C, the reaction product was precipitated on standing. The crude product was collected by filtration and then purified by recrystallization from hexanes–ethanol. Yield: 83%. Mp: 116 °C. ^{1}H NMR ($CDCl_3$, δ from TMS): 0.98 (m, 4×CH_3), 1.36 (br, 2×CH_2), 1.58 (m, 2×∠CH_2–), 2.21 (s, –CH_2–), 2.42 (s, –CH_2–), 3.21 (br., 2×CH_2N), 5.30 (d, NCH═), 6.34 (s, ═CH), 7.01 (d, ═CH). UV/vis. (in methylene chloride): λ_{max} = 480 nm.

Sample Preparation. The polymer composite employed in the current study was based on photoconducting carbazole-substituted polysiloxane (PSX-Cz) doped with DB-IP-DC chromophore and 2,4,7-trinitro-9-fluorenone. The composition of polymeric materials was PSX-Cz: DB-IP-DC: TNF in a ratio of 69:30:1 by wt %. For device preparation, the mixture was dissolved in dichloromethane and the solution was filtered through a 0.2 μm filter. The composite was casted on an indium tin oxide (ITO) glass plate with an etched electrode pattern, dried slowly for 6 h at ambient temperature, and subsequently heated in an oven at 90 °C for 24 h to completely remove the residual solvent. Then, the composite was softened by placing it on a hot plate at 100 °C, followed by sandwiching between ITO-coated glasses under light pressure to yield a film with uniform thickness. The thickness of the film was controlled by an inserted Teflon spacer between two ITO glass plates.

Measurements. The photorefractive property of the composite was characterized by the two-beam coupling (2BC) and degenerate four-wave mixing (DFWM) methods using the

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60μm-thick film.[2,8,12] For 2BC measurement, two coherent laser beams were irradiated at sample in the tilted geometry with the incidence angle of 30° and 60° with respect to sample normal. The *p*-polarized laser beam at the wavelength of 632.8 nm (He−Ne laser) with an intensity of 20 mW/cm^2 was used. The asymmetric energy coupling between two laser beams is evaluated by the gain (γ) defined as $\gamma = I_2\ (I_1 \neq 0)/I_2\ (I_1 = 0)$, where I_1 and I_2 are a pump beam and a signal beam, respectively. And the gain coefficient (Γ) employed as the measure of photorefractive performance was calculated from the measured value of gain (γ) according to the following equation.[12]

$$\Gamma = \frac{1}{L}\left[\frac{\ln \beta\gamma}{\ln(1+\beta-\gamma)}\right] \qquad (1)$$

where L is the beam path length and β is the intensity ratio of incident laser beams ($I_1/I_2 = 1.17$ in our work).

The diffraction efficiency of photorefractive grating was determined by the DFWM experiments. Photorefractive grating was formed by the irradiation of two *s*-polarized beams with the intensity of 20 mW/cm^2 in order to minimize the beam coupling between the writing beams, which causes the variation of photorefractive grating throughout the sample. And the recorded photorefractive grating was read out by a *p*-polarized counter-propagating probe beam. The sample geometry such as incident angles of two writing beams and the wavelength of the laser employed in the DFWM method are the same as those in 2BC measurement. The magnitude of the internal diffraction efficiency (η_{int})[12] was determined from the measured transmitted and diffracted intensities of the reading beam, using the relation

$$\eta_{\text{int}} = I_{\text{R,diffracted}}/(I_{\text{R,diffracted}} + I_{\text{R,transmitted}})$$

The photoconductivity of the composite was measured at a wavelength of 632.8 nm using a simple photocurrent method. The current flowing through the sample was measured during the illumination of light with an intensity of 20 mW/cm^2 at the applied field of 30 V/μm. The absorption coefficient of the composite was determined using a UV−Vis spectrometer (Duksan Mechasys, Optizen III). The glass transition temperature (T_g) of the composites was determined by differential scanning calorimetry (Perkin-Elmer DSC7) at the heating rate of 10 °C/min. The polymer composite containing 30 wt % of DB-IP-DC chromophore showed a glass transition temperature of 27 °C without the addition of any extra plasticizer. The chemical structure of the molecules was characterized by ^{1}H NMR spectrometry (Varian, INOVA, 400 MHz) and FT-IR spectrometry (Perkin-Elmer, Paragon 500).

Results and Discussion

It is a well-accepted fact that the polymeric composite systems with the low glass transition temperature (T_g) possess high photorefractive properties, due to the in situ reorientation of the birefringent chromophore molecule under the spatially modulated space−charge field.[6−8] In the case of low T_g polymeric photorefractive composites, the modulation of refractive index arises predominantly from the birefringence effect, rather than Pockels effect as in inorganic crystals.[14−16] Consequently, the chromophore with a large dipole moment (μ) and a high polarizability anisotropy ($\Delta\alpha$) is considered to be desirable for the low T_g photorefractive composite.[15,16]

Table 1. Dipole Moment (μ), Polarizability Anisotropy ($\Delta\alpha$), and Hyperpolarizability (β) of Chromophore Calculated Using MOPAC 6

conjugation bridge of NLO chromophore	μ (D)	$\Delta\alpha$ (AU)	β (10^{-30} esu)
isophorone[a]	8.00	216.6	34.2
benzene[b]	6.02	165.5	22.6

[a] 2-{3-[(*E*)-2-(Dibutylamino)-1-ethenyl]-5,5-dimethyl-2-cyclohexenylidene}malonitrile (DB-IP-DC). [b] 4-Dibutylaminobenzylidenemalononitrile (DB-Bz-DC).

Following the above strategy, we designed a 2-{3-[(*E*)-2-(dibutylamino)-1-ethenyl]-5,5-dimethyl-2-cyclohexenylidene}malononitrile (DB-IP-DC) chromophore for photorefractive application. The isophorone moiety was chosen as a conjugation bridge of chromophore, since polyene-based chromophore is known to possess a larger dipole moment and polarizability anisotropy than an aromatic ring.[16] When a strong electron-donor (dialkylamine) and strong electron-acceptor (dicyano group) are incorporated at both ends of the isophorone conjugation bridge, the extensive charge transfer is able to occur along a π-conjugated bridge, which is expected to endow the large polarizability anisotropy ($\Delta\alpha$) to NLO chromophore. And the significant charge separation in the ground state may enable the DB-IP-DC chromophore to possess a large dipole moment (μ).

In addition, the isophorone structure provides another advantage over the linear polyene-based conjugation bridge. The steric hindrance associated with the ring structure as well as the dimethyl substituents of an isophorone unit is expected to hinder the crystallization of the chromophore. This may allow the composite film to retain its optical clarity for a prolonged period, due to the reduced tendency of self-aggregation. Furthermore, the relatively long dibutyl chains incorporated on the electropositive end of the chromophore is expected to enhance the solubility of the polar chromophore in nonpolar photoconducting medium and to facilitate the orientation of the chromophore under the influence of an electric field.

To demonstrate the validity of our concept, the optical parameters of DB-IP-DC chromophore were evaluated by the semiempirical quantum chemical calculation method, MOPAC 6, with the PM3 procedure for geometry optimization in the ground state. As shown in Table 1, the calculated result implies that DB-IP-DC will possess a high dipole moment and polarizability anisotropy. For comparison, the calculated result on the chromophore based on a benzene moiety are presented together. 2-{[4-(Dibutylamino)phenyl]methylene}malononitrile (DB-Bz-DC) chromophore consists of the same dibutylamine electron-donor and dicyano electron-accept groups as DB-IP-DC chromophore, except the type of conjugation bridge. As we expected, the isophorone-based chromophore exhibits a much improved optical property, as compared with the corresponding benzene-based chromophore, since the more feasible charge transfer may occur along the polyene moiety rather than the benzene bridge. The calculated results presented in Table 1 may provide the basis to estimate how much

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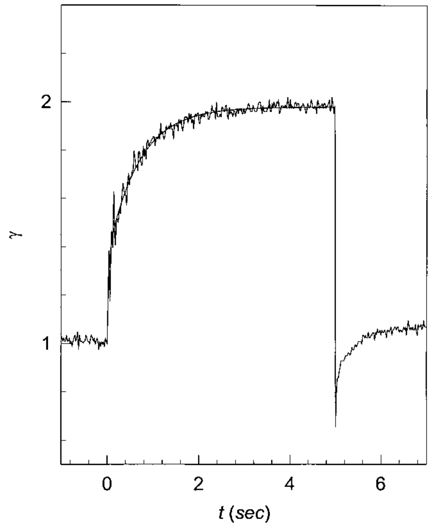

Figure 2. Two-beam coupling gain of the composite containing DB-IP-DC chromophore determined at the applied field of 100 V/μm.

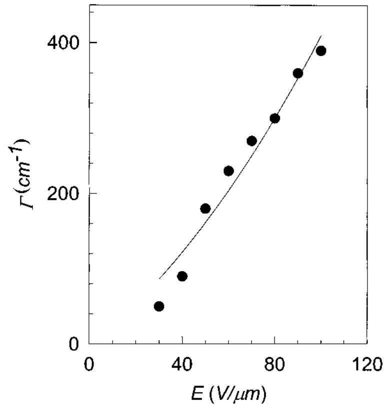

Figure 3. Steady-state gain coefficient of composite containing DB-IP-DC chromophore at various applied electric fields.

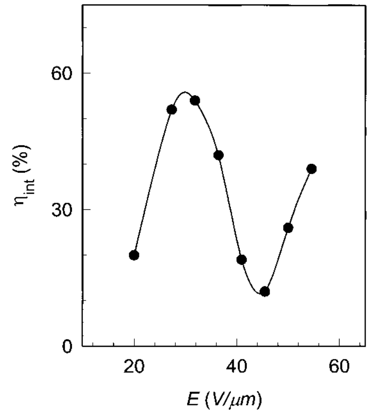

Figure 4. Steady-state diffraction efficiency of composite containing DB-IP-DC chromophore at various applied electric fields.

the optical nonlinearity of the chromophore is improved by the variation of the conjugation bridge.

Figure 2 exhibits the gain coefficient of the composite containing 30 wt % of DB-IP-DC chromophore at the applied field of 100 V/μm. The measured value of gain is observed to be ca. 2, which means that the pump beam is almost transferred to the signal beam. Be reminded that the maximum gain value attainable ideally from a two-beam coupling measurement is ($1 + \beta$), where β is the intensity ratio of two incident beams ($I_{\text{pump beam}}/I_{\text{signal beam}}$). Figure 3 exhibits the gain coefficient of the DB-IP-DC composite at the various applied electric fields. Even at the moderate electric field of 50 V/μm, the gain coefficient of the composite is as high as ca. 180 cm^{-1}. At the applied field of 100 V/μm, the gain coefficient is observed to be 390 cm^{-1}. Even though absorption loss of the composite ($\alpha = 60$ cm^{-1} at 632.8 nm) is taken into account, the net gain coefficient is as high as 330 cm^{-1} at 100 V/μm. For the case of a composite containing 30 wt % of DB-Bz-DC chromophore ($T_g = 5$ °C), the gain coefficient is observed to be 120 cm^{-1} at the applied electric field of 70 V/μm, which is much lower than the 280 cm^{-1} of the DB-IP-DC composite. (In the case of DB-Bz-DC composite, the maximum external field applicable to the device was 70 V/μm. There is no experimental data available at the applied field of over 70 V/μm due to a breakdown of the device.) It is speculated that the higher photorefractive property of the DB-IP-DC composite over the DB-Bz-DC composite may reflect the better optical nonlinearity of the DB-IP-DC chromophore.

The results given in Figures 2 and 3 demonstrated that the current composite doped with the DB-IP-DC chromophore possesses an excellent photorefractive property, which is one of the best performances obtained to date in the field of polymeric photorefractive materials. Note that well-known photorefractive composites with high performance such as PVK:DMNPAA:ECZ:TNF (37:50:16:1 by wt %) composite and PVK:AODCST:BBP:C_{60} (49.5:35:15:0.5 by wt %) composite showed a gain coefficient of over 200 cm^{-1} only when the external applied field was as high as 100 V/μm.[6,8]

Diffraction efficiency was determined using a 60 μm thick film as a function of an applied electric field, as shown in Figure 4. The maximum diffraction efficiency ($\eta_{\max}$) obtained was 56% and it was observed at the relatively low field of 30 V/μm. The electric field at a diffraction efficiency maximum, $E(\eta_{\max})$, of the current composite can be decreased further with the increase of film thickness, say up to 100 μm, since the diffraction efficiency depends on the thickness of the sample as follows,[2]

$$\eta = \sin^2\left[\frac{\pi d \Delta n \cos(\theta_2 - \theta_1)}{\lambda\sqrt{\cos\theta_1 \cos\theta_2}}\right] \qquad (2)$$

where d is the sample thickness, Δn is the refractive index modulation, λ is the wavelength, and θ_1 and θ_2 are internal angle of incidence of the two writing beams. When the steady-state performance of the photorefractive materials is evaluated, $E(\eta_{\max})$ can be used for a parameter: $E(\eta_{\max})$ is decreased with the improvement of the photorefractive property of the material.[12] The low value of $E(\eta_{\max})$ shown in Figure 4 proved the high performance of the polymer composite containing DB-IP-DC chromophore, together with the high gain coefficient.

The response time of the photorefractive composite was evaluated from the build-up of the beam intensity of the 2BC measurement. Time constants, τ_1 and τ_2, were calculated by fitting the evolution of the growth

Table 2. Photoconductivity and Response Time of Composites at 632.8 nm

composite	photoconductivity,[a] nA	time constant τ_1,[b] ms 70 V/μm	time constant τ_1,[b] ms 100 V/μm
PSX-Cz:TNF 69:1	77.0		
PSX-Cz:TNF:DB-IP-DC 69:1:30	45.0	67	33
PSX-Cz:TNF:DB-Bz-DC 69:1:30	10.0	490	

[a] At $I = 20$ mW/cm^2 and $E = 30$ $V/\mu m$. [b] At $I = 40$ mW/cm^2.

of the gain, $g(t)$, with the following biexponential function,[10]

$$g(t) = 1 + a_1\{1 - \exp(-t/\tau_1)\} + a_2\{1 - \exp(-t/\tau_2)\} \quad (3)$$

where τ_1 and τ_2 are the fast and slow time constants, respectively. As can be seen in Figure 2, the transient is well-fitted with a biexponential function. DB-IP-DC composite shows the fast time constant of 33 ms and the slow time constant of 680 ms at 100 V/μm and 40 mW/cm^2. The response time of DB-Bz-DC composite was also determined, and the result is given in Table 2, along with the photoconductivity at 30 V/μm and 20 mW/cm^2.

Photorefractive grating formation consists of (1) a build-up of space−charge field involving photogeneration of charges and their redistribution and (2) modulation of the refractive index via an electrooptic effect. As a result, the response time of low T_g photorefractive materials is limited by the photoconductivity and the orientational mobility of the chromophore, and it was suggested that the fast time constant (τ_1) is related to the photoconductivity of the material.[8,10,17,18] For the case of photorefractive materials containing a large amount of chromophores, in addition to hole-conducting molecules, a chromophore generally plays an important role in determining the speed of grating formation, since hole mobility is significantly influenced by the addition of chromophore.[19,20] As presented in Table 2, the moderate response time of the DB-IP-DC composite ($\tau_1 = 33$ ms at 100 V/μm) may be attributable largely to the relatively low photoconductivity of the carbazole-pendant polysiloxane medium. DB-Bz-DC composite having the lower photoconductivity shows the slower response, as compared with the DB-IP-DC composite. However, in the case of the DB-IP-DC composite, it is noteworthy that the reduction of photoconductivity of the polysiloxane matrix by the addition of 30 wt % of chromophore (from 77 to 45 nA) seems to be not so serious if the dilution of hole-transporting molecules is taken into account.

Finally, it should be mentioned that this composite was observed to possess long-term stability. The composite containing 30 wt % DB-IP-DC retains the optical clarity without any phase separation for over a year. This may arise from the improved compatibility of the chromophore in a nonpolar medium due to the long alkyl chain attached on the positive end of the chromophore and the reduced inclination of the isophorone ring toward crystallization.

Conclusions

In this work, we successfully prepared an improved polymeric photorefractive composite with a long storage time. Due to the enhanced optical property of chromophore and the good solubility in a polymer matrix, the photorefractive composite doped 30 wt % of 2-{3-[(*E*)-2-(dibutylamino)-1-ethenyl]-5,5-dimethyl-2-cyclohexenylidene}malononitrile chromophore (DB-IP-DC) showed photorefractive properties high enough for optical applications under moderate experimental conditions. The DB-IP-DC composite showed a high gain coefficient of 180 cm^{-1} at the moderate electric field of 50 V/μm. And the diffraction efficiency of the 60 μm thick film showed the maximum value of 56% at the relatively low field of 30 V/μm. In addition, the composite film retained optical clarity over a year when stored at room temperature. Therefore, we think the current polymeric composite containing DB-IP-DC exhibits promising results as a highly efficient photorefractive material and puts research one step closer to the application of polymeric materials to various optical applications.

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