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Synthesis and characterization of novel photoconducting carbazole derivatives in main-chain polymers for photorefractive applications

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Abstract

We have prepared hole-transporting polymers that have carbazole and 3,3′-dicarbazole in the main chain by polycondensation based on Fridel–Craft reaction via cations generated by proton of *p*-toluene sulfonic acid catalyst. In the device, they display high diffraction efficiency at low external electric field. The DiCz composite had a high diffraction efficiency of 82.4% at 52 V/μm and a photorefractive response time constant of 1.18 s at an electric field of 50 V/μm and a writing intensity of 60 mW/cm^2. The samples have excellent properties with respect to optical quality and shelf-lifetime.
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Keywords: Carbazole; Photorefractive effect; Main-chain polymers

1. Introduction

Carbazole compounds are one of the most important fundamental structures in the field of organic electrical and optical materials. In particular, carbazole compounds attract wide interest due to their potential application in areas such as optical data storage and information processing in organic photorefractive (PR) devices [1,2,9b]. The field of organic PR materials has existed for three decades. There are four kinds of organic PR materials: polymeric PR composites, fully functionalized polymers, small molecules, and metal-organic complexes. Over the last decade, a considerable number of studies have been conducted on the polymeric PR composites. One of the reasons why the polymeric PR composite has been studied in the fields of PR materials is that it exhibits the most promising results [1,2].

The PR effect refers to the spatial modulation of the refractive index of a material due to the light-induced redistribution of the electronic charge. The main characteristics governing the PR are the electro-optical activity and the photoconductivity of a material. A high-speed holographic response to patterned optical illumination in PR polymers depends on sufficient charge generation and charge mobility, and then, on the fast rotational diffusion of a nonlinear optical (NLO) chromophore [2b].

To date, poly(*N*-vinylcarbazole) (PVK)-based PR composites have been the main focus of interest in this area, in conjunction with various other chemicals, such as NLO chromophores, plasticizers, and photosensitizers [2,3,9b]. Although these PVK-based PR composites have been vigorously studied their unsuitability for use in PR applications has not been overcome. Especially, PVK-based PR composites tend to form chromophore aggregates on heating during device formation or operation, leading to a smaller PR figure-of-merit. In these respects, the development of new PR polymeric materials and their applications is strongly needed for commercialization.

By far the PR composites in the main-chain photoconducting polymers [2e] have received less attention, in spite of the presence of a tremendous number of reports about

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PVK-based PR composites. For this purpose, we have designed a new polymer where the main chain is sufficiently bulky to prevent the formation of π-stacking groups, for a fast orientation of the NLO chromophore, and helps to prevent aggregation of the NLO chromophore to increase the stability of the composites in a working device as mentioned above. It is possible that this may be overcome by attaching a bulky alkyl branch group at the 9-position of the carbazole moiety. Recently, Wang et al. reported a novel triarylamine-based polymer in the main chain [4], and shown to be useful as various hole-transporting material design. To improve device stabilities of PR composites, the replacement of the triarylamine with carbazole unit leads to new hole-transporting polymers.

In an attempt to improve on photorefractive properties, we have synthesized a new class of charge-transport polymers with carbazole and 3,3′-dicarbazole groups (Scheme 1). Unlike previous PR composite system of main-chain polymer [2e], these polymers are expected to improve photorefractivity and device stabilities. This paper describes measurements made on these polymers doped with the NLO chromophore P-IP-DC.

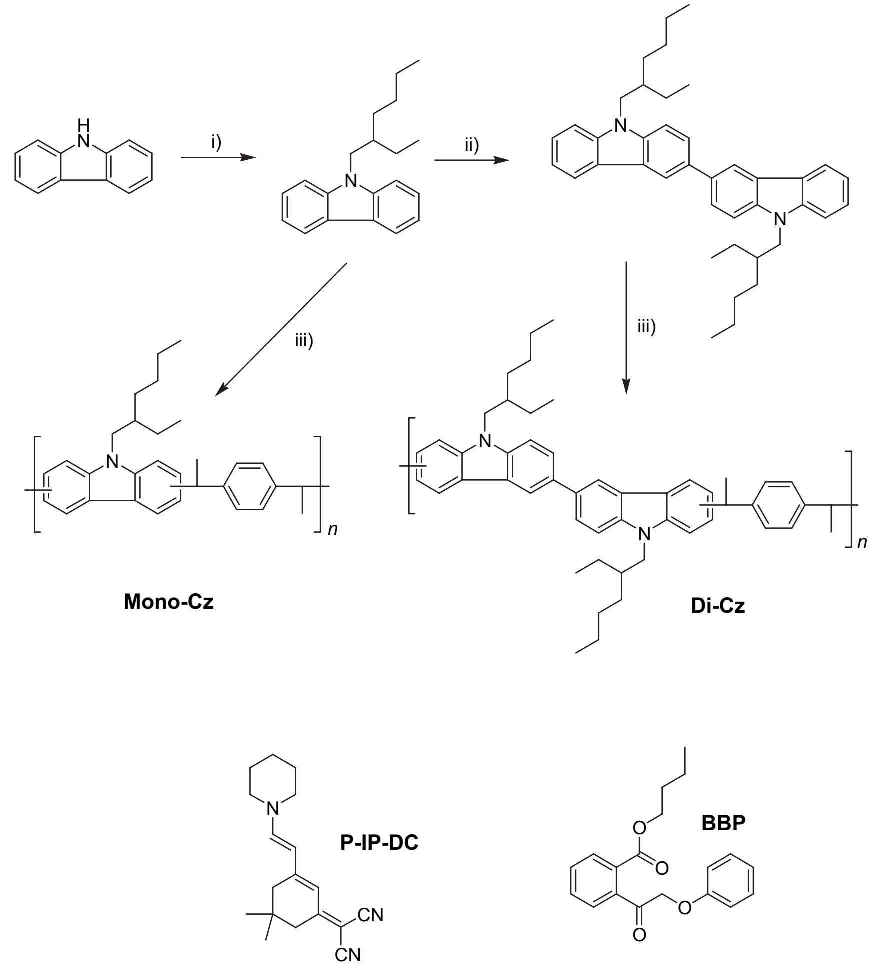
2. Experimental

2.1. General characterization

^{1}H NMR spectra were recorded using a Varian 400 MHz spectrometer with $(CH_3)_4Si$ as an internal reference. The absorption maximum (λ_{max}) of molecule and polymer in CH_2Cl_2 solution was recorded in Duksan Mechasys, Optizen III. Differential scanning calorimetry (DSC) was carried out using a Perkin–Elmer DSC7 analyzer with a heating rate of 10 °C/min under a nitrogen atmosphere. The number- and weight-average molecular weights of polymers were determined by gel-permeation chromatography (GPC) on a Waters GPC-150C instrument, using tetrahydrofuran (THF) as eluent and polystyrene as standard.

2.2. Materials

All chemicals were obtained from commercial suppliers and used as received unless otherwise noted. 9-(2-Ethylhexyl)carbazole, bis[9-(2-ethylhexyl)carbazole-3-yl], and polymers (MonoCz and DiCz) were synthesized according to the literature [4,5].



Scheme 1. Synthesis of carbazole-based polymers by Fridel–Craft reaction. *Reaction conditions*: (i) 2-ethylhexylbromide/NaH/DMF; (ii) $FeCl_3/CHCl_3$; (iii) 1,4-divinylbenzene/*p*-toluenesulphonic acid/chlorobenzene.

2.3. Synthesis

2.3.1. Bis[9-(2-ethylhexyl)carbazol-3-yl]

A stirred solution of 10 mmol of 9-(2-ethylhexyl)carbazole in 70 ml chloroform under a nitrogen atmosphere was cooled to 0 °C, and 40 mmol of $FeCl_3$ was then added to the mixture. After stirring the mixture at room temperature for 4 h, 150 ml of water was added. The organic layer was separated, dried over $MgSO_4$, filtered, and then concentrated. The mixture was purified using column chromatography (SiO_2, hexane/ethyl acetate, 98/2, v/v). A yield of 89% of the product was obtained as a colorless oil. ^{1}H NMR ($CDCl_3$, ppm): δ 10.09 (s, 1H, −CHO), 8.68 (d, 1H, ArH), 8.46 (d, 1H, ArH), 8.39 (d, 1H, ArH), 8.17 (d, 1H, ArH), 8.02 (d, 1H, ArH), 7.89 (d, 1H, ArH), 7.81 (d, 1H, ArH), 7.52−7.40 (m, 5H, ArH), 7.26 (m, 1H, ArH), 4.23 (m, 4H, $-NCH_2CH(Et)-$), 2.11 (m, 2H, $-NCH_2CH(Et)-$), 1.40 (m, 16H, $-CH_2-$), 0.94 (m, 12H, $-CH_3$).

2.3.2. General polymerization procedure

A glass ampoule flushed with dry nitrogen gas, containing the carbazole derivatives and 1,4-divinylbenzene in equal molar ratios, along with *p*-toluene sulfonic acid (3 mol%), was used to dissolve the contents in chlorobenzene (2 mol/L). The ampoule was then sealed, and the reaction mixture was heated at $T = 90$ °C for 5 h, and the contents were then poured into a methanol/acetone (5:1) mixture. The obtained solid was dissolved in a minimum amount of $CHCl_3$ and then poured into methanol/acetone mixture twice. The polymers are purified further by washing for 2 days in a Soxhlet apparatus with methanol. The final polymers were obtained after drying in vacuo at room temperature, yielding 63% MonoCz and 79% DiCz.

2.4. Device fabrication and measurements

A predetermined mass of the components was dissolved in 1,1,2,2,-tetrachloroethane, and the resulting solution was filtered through a 0.2 μm filter. The composite was cast on indium tin oxide (ITO) glass plates, dried for 12 h at ambient temperature, and subsequently heated in an oven at 50 °C for 24 h to remove any residual solvent. Then, the composite was softened by placing it on a hot plate at $T = 100$ °C. This was then covered with a second ITO-coated glass. The thickness of the film was controlled using a Teflon spacer between the two ITO glass plates.

3. Results and discussion

The non-π-conjugated main-chain polymers containing the carbazole were targeted to increase compatibility with NLO chromophore, the charge mobility, the device stability, and decrease the glass transition temperature. Two types of structures were used: carbazole system and 3,3′-dicarbazole systems wherein 3,3′-dicarbazole structure expect to increase the polymer's photoconductivity by a combination of conjugation length and ionization potential. The synthetic procedures used to prepare the monomers and polymers are outlined in Scheme 1. The introduction of the 2-ethylhexyl groups onto the 9-position of the carbazole groups was achieved using a procedure described in the literature [5], starting from the carbazole complex. Bis[9-(2-ethylhexyl)carbazol-3-yl] was synthesized by oxidative coupling of the corresponding monomers in the presence of a $FeCl_3$ catalyst in $CHCl_3$ to afford 3,3′-dicarbazole in a high yield.

In contrast, the polymer MonoCz with random connectivity by 1,4-divinylbenzene was synthesized by polycondensation based on Fridel−Craft reaction via cations generated by proton of *p*-toluene sulfonic acid catalyst. Similarly, polymer DiCz was synthesized from bis[9-(2-ethylhexyl)carbazol-3-yl] and 1,4-divinylbenzene in the presence of *p*-toluene sulfonic acid catalyst. The resulting polymers repeated reprecipitation from methanol/acetone mixture twice. The polymers are purified by washing for 2 days in a Soxhlet apparatus, with methanol to remove the low molecular weight fractions.

The resulting polymers MonoCz and DiCz were obtained as white solids. The copolymers were soluble in standard organic solvents such as chloroform, THF, and toluene and exhibited good film formation. This is partially due to the 2-ethylhexyl side chain attached to the carbazole moiety. The structural analysis was made by ^{1}H NMR and UV−vis spectroscopy. All the polymers of the methyl proton signals and the methine proton signals from 1,4-divinylbenzene unit appeared separately at around δ 1.72 and δ 4.06, respectively. The small signals indicated the presence of the unexpected structures; the linkage between carbazole unit and 1,4-divinylbenzene unit is not only at *p*-position but also at other positions.

The UV−vis spectra of the polymers are depicted in Fig. 1. The UV−vis absorption spectra of polymers were studied in $CHCl_3$. The absorption maxima of the polymer solution occurred at 243, 271, 300, 340, and 351 nm for MonoCz and 247, 271, 303, and 345 nm for DiCz. These polymers present a broad and strong absorbance band like carbazole-molecules in the UV−vis region. As expected DiCz polymer exhibits smaller red shift than MonoCz owing to the increased conjugation length of carbazole.

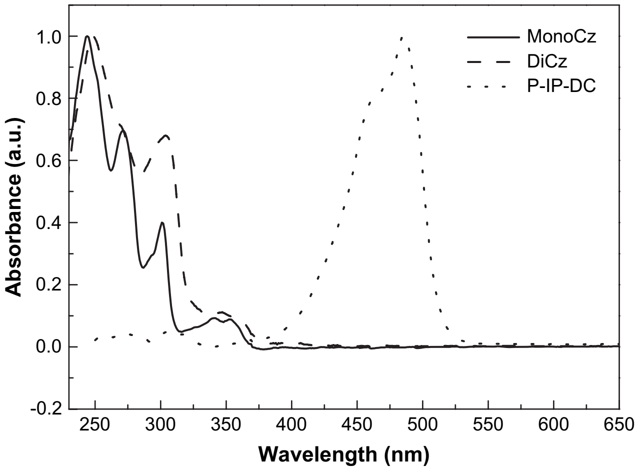


Fig. 1. UV−vis spectra of MonoCz, DiCz, and P-IP-DC in $CHCl_3$.

Table 1
Characterization data of the materials used

	MonoCz	DiCz
λ_{max}[a] (nm)	271, 300, 351	310, 343
HOMO/LUMO[b] (eV)	−5.92/−2.42	−5.38/−2.07
M_n ($\times 10^3$)/polydispersity (P.D.)	7.2/4.04	11.6/6.18
T_g[c] (°C)	64.5	92.5
T_g[d] (°C)	20	22
Photoconductivity[e] (pS/cm)	0.73	1.24
Δn[f] ($\times 10^{-3}$)	2.56	2.62
η_{max}	69.5[g]	82.4[h]
τ_{FWM}^{-1},[i] (s)	2.9	1.18
P-IP-DC[j]	μ (10^{-30}) = 26.7 $\Delta\alpha$ (10^{-40} cm^2/V) = 71.3 β (10^{-50} cm^3/V^2) = 12.7	

[a] Absorption spectrum in $CHCl_3$.

[b] HOMO energy values were calculated using HOMO Fc (ferrocene) (=−4.4 eV)/value of the HOMO and band gap of the absorption edge.

[c] Pure polymer value was determined from the second heating cycle in the DSC using a heating rate of 10 °C/min.

[d] Polymer composite value was determined from the second heating cycle in the DSC using a heating rate of 10 °C/min.

[e] The PR polymer composite value was determined using a DC current under a potential of 50 V/μm and a power of 10 mW/cm^2.

[f] The PR polymer value was determined using transmission ellipsometry under a potential 50 V/μm and a power of 10 mW/cm^2.

[g] Value obtained under a potential of 45 V/μm and a power of 45 mW/cm^2.

[h] Value obtained under a potential of 52 V/μm and a power of 40 mW/cm^2.

[i] Value determined at T_g.

[j] Calculated using the MOPAC 6 software package.

The average molecular weights (M_n) of the polymers were determined using gel-permeation chromatography (GPC) employing a polystyrene standard (Table 1). The MonoCz and DiCz copolymers had $M_n = 7.2 \times 10^3$ and 11.6×10^3, and a polydispersity of 4.04 and 6.18, respectively. The thermal properties of these polymers were studied using differential scanning calorimetry (DSC). The glass transition temperatures (T_g) of the MonoCz and DiCz copolymers were $T_g = 64.5$ and 92.5 °C, respectively. The higher glass transition temperature of DiCz versus MonoCz can be attributed to the rigidity of the 3,3-dicarbazole unit.

Cyclic voltammetry (CV) was used to assess the ionization potentials and the electrochemical stability of these polymers. The polymers were coated onto a platinum electrode to form a thin film. Then, these were immersed in a 2 mM tetra-*n*-butylammonium tetrafluoroborate acetonitrile solution. The potentials were recorded against an Ag/AgCl as reference electrode and each measurement was using the ferrocene/ferrocenium (Fc) redox system as an internal standard. The first oxidation potential increases with π-conjugation length of the carbazole, i.e., MonoCz (5.92 eV) > DiCz (5.38 eV). The low oxidation potentials of these materials can facilitate their use as hole transport materials in PR devices. Table 1 provides a summary of the HOMO levels of MonoCz and DiCz measured using CV (not shown). The HOMO and LUMO of DiCz are lower by 0.54 and 0.35 eV, respectively, than the HOMO and LUMO of MonoCz. Evidently, this is because of the extended π-conjugation extension of carbazole unit in DiCz.

To study the PR properties in MonoCz and DiCz, polymeric composites were prepared from a mixture of the photoconducting polymer (54 wt%), NLO chromophore (30 wt%), butylbenzyl phthalate (BBP) plasticizer (15 wt%), and C_{60} (1 wt%). The T_g values of the MonoCz and DiCz composites from the DSC data were $T_g = 20$ and 22 °C, respectively, which assure the facile orientation of the NLO chromophore at temperatures around T_g. Note that, in the case of a low T_g material, the glass transition temperature should be in the vicinity of, or lower, the measuring temperature, to take advantage of any potential orientation enhancement. The mixture of the composite was sandwiched between two indium tin oxide glass plates to form a 50 μm thick film along with a Teflon spacer.

Photoconductivity measurements ($\lambda = 633$ nm) were carried out on the two samples, and showed photoconductivities of $\sigma_{photo} = 0.73$ pS/cm for the MonoCz composite and $\sigma_{photo} = 1.24$ pS/cm for the DiCz composite, using a light intensity of 10 mW/cm^2 and an applied electric field of 50 V/μm (Fig. 2). The observed nonlinear dependence on the electric field strength is thought to be due to the fact that both the quantum efficiency and the charge mobility depend strongly on the electric field strength. Comparing the photoconductivity of the MonoCz composite with that of the DiCz composite shows that the former is about 1.7 times larger. This result may be explained by a previously reported study [2c,d]. The reason for the different photoconductivities for the different charge-transport molecules has a deep connection with the chromophore HOMO. If the HOMO of the chromophore is higher in energy than that for the charge-transport molecule, the chromophore can donate an electron from its HOMO to a nearby the charge-transport molecule HOMO. Thus, the chromophore acts as a trap for holes. That is, the depth of the chromophore HOMO as a hole trap can affect the charge mobility, and then turn affects the photoconductivity, with lower photoconductivity for deeper hole traps. It is shown from the Table 1, the HOMO level of DiCz (−5.38 eV) is 0.54 eV lower than that of MonoCz (−5.92 eV) and is very close to that of P-IP-DC (−5.32 eV). Therefore, the lower HOMO level of DiCz,

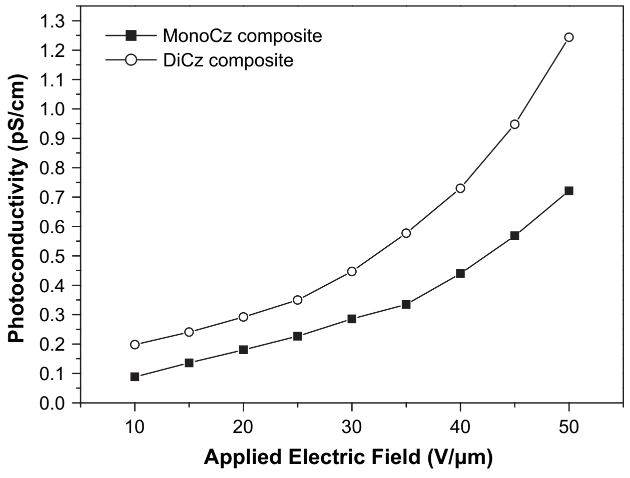


Fig. 2. Photoconductivity of MonoCz composite and DiCz composite as a function of external electric field strength.

compared with MonoCz, may lead to larger photoconductivity, which is consistent with our experiment results.

The electro-optical properties of the polymeric composites were determined using the transmission ellipsometric method ($\lambda = 633$ nm). The sample was tilted by $\theta = 45°$, and placed between the polarizer and the analyzer, with the polarization set to $+45°$ and $-45°$. The value of Δn of composite was determined from the variation of the transmitted intensity (T) through the crossed polarizers upon the application of the electric field, as described by the following equation: $T = \sin[\sin^2(2\pi/\lambda)l\Delta n]$, where λ is the wavelength, and l is the light path length. The field-induced birefringence of the PR polymer system was characterized using transmission ellipsometry under various applied fields. These data from the transmission ellipsometer experiments can be used to predict both the steady-state holographic contrast of the PR composite and to quantify the rotational freedom of the chromophores within the sample. As shown in Fig. 3, the birefringence (Δn) of a composite containing the P-IP-DC chromophore [4] increased quadratically with increasing applied field. At an applied potential of 50 V/μm ($I = 10$ mW/cm), $\Delta n = 2.62 \times 10^{-3}$ for MonoCz composite and 2.56×10^{-3} for DiCz composite, which are sufficiently large values for the preparation of efficient PR materials. Since the chromophores are rotating within an amorphous medium, they typically exhibit a non-exponential dynamic behavior.

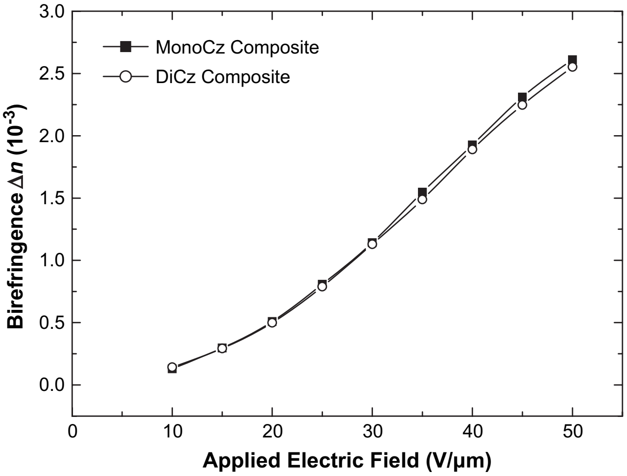


Fig. 3. Electric field-induced birefringence of MonoCz composite and DiCz composites versus applied electric fields.

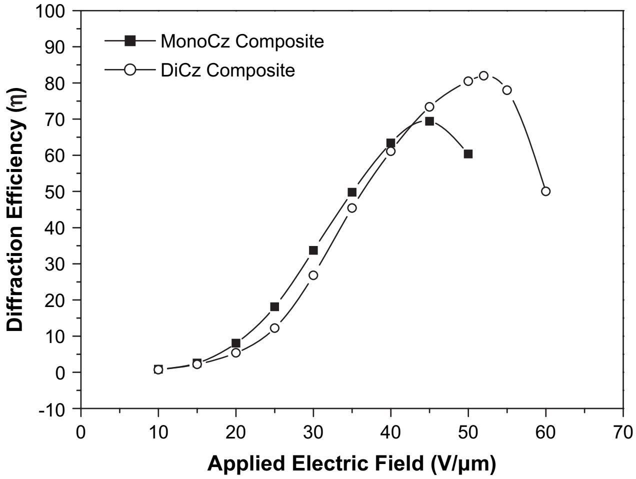


Fig. 4. Steady-state diffraction efficiency of MonoCz and DiCz composites under various applied electric fields.

The diffraction efficiency of the PR materials was determined using a degenerate four wave mixing (DFWM) experiment. Two coherent laser beams with $\lambda = 633$ nm were irradiated on the sample in the tilted geometry at an incident angle of $\theta = 30°$ and 60° with respect to the sample's normal axis. The intensity of s-polarized writing beams was 60 mW/cm^2. The recorded PR grating was read by a p-polarized counter-propagating beam. An attenuated reading beam with a very weak intensity of 0.1 mW/cm^2 was used. The thickness of sample was 50 μm and measuring temperature was at T_g. The internal diffraction efficiency (η_{int}) of the PR material was determined using the following equation

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

where $I_{R,diffracted}$ and $I_{R,transmitted}$ are the diffracted and transmitted intensities of the reading beam, respectively. The diffraction efficiency, η as a function of applied electric field, E, for each sample is shown in Fig. 4. At an external field of 50 V/μm at T_g, the values of the maximum diffraction efficiency (η_{max}) of guest-host systems containing MonoCz and DiCz were 69.5% at $E = 45$ V/μm and 82.4% at $E = 52$ V/μm, respectively. The MonoCz:P-IP-DC:BBP:C_{60} composite and the DiCz:P-IP-DC:BBP:C_{60} composite showed high diffraction efficiencies under low external electric field (Fig. 4). In addition, under identical experimental conditions, such as NLO chromophore (Δn), sensitizer, plasticizer, and experimental temperature at T_g and the PR properties of guest-host systems were largely determined by the magnitude of the photoconductivity. Of course, in the case of the P-IP-DC chromophore, the high electro-optic properties may be due to a large dipole moment induced, as well as to the high polarizability anisotropy of the chromophores due to effective conjugation of the polyene [6].

One of the major properties of PR composites has been the response time of the diffraction efficiency. This parameter is very important for real applications such as a real-imaging and real-data processing. To investigate the fast response time of PR devices, we measured the temperature dependence of the response time of the diffraction efficiency. The temperature dependence of the response time of the diffraction efficiency is shown in Fig. 5. In these experiments, an electric field of 50 V/μm for DiCz composite was applied to the sample, and a writing and a reading beam illuminated the samples. After a period of 200 s, a second writing beam was applied, and the diffracted reading beam monitored. The time constants, τ_1 (the fast time constant, corresponding to the time of internal electric field build-up) and τ_2 (the slow time constant, corresponding to the reorientation time of the internal space-charge field), were calculated by fitting the evolution of the growth of the diffraction signal, $\eta(t)$ [7]. The response

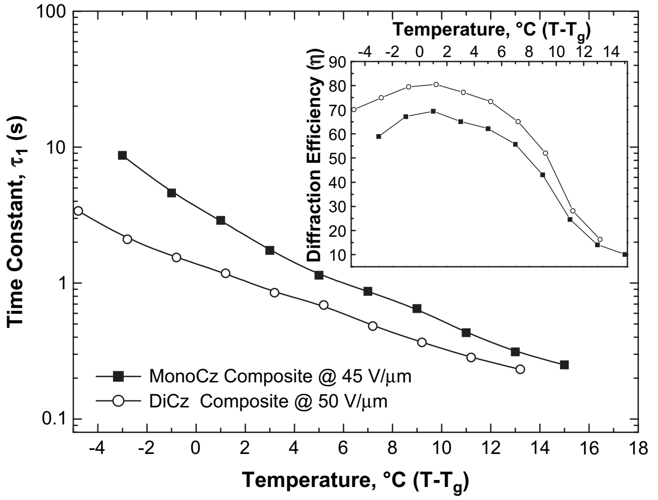


Fig. 5. Temperature dependences of the response time of the diffraction efficiencies. The inset shows the temperature dependences on the grating formation in PR polymeric composite.

time of the diffraction efficiency increased as the temperature increased above the polymer composite T_g value. At higher temperatures, the film softened and could be polarized easily by the external electric field, resulting in a larger induced electro-optic effect. In addition, the NLO chromophore becomes more mobile (see Table 1). As shown in Fig. 5, the devices exhibited not particularly fast response time and the sensitivity was not overly high. 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 electro-optic effect. As a result, the response time of low T_g PR materials is limited by the photoconductivity and the orientational mobility of chromophore and it was suggested that the fast time constant (τ_1) is related to the photoconductivity of the material [1c,2c,8]. For the case of PR 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 [9]. As displayed in Fig. 5, the moderate response time of the MonoCz composite having the lower photoconductivity shows the slower response, as compared with the DiCz composite.

Similarly, temperature dependence on the grating formation of MonoCz composite and DiCz composite was determined at 45 V/μm and 52 V/μm, respectively, and the results are shown in the inset of Fig. 5. For PR polymeric materials, temperature is one of the most important factors together with the external electric field, because it is closely related with photogeneration efficiency, carrier mobility, electro-optic coefficient tensor, and so on. The diffraction efficiency of the PR composite decreased with increasing temperature. It may be attributed to the decreases of space-charge field and/or electro-optic coefficient with increasing temperature [10].

Finally, it should be mentioned that these composites were observed to possess the long-term stability. The composite containing 30 wt% of P-IP-DC retains the optical clarity without any phase separation over a year. It may arise from the improved compatibility of chromophore in a nonpolar medium due to the long branched-alkyl chain attached on the carbazole derivatives and the reduced inclination of P-IP-DC toward crystallization.

DiCz composite showed a high diffraction efficiency of 82.4% at rather low electric field ($E = 52$ V/μm). These results are comparable to those of the best PR composite from among the main-chain systems reported so far. Unfortunately, the response time is not particularly fast and the sensitivity is not overly high. However, these results demonstrate that the ability to control and systematically alter the features of ionization potential energy with molecular design can provide opportunity to investigate a fast response time in *photorefractive materials*.

4. Conclusion

Here we have successfully prepared a novel polymeric PR composite with a long storage time. Because of the enhanced optical properties of the chromophore and the high solubility in a polymer matrix, a PR composite doped with 30 wt% of P-IP-DC showed good enough PR properties for optical applications under moderate experimental conditions. The DiCz composite showed a high diffraction efficiency of 82.4% in a moderate electric field of 52 V/μm, with a response time of the diffraction efficiency of 1.2 s in an applied field of 50 V/μm, a very weak intensity of 0.1 mW/cm^2 (reading beam), at T_g. In addition, the composite film retained optical clarity for over a half year when stored at room temperature. Therefore, we believe that the PR composite containing DiCz of the main chain of the polymer shows promise as a highly efficient PR material, and takes our research one step closer to the goal of finding a polymeric material that can find application in various optical devices.

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