High-Performance of PVK-based Photorefractive Polymers by High-Temperature Casting

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To achieve high performance in molecularly dispersed photorefractive polymer films, it is essential to have a large electro-optic coefficient (r_{33}), which is obtained by orientating nonlinear optic (NLO) molecules in an external electric field applied across the film. We investigated high-temperature casting, which is a new material fabrication technique for this purpose. We found that samples prepared by casting at higher temperatures showed a larger value of r_{33}, which was due to an increasing number of unpaired NLO molecules in the polymer matrix that were able to orientate in an external electric field. This was caused by releasing stable anti-parallel pairs that were formed between the NLO molecules due to their large dipole moment. Therefore, our samples showed a large improvement in their photorefractivity in four-wave mixing (FWM) experiments.

Over the last three decades, photorefractive (PR) materials have attracted considerable interest for use in optoelectronic and photonic applications, such as data storage, and in optical-processing applications, such as optical correlation and dynamic transient holograms.[1–4] In the last decade, many of the various classes of organic photorefractive materials have been investigated for photorefractivity, including organic crystals,[5] liquid crystals,[6,7] other monolithic glasses,[8,9] and polymers.[10–13] In particular, following the first report of host/guest polymer composites,[14] PR polymers are now a subject of wide interest, because these systems possess many advantages, such as the availability of a wide variety of guest molecules, their low-cost, and their ease of fabrication of large-area films.

The photoconductive poly(*N*-vinylcarbazole) (PVK)/2,4,7-trinitro-9-fluorenone (TNF)-based PR polymer, incorporating a nonlinear optic (NLO) compound and 9-ethylcarbazole (EtCz) as a hole transportable plasticizer exhibits high performance with almost 100% diffractivity.[15] Such a high diffractivity in this type of PR polymer is achieved by two well-defined NLO orientations. One is the NLO orientation towards an externally applied electric field by poling, by which the PR film exhibits an electro-optic (EO) behavior due to the Pockels effect; the other orientation is the so-called, "orientational enhancement effect", in which the NLO molecules reorientate themselves towards the space-charge field built-in by photoconduction, resulting in an enhanced change in the refractive index.[16,17]

The latter effect requires a substantial molecular rotation of the NLO molecules in a solid-state film. This is the reason why a low glass transition temperature (T_g) is preferred for a PR polymer, and why the hole transportable plasticizer EtCz is added to PVK-based PR polymers, since it ensures a lower T_g value. However, upon adding an easily crystallized plasticizer to this system, a serious problem arises, in that the added EtCz crystallizes too easily, which results in an optically opaque film. A potentially serious problem of thermal instability in low-T_g polymer composites is resolved by replacing EtCz with 1,3-bis(9-carbazolyl)propane (BisCzPro),[18] or by using a liquid plasticizer,[19–21] which results in a highly stable PR polymer. Another problem in PVK-based PR polymers is their slow response time, which is due to the need to reorientate the NLO molecules in the orientational enhancement process. Recently, this problem was resolved by the development of new NLO compounds, such as 4-(1-perhydroazepinyl)benzylidenemalononitrile (7-DCST) and fluorinated cyanotolane chromophore (FTCN).[22,23] However, such high PR properties are achieved only under severe external conditions, for example, applied electric fields of ca. 100 V/μm and light intensities of ca. 1 W/cm^2.

To further the practical use of organic PR polymers, it is important that high diffraction efficiencies and fast response times are realized under conditions that are more moderate. One of the ways to improve these is to increase the contribution of the Pockels effect, i.e., to orientate the NLO molecules in an external applied electric field as much as possible, to yield a large electro-optic coefficient, r_{33} (the component orientated perpendicular to the film), of the PR film. To achieve this, we have developed a high-temperature casting method to prepare PR films. The idea behind introducing high-temperature casting is based on the following concept. Since, generally, NLO molecules consisting of a donor–acceptor conjugated π-electron system have a large dipole moment, it is easily imagined that such NLOs dispersed into the host polymer at high density, typically 30 wt %, may couple to form energetically stable anti-parallel pairs. These do not respond to, nor orientate towards, an external applied electric field by poling. The equilibrium between paired and unpaired NLO molecules in a spissated solution at a given casting temperature will be fixed in the resulting cast film. Therefore, a higher casting temperature increases the number of higher energy unpaired NLO molecules. These unpaired molecules can orientate towards an externally applied electric field, and thus increase the r_{33} value

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of the PR film. Similar observations based on this concept have been reported in the literature,[24,25] where the number of higher energy excimer site conformations formed between adjacent π-electron chromophores of vinyl polymers in a cast film increased with a higher casting temperature. In a previous paper,[26] we reported that PVK-based PR polymer films incorporating molecularly dispersed *N*-[4-(diethylamino)benzylidene]-2-methyl-4-nitroaniline (DBMNA), prepared using a higher casting temperature, showed higher r_{33} values, and therefore higher diffraction efficiencies.

In this work, we attempted to confirm the effect of using a high casting temperature to improve the PR performance of the same PVK-based polymer dispersed with two different types of NLO molecules: DBMNA and 7-DCST. For both NLO molecules, we observed that high-temperature casting is very effective for improving the performance of a PR polymer composite.

Experimental

NLO Molecules and Plasticizers. All of the reagents used in the syntheses were obtained commercially, and were used without any further purification, unless otherwise noted.

9-Ethylcarbazole. EtCz was purchased from the Aldrich Chemical Co., (USA). The dark-brown plate-like crystals were purified by recrystallizing four or five times using a 1:2 tetrahydrofuran:methanol solution to obtain pure white needle-like crystals.

1,3-Bis(9-carbazolyl)propane. First, 4 g (24 mmol) of carbazole, which was recrystallized twice using acetone, was added to a 100 mL flask fitted with a magnetic stirrer and a condenser and 2.5 g (12.7 mmol) of 1,3-dibromopropane dissolved in 30 mL of benzene. Then, 0.07 mg (0.3 mmol) of benzyltriethylammonium chloride (BTEAC), acting as a catalyst, and 10 mL of 50% sodium hydrate solution were added to the resulting mixture; this was then heated under reflux for a period of 4 h. After allowing the mixture to cool to room temperature, the precipitate was collected by filtration. The residual product was purified by recrystallization using a 1:1 mixture of tetrahydrofuran:methanol to yield 2.2 g (5.9 mmol, 46%) of BisCzPro. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.10 (d, $J = 7.6$ Hz, 4H), 7.35–7.42 (m, 4H), 7.21–7.25 (m, 8H), 4.34 (t, $J = 7.3$ Hz, 4H), 2.46 (m, $J = 7.2$ Hz, 2H).

***N*-[4-(diethylamino)benzyliden]-2-methyl-4-nitroaniline.** A mixture of 7.08 g (40 mmol) of 4-diethylaminobenzaldehyde, 6.08 g (40 mmol) of 2-methyl-4-nitroaniline, and 1.9 g (10 mmol) of *p*-toluenesulfonic acid monohydrate was dissolved in 350 mL of dry toluene in a 500 mL flask equipped with a Dean–Stark trap. The reaction mixture was stirred under reflux for a period of 8 h. After evaporation of the solvent using a rotary evaporator, the residual precipitate was purified by recrystallizing three times in ethanol to yield 4.0 g (12.8 mmol, 32%) of DBMNA. ^{1}H NMR (270 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.09 (s, 1H), 8.05 (d, $J = 2.64$ Hz, 1H), 7.77 (d, $J = 8.9$ Hz, 2H), 6.94 (d, $J = 8.9$ Hz, 1H), 6.71 (d, $J = 8.9$ Hz, 2H), 3.45 (q, $J = 6.9$ Hz, 4H), 2.38 (s, 3H), 1.23 (t, $J = 6.9$ Hz, 6H).

4-(1-Perhydroazepinyl)benzylidenemalononitrile. The 7-DCST used was synthesized according to a literature procedure given in Ref. 11.

PR Sample Preparation and Measurements. We employed a thermally stable, molecularly dispersed PVK/TNF photoconducting polymer, incorporating a mixture of EtCz and BisCzPro (typically in a ratio of 3:1) as the hole transportable plasticizer, with either 7-DCST[11,19] or DBMNA as a nonlinear optic compound. The chemical structures of these compounds used are shown in Fig. 1.

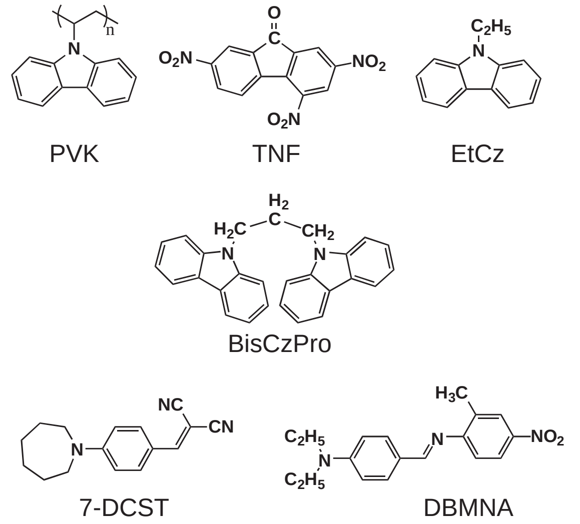

Fig. 1. Chemical structures of compounds used in this study.

DBMNA has an advantage in being easy to synthesize (see above). The photoconducting PVK host polymer was loaded with 35 wt % of the NLO compound, 32 wt % of the EtCz and BisCzPro plasticizer, and 1 wt % of TNF acting as a sensitizer. These compounds were dissolved in toluene, and filtered using a microfilter before being cast on an indium tin oxide (ITO) electrode at room temperature. The resulting cast film was dried in vacuo overnight. PR samples were prepared in a sandwich-type structure by hot pressing the cast film at 130 °C between two optically transparent ITO electrodes, with a polyimide spacer of 100 µm thickness. To study different casting temperatures (T_{ca}), the polymer solution and ITO substrate were maintained at a given temperature in a thermostatic chamber for a long period, typically 1 hour; the solution was then cast on an ITO substrate at the same temperature.[23] After evaporation of the solvent, the films were dried in vacuo overnight, and a sample cell was constructed by the usual method.

Diffractivity measurements on a sample were carried out using a four-wave mixing procedure under an external DC applied voltage, in which the initially randomly oriented NLO compounds were aligned perpendicular to the film's surface to confer an electro-optic effect on the polymers. Holographic gratings were written in polymers using a He–Ne laser ($\lambda = 633$ nm) with a power density of 22 mW and a beam diameter of 2 mm that overlapped on the sample film at incidence angles of 60° and 30° to the normal direction. A reading beam (power = 0.5 mW) was aligned so that it propagated in the opposite direction to one of the writing beams. The diffraction efficiency was calculated by monitoring the ratio of the intensity of the diffraction beam to that of the reading beam. The diffraction response was monitored on an oscilloscope that read the voltage from the photodiode output of the diffraction beam, and was estimated by employing an exponential curve-fitting procedure, as previously reported in the literature.[11,13]

The electro-optic effect can be observed by passing an oblique light beam through a film that is linearly polarized at an angle of 45° with respect to the plane of incidence. A voltage applied across the film has a different effect on the *p*- and *s*-phase polarized light. Therefore, the values of the electro-optic coefficient,

r_{33}, were obtained from the rate of change of the relative phase shifts of the *p*- and *s*-phase polarized light with the applied voltage, according to a method reported by Schildkraut,[27] and calculated using

$$\frac{\Delta\Psi}{\Delta V} = \frac{2\pi \cdot r_{33}}{3 \cdot \lambda} n^3 \tan\phi \sin\phi, \tag{1}$$

where $\Delta\Psi/\Delta V$ is the phase difference between the *s*- and *p*-polarized waves of the output beam in terms of the applied DC voltage, *n* is the refractive index of the NLO, and ϕ is the refraction angle.

Results and Discussion

Properties of DBMNA and 7-DCST. Figure 2 shows the diffraction efficiency of PR polymer samples dispersed with two types of NLO: 7-DCST and DBMNA. These samples were prepared by casting at room temperature, and measured using the same experimental conditions. As is commonly observed, the diffraction efficiency increased with increasing external applied electric field in both cases. This was mainly due to the increased EO effect resulting from an increased alignment of the NLO molecules in the polymer with increasing electric field. However, when the performances of the 7-DCST and DBMNA systems were compared, the 7-DCST sample showed a higher diffraction efficiency than the DBMNA sample at the same electric field. This difference was apparently derived from the types of NLO, because the T_g values of both polymers were almost the same, $T_g \approx -5$ °C.

The electro-optic coefficient, r_{33}, is shown in Fig. 3 for these two samples. The value of r_{33} increased with increasing temperature in both cases. The higher measuring temperature may facilitate the orientation of NLO compounds within a softer polymer matrix. Furthermore, the composite with 7-DCST exhibited a relatively larger value of r_{33} than that for a polymer with DBMNA. It is reasonable to explain this result by the fact that the relative diffraction efficiency of 7-DCST was larger than that of DBMNA.

However, the difference in the molecular susceptibility, β, of 7-DCST and DBMNA obtained from MOPAC (PM3) molecular orbital calculations compared to the experimental r_{33} values is curious. Table 1 lists the NLO properties of 7-DCST and DBMNA, showing the values of β, the dipole moment, μ, and the PR properties for both NLO molecules. Interestingly, DBMNA has a much larger value of β than 7-DCST. In general, the magnitude of the EO effect correlates with the value of β. Nevertheless, the system with 7-DCST exhibits a large value of r_{33}, and consequently a high diffraction efficiency. Therefore, theoretically, the DBMNA system would be expected to exhibit a relatively much larger value of r_{33} than that of the 7-DCST system under the same experimental conditions. Another contrast can be found in the value of the dipole moment, μ, between these two NLO compounds. The dipole moment of DBMNA is larger than that of 7-DCST, and therefore we focused on the difference in the dipole moments to understand why the value of r_{33} for the DBMNA-containing films was small in spite of a large value of β.

Effect of High-Temperature Casting. When NLO molecules possessing a large dipole moment are dispersed at a high density in a polymer, it can be easily imagined that such NLO molecules may couple with an adjacent NLO molecule to form an energetically stable anti-parallel pair due to large dipole–di-

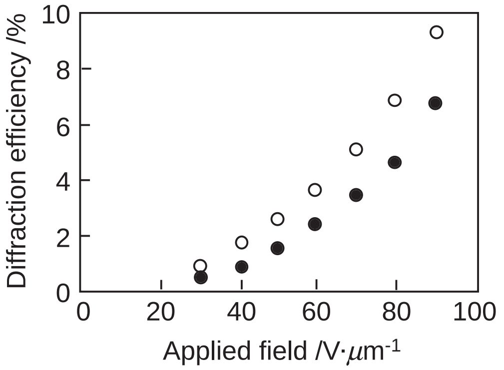

Fig. 2. Applied field dependence of diffraction efficiency, at 20 °C for 7-DCST (open circle), and DBMNA (closed circle). Each sample was made with the usual room temperature casting method and measured under the same conditions.

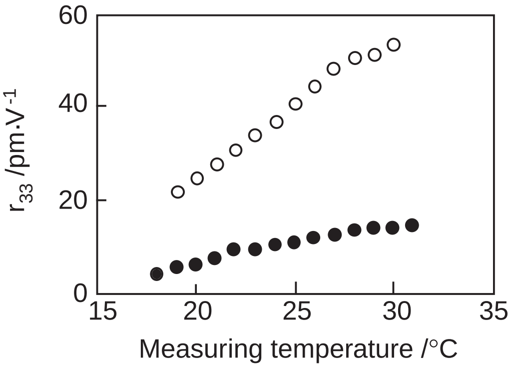

Fig. 3. The r_{33} values of two polymers measured at various temperatures under an applied field of 83.3 V/µm. 7-DCST (open circle) and DBMNA (closed circle). Each sample was made with the usual room temperature casting method and measured under the same condition.

Table 1. NLO Properties of 7-DCST and DBMNA and Their PR Performance

NLO	Dipole moment/debye	$\beta^{a)}/10^{-30}$ esu	$r_{33}{}^{b)}/\mathrm{pm \cdot V^{-1}}$	D.E.$^{c)}$/%
7-DCST	7.49	19.98	22.5	9.2
DBMNA	10.19	52.74	7.2	6.8

a) The molecular susceptibility (β) was calculated using $\beta = 3\mu_g{}^2(\mu_e - \mu_g)/2E^2$, where μ_g is the ground state dipole moment, μ_e is the excited state dipole moment, and E is the transition energy. b) r_{33} was measured in an applied field of 83.3 V/µm at 20 °C. c) The diffraction efficiency was measured in an applied field of 90 V/µm.

pole interactions. In a 35 wt % dispersion, the intermolecular distance of NLO is about 10 Å, and therefore, any anti-parallel NLO pairs would not be affected by an external applied electric field, because of cancellation of the dipole moments with each other. Thus, the value of r_{33} of a cast polymer film would be small for a composite dispersed with NLO molecules having a large dipole moment, such as DBMNA, in spite of a large value of β, since there would exist a large number of anti-parallel NLO pairs, which would not respond to the external applied electric field. In the opposite sense, however, this means that even in such a case, it would be possible to increase the value of r_{33} by increasing the molar fraction of isolated NLO molecules by some means. As mentioned in introduction, the equilibrium between paired and unpaired NLO molecules in a spissated solution at a given casting temperature should be fixed in the resulting cast film. Therefore, a higher casting temperature increases the number of high-energy unpaired NLO molecules. To confirm this proposition, and to increase the molar fraction of isolated NLO molecules dispersed in a polymer host, we attempted to introduce a new method of high-temperature casting in the sample-preparation process.

First, the effect of high-temperature casting on the value of r_{33} is shown for the DBMNA system. As can be seen from the data shown in Fig. 4, a larger value of r_{33} was obtained for samples cast at higher temperatures. In particular, a polymer cast at $T_{\mathrm{ca}} = 70$ °C showed very large r_{33} values measured at room temperature, near to 60 pm/V. This value is almost six-times larger than that of a room temperature cast film (where typically, $r_{33} \approx 10$ pm/V in the case of DBMNA, see Fig. 3), and far exceeds the value of $r_{33} \approx 20$ pm/V of the 7-DCST system. This result strongly supports the idea that a large number of anti-parallel pairs exist in the film cast at room temperature, and that high-temperature casting can uncouple such pairs into isolated moieties, which, as a consequence, leads to a higher value of r_{33}.

After evaluating the improvement in the value of r_{33} by high-temperature casting, the effect on the PR performance was examined. Figure 5 shows typical PR transients for samples cast at various temperatures from FWM experiments under an applied field of 90 V/μm. The samples cast at higher temperatures showed higher diffraction efficiencies, reflecting an increase in their r_{33} values. The system cast at $T_{\mathrm{ca}} = 70$ °C exhibited an increase in the diffraction efficiency of over three-times more than that of the system cast at room temperature. Thus, high-temperature casting provides a very effective method to ameliorate the PR performance of a polymer composite.

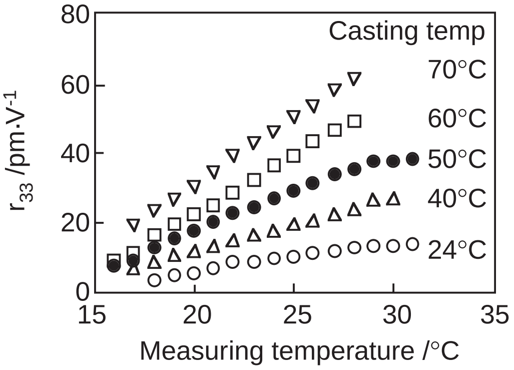

Fig. 4. The r_{33} values of DBMNA dispersed samples cast at 24 °C (open circles), 40 °C (open triangles), 50 °C (closed circles), 60 °C (open squares), and 70 °C (open inverted triangles). The abscissa denotes the measuring temperature. Applied field = 83.3 V/μm.

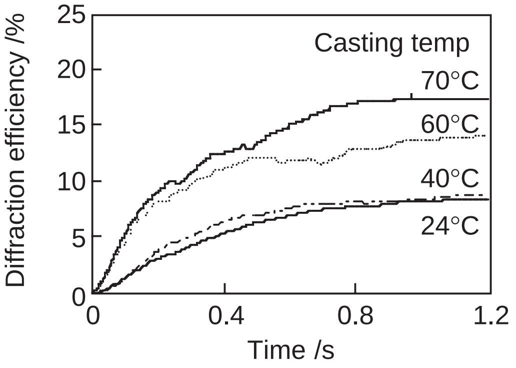

Fig. 5. Photorefractive transient response in the system dispersed with DBMNA for various casting temperatures. Applied field = 90 V/μm.

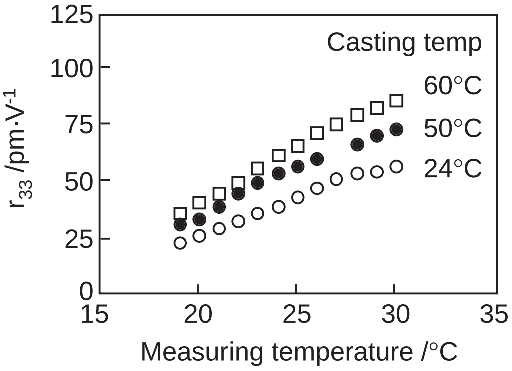

Fig. 6. The measuring temperature dependence of r_{33} of the 7-DCST sample for casting at 24 °C (open circles), 50 °C (closed circles), and 60 °C (open squares). Applied field = 83.3 V/μm.

The same high-temperature casting experiment was also carried out for the 7-DCST system, as shown in Fig. 6. In this case, the effect of high-temperature casting on the value of r_{33} was not as clear as that for the DBMNA system (see Fig. 4). Since both the dipole moment and the value of β of 7-DCST are not as large as those of DBMNA, the 7-DCST molecules are most likely distributed as isolated moieties in the polymer matrix, even when cast at room temperature. This result can also explain that the higher value of r_{33} and a higher PR performance are obtained, even for films cast at room temperature.

Evaluation of the Activation Energy. Our hypothesis concerning the two dipole state is also supported by an evaluation of the activation energy. Figure 7 shows Arrhenius plots of the value of r_{33} versus the inverse of the casting temperature for a fixed applied electric field for the DBMNA polymer. The Arrhenius plots show that a linear relationship existed, with the activation energy, E_{a}, estimated to be in the range $E_{\mathrm{a}} =$

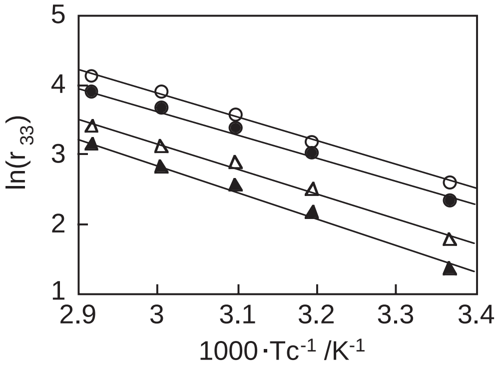

Fig. 7. Arrhenius plot of r_{33} against the casting temperature for the polymer composites containing DBMNA, measured at 18 °C (filled triangles), 20 °C (open triangles), 25 °C (filled circles), and 28 °C (open circles).

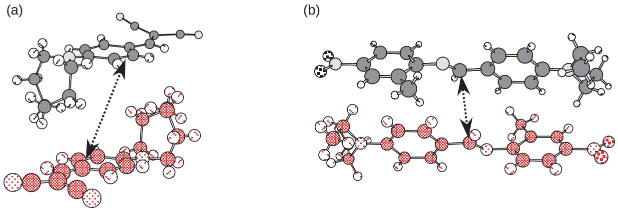

Fig. 8. Molecular arrangements of the nearest neighbor NLO molecules from X-ray analysis. (a) 7-DCST, and (b) DBMNA. Both NLO molecules have a center of inversion. The adjacent molecular distance is 12.2 Å for 7-DCST and 6.0 Å for DBMNA, respectively.

0.3–0.35 eV. Results for the 7-DCST polymer showed $E_a =$ 0.08–0.1 eV, which is almost one-third of the value of the polymer containing DBMNA.

If the increase in the value of r_{33} is caused by thermal activation of the energetically most stable anti-parallel paired NLO state to the higher-energy isolated state, then the experimental activation energy (E_a) should represent the energy difference (E_c) between the two dipole states in a parallel alignment,[28,29] as given by

$$E_c = \frac{|\mu|^2(1 - 3\cos^2\theta)}{\varepsilon \cdot \varepsilon_0 \cdot r^3}, \qquad (2)$$

where μ is the dipole moment of the NLO compound, ε and ε_0 are the dielectric constants of the film medium and of a vacuum, respectively, r is the inter-molecular stacking distance, and θ is the stacking angle. To obtain information about the molecular packing of paired NLO molecules in a crystal, the molecular stacking of the nearest-neighboring molecules was calculated from an X-ray crystal structure analysis, as shown in Fig. 8. For both types of NLO, the intermolecular stacking was found to have a center of inversion in the form of an anti-parallel pair. However, the inter-molecular stacking distance of the DBMNA was only 6.0 Å, being about half the distance of the 7-DCST, which had an inter-molecular stacking distance of 12.2 Å. This is probably due to a steric hindrance from the 1-perhydroazepinyl substituent. This means that the dipole–dipole interaction between DBMNA molecules, having a large dipole moment, must be much stronger than that between 7-DCST molecules; it is easy to imagine that there must be a large number of anti-parallel NLO pairs in a molecularly dispersed PR polymer containing DBMNA. From the data shown in Fig. 8, the value of θ of DBMNA and 7-DCST was estimated to be $\theta = 60°$ and $90°$, respectively. Substitution of these values into Equation 2 gives $E_c = 0.31$ and 0.1 eV for DBMNA and 7-DCST, respectively. Surprisingly, these E_c values are in good agreement with their respective experimental E_a values, because both values of E_a and E_c for 7-DCST are almost one-third those of DBMNA. This result indicates that the Boltzmann distribution between the paired and isolated dipole states in the spissated solution just before solidification is frozen into the resulting cast polymer film. Moreover, the good agreement between the different theoretical E_a values between DBMNA and 7-DCST also provides strong support for the concept of high-temperature casting.

Finally, we examined the effect of high-temperature casting on the improvement of the PR performance. Figure 9 shows the diffraction efficiency and response speed for various casting temperatures for both systems containing DBMNA and 7-DCST. In the DBMNA system, the diffraction efficiency was greatly improved by casting at higher temperatures. The sample cast at $T_{ca} = 70$ °C showed almost the same diffraction characteristics as the 7-DCST system at room temperature. In the case of 7-DCST samples, the effect of high-temperature casting seems to be saturated against the casting temperatures, since the difference in energy (E_c or E_a) between the two dipole states was only about 0.08–0.1 eV. Therefore, high-temperature casting is much more effective for systems dispersed with an NLO, such as DBMNA, which has a large dipole moment and a large molecular susceptibility.

In a comparison of two polymer samples showing almost the same diffraction efficiency of 15%, for a DBMNA film cast at $T_{ca} = 70$ °C and a 7-DCST film cast at $T_{ca} = 50$ °C, both samples exhibited the same value of r_{33}, i.e., $r_{33} = 50$ pm/V in the same applied field (see Fig. 4 for the DBMNA sample and Fig. 6 for the 7-DCST sample). This observation was consistent in the sense that samples having almost the same value of r_{33} also had the same diffraction efficiency.

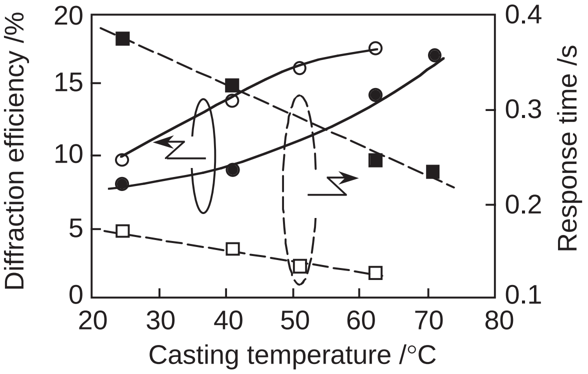

Fig. 9. Photorefractive characteristics against the casting temperature. Applied field = 90 V/μm, observed at 24 °C. The open and filled circles represent the diffraction efficiency of 7-DCST and DBMNA, respectively. Similarly, the open and filled squares represent the response time of 7-DCST and DBMNA, respectively.

The response time was also improved with increasing the casting temperature for the two NLO polymers. However, the rate of improvement in the response time with increasing casting temperature was more marked for the DBMNA compared to the 7-DCST. This is the first time that a high response speed of near to 0.2 s has been achieved in a PVK-based composite polymer containing DBMNA under the same measurement conditions for the beam intensity and in an external applied field. However, the 7-DCST sample showed a much faster response time of near to 0.1 s compared to a sample containing DBMNA (about 0.2 s), and overall, the 7-DCST sample exhibited higher response speeds. This strongly suggests that the difference in the response speed may be caused by the different reorientation speeds caused by an orientational enhancement effect, which involves a substantial rotational movement of the NLO molecules. Therefore, the long stick-like shape of the DBMNA molecule is sterically unfavorable for reorientating in the space-charge field in a polymer matrix. It would be worthwhile, however, to show that the high-temperature casting technique can be used to obtain a large r_{33}-value PR polymer composite, which is one of the most important properties for a high-performance PR polymer.

Conclusion

With an aim of achieving a high-performance PR polymer, we examined the performance of PVK-based PR polymers and their dependence on two types of NLO molecules. We found that the electro-optic coefficient, r_{33}, which governs the PR performance, was not directly proportional to the susceptibility of the NLO compounds, due to the formation of anti-parallel pairs by the NLO molecules in the polymer matrix. By introducing a new method, high-temperature casting, we found that the r_{33} values were greatly improved, owing to an increase in the number of unpaired NLO molecules. This was especially so in the case of NLO molecules with large dipole moments. As a result, the diffraction efficiency improved greatly. However the response time in molecularly dispersed PR polymers was still dominated by the orientation enhancement effect: smaller-sized NLO molecules with a large molecular susceptibility are preferred to obtain the fastest response time.

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