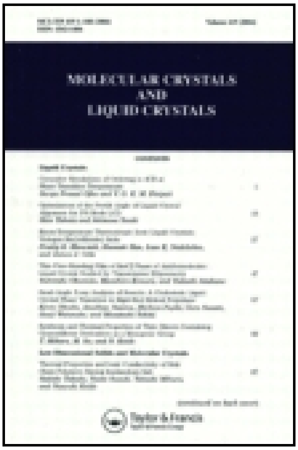

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High Performance in Molecularly Doped Photorefractive Polymers - High Temperature Casting Effect of r_{33}

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High Performance in Molecularly Doped Photorefractive Polymers – High Temperature Casting Effect of r_{33}^{-}

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To achieve high performance in molecularly dispersed photorefractive polymers, it is essential for the sample films to show the large electro-optic coefficient (r_{33}), which is emerged by orientating nonlinear optic (NLO) molecules incorporated toward the external electric field applied across the film. In this work, the effect of casting temperature in preparing the sample films was examined. It was found that the samples prepared by casting at the higher temperature showed the larger r_{33}. In the samples thus prepared, the diffraction efficiency and response in FWM experiments were much improved.

Keywords: Photorefractive polymer; Electro-optic coefficient; Casting temperature effect;

INTRODUCTION

Recently, organic photorefractive (PR) polymers have attracted considerable attention as photonic materials [1]. Among these, the PVK(poly-*N*-vinylcarbazole)-based molecular dispersion PR polymers with low glass transition temperature (Tg) have been focused and studied extensively so far [1,2]. The low Tg PR polymers have the features that large refractive index change can be realized by birefringence effect in addition to Pockels effect, because NLO molecules incorporatedare easily rearranged toward the space charge field formed in the polymer, so-called "orientational enhancement effect" [1]. In fact, the PVK-based PR polymer doped with *N*-EtCz (N-ethylcarbazole) as a plasticizer exhibited nearly 100% diffraction efficiency under a certain condition [2]. However, this PR polymer had a serious problem that doped small molecules are easily crystallized. In our previous work [3], we solved this problem and successfully developed thermally stable PR polymer by replacing EtCz with BisCzPro (bis-*N*-carbazolylpropane), dimer compound of carbazole, or the mixture of EtCz and BisCzPro. But the response speed for the grating formation was not improved so much because the reorientation of NLO molecules is still predominant over Pockels effect. One of the ways to improve this is to increase the contribution of Pockels effect, i.e., to orientate the NLO molecules to the external electric field direction as much as possible to yield large electro-optic coefficient r_{33} of the PR films. In the present work, therefore, the effect of casting temperature in preparing the sample films was examined to ensure the well-defined molecular dispersion of the NLO molecules in the films. It was found that the samples prepared by casting at the higher temperature showed the larger r_{33} and also improved diffraction efficiency as well as response speed in FWM experiments.

Samples and Sample Preparation

The PR polymer used in this study was consisted of 35wt% 4'-(*N,N*-diethylamino)benzyliden-2-methyl-4-nitroaniline (DBMNA) as an NLO, 1wt% TNF, charge generation sensitizer, 24 wt% EtCz and 8wt% BisCzPro, plasticizer, and 32wt% PVK. The chemical structures of these materials are shown in Fig. 1. These compounds were dissolved in toluene before being cast on indium tin oxide (ITO) electrodes. To change the casting temperature, the solution and ITO substrates were kept at a given temperature for a long

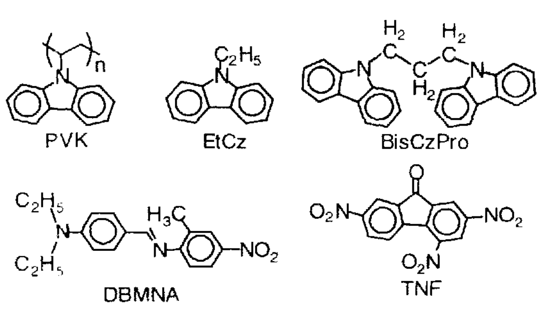

FIGURE 1 Chemical structures used in this study.

while, and then at the temperature casting was carried out as usual. Cast samples were dried *in vacuo* for overnight and heated up to about 130°C to make a sandwiched sample cell with two ITOs. Polyimide spacers were used to maintain a uniform thickness of 100μm.

Optical Measurements

The electro-optic coefficients, r_{33}, an effective component for PR effect, were obtained according to the method reported by J. S. Shildkraut [4]. The evaluation of the photorefractivity was made by four-wave mixing (FWM) experiments. Holographic gratings were written in the polymers using two beams of equal intensity from 22 mW He-Ne laser (633 nm) overlapped in the sample film at incidence angles of 60° and 30° to the normal direction, respectively. In FWM experiments, the reading beam (0.5 mW) was aligned so as to propagate in the opposite direction to one of the writing beam.

Results and Discussion

In Fig.2 are shown the temperature dependence of r_{33} for the samples cast at various temperatures. Very interestingly, the value of r_{33} increased with rising the casting temperature, and in a sample cast at 70°C it reached 60 pm/V, which had never been observed in the room temperature cast (typically, ~10 pm/V in the case of DBMNA). It should be noted that similar behavior was also observed for other NLOs, although the rates of increase depend on the kind of NLOs. When NLO molecules having a large dipole moment are dispersed to the polymer in a high density , it is easily pictured that NLO molecules may form energetically stable anti-parallel pairs due to the dipole-dipole

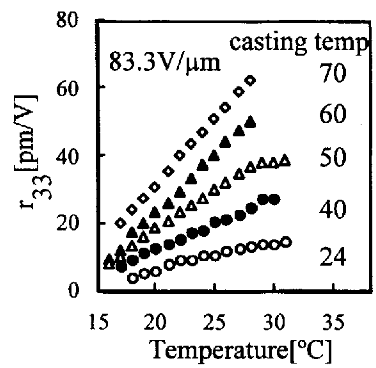

FIGURE 2 Temperature dependence of r_{33} for various casting temp.

interaction, which do not respond to external field applied for the electro-optic effect emergence. In the 35wt% dispersion, indeed, the inter-molecular distance becomes less than 10 Å. Thus, high temperature casting makes NLO molecules embedded in the polymer to be isolated from each other and increases the fraction of NLOs, which can orient toward external field to give the large r_{33} in consequence. The detailed analysis will be given in the forthcoming paper.

Fig.3 shows typical PR transients for these samples cast at various temperatures in FWM experiments under applied field of 90 V/μm. Apparently, the higher temperature casting sample gave the higher diffraction efficiency and response speed, reflecting the increase of r_{33}. Thus, the high temperature casting technique will provide one method to improve the performance in molecularly dispersed PR polymers.

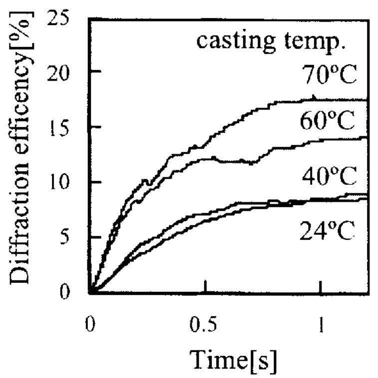

FIGURE 3 Typical PR resopnse. Applied field=90V/μm.

Conclusion

In this study, aiming at high-performance of molecularly dispersed PR polymers, we examined the casting temperature dependence of PVK-based PR polymer. It was found that the electro-optic coefficient r_{33} was greatly increased by casting the PR films at high temperature. In the samples thus prepared, the diffraction efficiency and response were much improved.

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