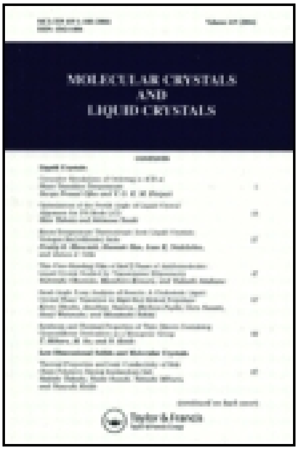

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Improved Long-Term Stability and Performance of Photorefractive Polymer Devices Containing Eutectic Mixtures of Electrooptic Chromophores

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ABSTRACT

Recently, amorphous organic photorefractive (PR) materials have attracted a lot of attention. However, since most of the high-performance PR organic materials are polymers blended with large amounts of low-molecular-weight components, their shelf-life time is limited due to phase separation. One way to improve the shelf-life time, which was proposed by us recently, is to use eutectic mixtures of two electrooptically active chromophores. However, in our earlier attempt in improved life time was achieved at the cost of a reduced performance due to increased absorption. In this paper, we apply this technique again with great success, not only improving the life time by a factor of 15, but at the same time improving the steady-state holographic performance by 30%.

Keywords: photorefractive polymers, eutectic mixtures, holography

INTRODUCTION

The PR effect is among the most promising mechanisms for reversible holographic applications such as real-time optical processing and holographic data storage [1]. The hologram is recorded as a spatial modulation of a recording material's refractive index induced by an internal electric field which develops as a result of charge carrier separation. Over the last years, amorphous organic photorefractive (PR) materials have attracted a lot of attention due to their excellent performance, including absorption-limited complete diffraction in only 100-150 μm thin films and net optical gain larger than in traditional inorganic PR materials [2]. Furthermore, organic materials offer the advantage of wide structural flexibility, they can be processed into

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devices of nearly arbitrary size with excellent reproducibility, and they are inexpensive.

Highly-doped composites based on the photoconductor PVK have so far shown the best PR performance among polymers [2-4]. However, a severe drawback of these materials is their limited shelf-life time, owing to the fact that they contain large amounts of low-molecular-weight components (e.g. a total of 67 % in [3]) and at the same time posses low glass-transition temperatures T_g. The latter allows the in-situ orientation of the nonlinear optical (NLO) chromophores by an externally applied electric field E_{dc}, necessary to obtain a macroscopic electrooptical (EO) effect in the material. Another advantage of the low T_g is that the PR performance in such materials is strongly enhanced by the so-called 'orientational enhancement mechanism' [5], enabling birefringence contributions to the index modulation amplitude.

The high loading of small molecules makes many of PR composites metastable, and their shelf-life time becomes limited by crystallization of one of the components. The life time of devices containing large quantities of small molecules was found to vary strongly, depending on (i) the compatibility of all components, (ii) the number of crystallization centers, such as dust particles, and (iii) the diffusional mobility of molecules in the matrix. The latter is mainly determined by the internal free volume which depends on the processing conditions such as the cooling rate. In soft materials it was observed that crystallization was induced by the application of the electric field and or by heating by the laser light.

Several techniques to improve the shelf-life time have been proposed in the past. One attempt was to use a polymeric binder with a lower T_g than PVK ($T_g \approx 200°C$) in order to avoid the addition of a plasticizer [6], but the life time of these highly-doped materials was only slightly improved. All other attempts involved the adjustment of the EO chromophores. For example, liquid chromophores [7] or some with solubilizing side chains [8] have been used. Another approach is to use chromophore mixtures, e.g. a random mixture of four EO isomers [9] or to specifically adjust the chromophore ratio to the optimum (eutectic) concentration by mixing two NLO chromophores [10]. However, in all these attempts longer life times were obtained so far at the cost of a reduced PR device performance.

The ideal materials to prevent the phase-separation problem are (nearly) monolithic systems, consisting mainly of just one component, thus excluding phase separation in the first place. Examples in this category include fully-functionalized PR polymers [11], PR liquid crystals (LC) [12,13], and multifunctional low-molecular weight glass-forming PR compounds [14,15]. However, each of those material classes exhibits specific disadvantages, such as lengthy synthesis, limited resolution, electrochemical instability, and/or slow response times. Furthermore, by limiting oneself to one multifunctional component, there is a tradeoff in performance since none of the functionalities is optimized in the same molecule. Thus, considering all aspects involved in the selection of a PR material for application, only PR composites can overcome the above mentioned disadvantages.

One of the most promising concepts for improvement of the life time of PR devices made from highly-doped composites seems the use of eutectic mixtures of two EO chromophores [10]. In our earlier work, the shelf-life time of PVK-based PR composites using the nonlinear optical (NLO) chromophore 2,5-dimethyl-4-(p-nitrophenylazo) anisole (2,5DMNPAA) was improved by one order of magnitude, the performance in terms of achievable Δn was almost unchanged, however, one disadvantage remained, namely the increased absorption of the second chromophore used earlier, the 3,5DMNPAA. Now, we choose another azo dye, 3-methoxy-4-(p-nitrophenylazo)anisole (MNPAA, see Fig. 1), which exhibits an absorption spectrum very similar to 2,5DMNPAA (for both $\lambda_{max} = 396$ nm).

EXPERIMENTAL

Binary mixtures of 2,5DMNPAA (1) and MNPAA (2) with varying molar fraction $X = m_1 / (m_1 + m_2)$ (where m_i are the weights of each chromophore) were prepared, and the melting temperatures were determined. The phase diagram shown in Fig. 1) indicates a eutectic mixture for x ≈ 0.50 with a melting temperature T_m = 130-132°C. For the eutectic composition, the melting point is the lowest for any binary mixture of the two chromophores, indicating the weakest possible interactions between dye molecules. Therefore, the eutectic composition is expected to be best to prevent crystallization in PR devices for longer times.

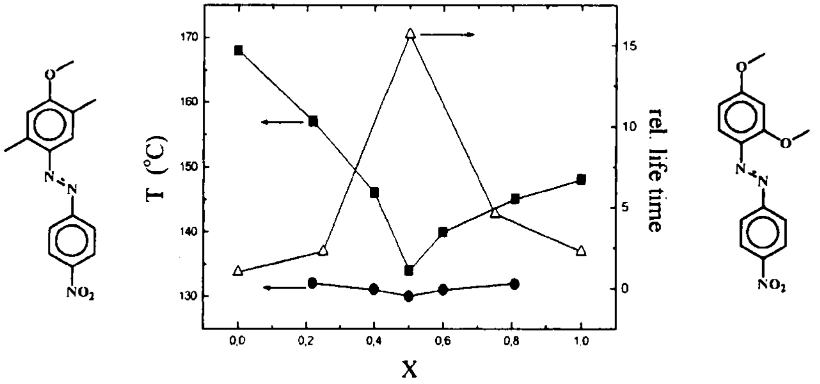

Fig. 1: Phase diagram of binary mixtures of 2,5DMNPAA and MNPAA: transition solid/2-phase (solid circles), transition 2-phase/liquid (solid squares) and relative life time of devices measured at 60°C (open triangles). The lines are guide to the eye. left/right: chemical structures of 2,5DMNPAA (left, x = 0) and MNPAA (right, $x = 1$), respectively.

A series of PR composites with constant total content of EO chromophore (39 %wt), but varying molar fraction x of the two chromophores, respectively, were prepared. The other components were PVK (45 %wt), the plasticizer N-ethylcarbazole (ECZ, 15 %wt), and the sensitizer 2,4,7-trinitro-9-fluorenon (TNF; 1 %wt). The detailed device preparation was given previously [3]. The PR properties were investigated by degenerate four-wave mixing (DFWM) experiments in a tilted geometry (tilt angle ψ_{ex} = 60°). The output of a 690 nm laser diode was split into two parts to form the writing beams, which were then overlapped inside the sample with an angle of $2\theta_{ex}$ = 20° to create a sinusoidal interference pattern. Both writing beams were s-polarized, had a diameter of approximately 1 mm and a power density of I_1 = 0.14 W/cm^2 and I_2 = 0.17 W/cm^2, respectively. The index grating recorded in the PR material was read out by diffracting a weak p-polarized probe beam ($I_3 \approx$ 0.05 mW/cm^2), which was counterpropagating with one of the writing beams. The diffraction efficiency η is defined as the ratio between the diffracted light intensity and the incoming readout intensity.

RESULTS AND DISCUSSION

Figure 2 shows the results of the DFWM experiments performed with the different devices. Complete internal diffraction occurs for the composite using pure 2,5DMNPAA an external electric field of $E(\eta_{max}) \approx$ 72 V/μm. The field of maximum diffraction indicates the identical index modulation amplitude Δn in all cases. It drops for increasing molar fraction X until the eutectic composition

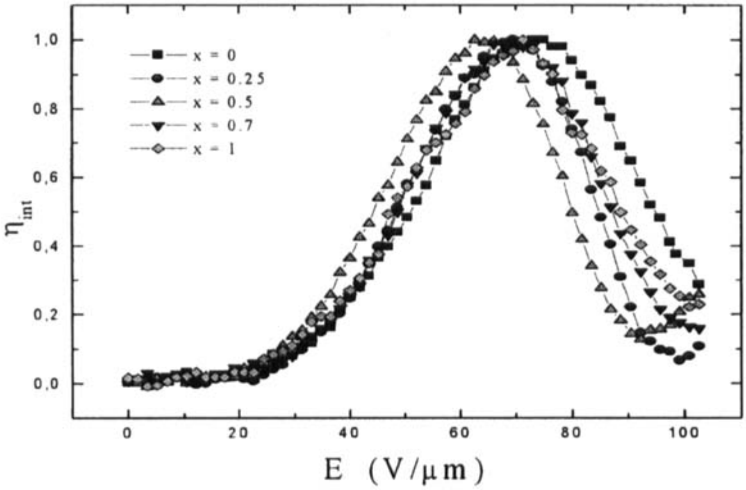

Fig. 2: Electric-field dependence of the normalized internal diffraction efficiency in devices dye/PVK/ECZ/TNF 39:45:15:1 %wt: x = 0.00 (squares), x = 0.25 (circles), x = 0.50 (up triangles), x = 0.71 (down triangles), and x = 1.00 (diamonds).

is reached, $E(\eta_{max}) \approx 64$ V/µm, and then increases again. Finally, for pure MNPAA $E(\eta_{max}) \approx 69$ V/µm is obtained. The index modulation amplitude reaches $5.1 \leq \Delta n \leq 5.8\ 10^{-3}$ at $E \approx 102$ V/µm (see Tab. 1 for details). The actual diffraction efficiencies η are absorption-limited. The absorption coefficient at 690 nm amounts to 7 cm^{-1}, corresponding to ca. 90 % external diffraction efficiency.

Obviously, the performance of the device using purely MNPAA is better than the one using only 2,5DMNPAA. Furthermore, the eutectic mixture shows the best performance. We attribute this result to the differences glass transition temperature, which allows better orientation of the chromophores in the eutectic mixture compared with the other compositions [16]. Assuming a quadratic dependence of the index modulation amplitude Δn on the applied electric field [5], this corresponds to a factor 1.3 larger Δn in the eutectic devices compared with those using 2,5DMNPAA.

The room-temperature life time of the devices is difficult to measure due to the slow crystallization rate. Therefore, the stability study of the devices was conducted at $T = 60°C$ by measuring the transmission of the devices as a function of time. An induction period is observed, during which the transmitted light intensity remains constant, followed by a crystal growth period during which T decreases. We define the life time of the devices as the intercept of the linear extrapolations of the induction and growth period. It corresponds to the first visible appearance of small crystallites in the polymer matrix.

The results of the stability investigation are summarized in Table 1. Clearly, the device life time $t(60°C)$ is by far the best for the eutectic composition. It is by more than 15 times better than for the reference device using exclusively 2,5DMNPAA (Tab. 1, Fig. 1). This compares to a 4.5 improvement when using 2,5/3,5DMNPAA eutectic mixtures [10], demonstrating the significant progress achieved here.

	x = 0	x = 0.25	x = 0.5	x = 0.75	x = 1
α (cm^{-1})	7	7	7	7	7
T_g (°C)	17	14	10	13	15
$E(\eta_{max})$ (V/µm)	73	69	64	70	71
Δn_p (10^{-3})	5.1	5.6	5.8	5.5	5.4
t(60°C) (sec.)	650	1,500	10,200	3,000	1,500

Table 1: properties of the investigated composites: α absorption coefficient, T_g glass transition temperature, $E(\eta_{max})$ external field for maximum internal diffraction, Δn_p index modulation amplitude at E = 102 V/µm, t life time of devices at 60°C.

CONCLUSION

In conclusion, we obtained PR polymer devices with tremendously improved shelf-life times by using a eutectic mixture of two isomeric EO chromophores. Unlike in our earlier attempt to use this technique, not only was the life time improved by more than one order of magnitude, but the performance was improved by about 30%. The shelf-life times at room temperature are unknown at this point.

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