

High-performance polysiloxane-based photorefractive polymers with nonlinear optical azo, stilbene, and tolane chromophores

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The performance of photorefractive (PR) polymers strongly depends on the incorporated nonlinear-optical chromophores. We compare three polysiloxane-based PR guest–host polymers with an azo, a stilbene, and a tolane type of chromophore. Characteristic properties such as diffraction efficiency η , gain coefficient Γ , phase shift ϕ , modulation of the index of refraction Δn , and response time are measured as a function of the external electric field. Orientational enhancement as well as the influence of photoisomerization is observed and analyzed quantitatively. The materials show high performance with $\Delta n > 1 \times 10^{-2}$, corresponding to external diffraction efficiencies of 60% for samples of only 40- μm thickness. © 1998 Optical Society of America [S0740-3224(98)00209-4]

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Photorefractive guest–host polymers belong to the most successful organic PR systems synthesized so far.^{1–4} Generally, a high doping level of nonlinear-optical chromophores in a photoconducting polymer–host provides good orientational mobility of the dopants. The reason for this is the low viscosity, which is due to a reduced glass-transition temperature near room temperature. As a consequence, the PR performance is improved by the orientational enhancement effect.⁵ Further improvements require a deeper understanding of the roles of the various chromophores. Here we compare the PR properties of three guest–host systems consisting of a photoconducting polysiloxane (PSX) host doped with trinitrofluorenone (TNF) and with three different chromophores based on azo, stilbene, and tolane moieties.

The photorefractive effect can be defined as a spatial modulation of the index of refraction Δn induced by a light-intensity pattern whereby the former is spatially shifted with respect to the latter.⁶ Two coherent diode laser beams at a wavelength of $\lambda = 670$ nm are intersected within the samples to yield an interference pattern with a grating period of 4 μm . The angle between the beams was 17°, and the sample was tilted at an angle of 60° with respect to the direction of incidence. We performed degenerate four-wave mixing experiments in which the induced Δn grating is probed by a third beam, which is diffracted off the grating. We measured the time- and E -field-dependent diffraction efficiencies, defined as the ratio between the diffracted and the incident power of the reading beam. The degenerate four-wave mixing experiments also allow for the determination of the response time and the magnitude of the modulation of refractive index Δn . We carried out two-beam coupling experiments to prove the phase-shift-induced energy transfer between the writing beams and to deduce the

gain coefficient Γ . A well-known technique based on grating translation⁷ was used to measure directly the phase shift ϕ between the light-intensity pattern and the refractive-index modulation. For these measurements the sample was translated along the direction of the induced Δn grating much faster than the response time of the material. As a result, a sinusoidal intensity variation of the two writing beams was recorded behind the sample.

To exhibit photorefractivity the PR materials must simultaneously provide generation, transport, and trapping of charges as well as electro-optical properties.⁸ In our case a photoconducting PSX host with pendant carbazole moieties was used as the charge-transport material. The PSX system is well known for its low light-scattering properties.⁹ Its synthesis was described elsewhere.¹⁰ Commercially available trinitrofluorenone (TNF) was added for the photogeneration of charges by means of a charge transfer complex with the carbazole moieties. The chromophores shown in Fig. 1 were used as nonlinear-optical molecules. No additional trapping sites had to be added to the material, because they are inherently present¹¹ as a result of polymer-chain ends, impurities, or the other functionalities. The glass-transition temperature was carefully adjusted to $T_g = 25$ °C to ensure high orientational mobility of the chromophores for optimum orientational enhancement.

Figure 2 depicts gain coefficient Γ versus the applied electric field E for the system PSX–azo–TNF. The E -field dependence is typical of all our systems and, in particular, the different signs of Γ for s - and p -polarized writing beams indicate the presence of the orientational enhancement effect.⁵ The maximum gain coefficients for the composites are listed in Table 1. Inasmuch as $\Gamma \sim \Delta n \sin(\phi)$, measurements of both phase shift ϕ and

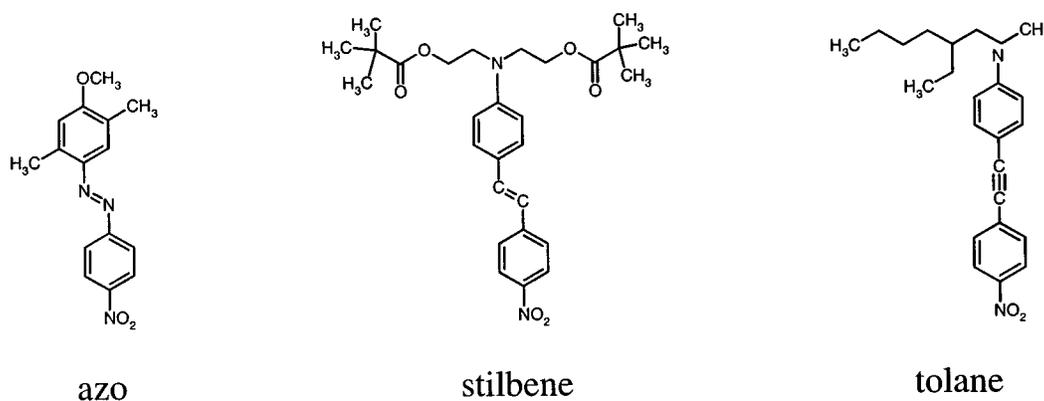
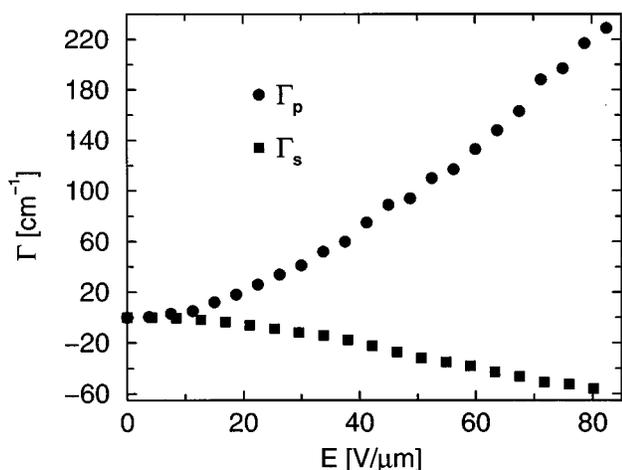


Fig. 1. Nonlinear-optical chromophores incorporated into our systems.

Fig. 2. Gain coefficient Γ versus external electric field for p - and s -polarized writing beams for the system PSX-azo-TNF.

the modulation depth of index of refraction Δn are necessary for a qualitative understanding of the different magnitudes of Γ . By the translation technique described above, phase shift ϕ as well as modulation Δn were determined. It should be noted that the measurements were carried out for s -polarized writing beams only for which the bending effects of the Δn grating could be neglected.⁶ A summary of the photorefractive properties of our three polymer systems is given in Table 1. Although the size of Δn_s for the stilbene and the azo systems is almost equal, gain coefficient Γ_s differs significantly for these two materials, as can be explained by different phase shifts ϕ , which are 4° for stilbene and 21° for the azo composite. Phase shift ϕ can be expressed as (for $E_D \ll E_0$, E_q)³:

$$\phi = \arctan\left(\frac{E_0^2 + E_D E_q}{E_0 E_q}\right), \quad (1)$$

where E_0 is the external electric field, $E_D = k_B T K_G / e$ is the diffusion field, and $E_q = e N_{\text{eff}} / (\epsilon_0 \epsilon_r K_G)$ is the trap-density-limited space-charge field. K_G denotes the wave vector of the grating, ϵ_0 is the vacuum permittivity (assuming that $\epsilon_r = 8$), k_B is Boltzmann's constant, and N_{eff} is the effective density of the pertinent traps. We can estimate the effective trap density N_{eff} (Table 1) by fitting Eq. (1) to the measured phase shift ϕ as a function of external field E . For each case N_{eff} is of the order of

10^{17} cm^{-3} , with increasing magnitude from the azo to the tolane to the stilbene composite. The reason for this tendency is not understood, but it may be connected to the chemical nature of the chromophore. Nevertheless, it is obvious that the chromophores play an important role in the microscopic trapping mechanism.

From the E -field dependence of the absolute Δn values in Fig. 3 the contribution of the photoisomerization grating¹² (chromophore reorientation owing to *trans-cis-trans* cycles) to Δn can be quantitatively determined. In the case of the azo system the modulation of the index of refraction starts with $\Delta n = 10^{-4}$ at zero field. At zero field no PR grating is present, and the measured Δn is due only to the E -field-independent *trans-cis* effect. At $\sim 10 \text{ V}/\mu\text{m}$, Δn drops to a minimum and increases again for higher E fields. The reason for this behavior is the buildup of the PR grating whose sign is opposite that of the *trans-cis* grating. For the stilbene polymer the *trans-cis* part of the system is of the order of $\Delta n = 10^{-5}$, whereas it completely disappears for the tolane polymer. This result is obvious because the threefold carbon-carbon bond prevents *trans-cis* isomerization for tolane.

The diffraction efficiency η for s - and p -polarized reading beams as obtained from the degenerate four-wave mixing measurements is plotted in Fig. 4 as a function of external field E for the system PSX-stilbene-TNF. The internal diffraction efficiency is given by⁶

$$\eta = \sin^2 \left[\frac{\Delta n \pi d \hat{e}_1 \cdot \hat{e}_2}{\lambda (\cos \Theta_1 \cos \Theta_2)^{1/2}} \right], \quad (2)$$

where Θ_1 and Θ_2 are the angles of incidence of the two writing beams, d is the thickness of the sample, and \hat{e}_1 and \hat{e}_2 are unit vectors directed along the electric field of the incident and the diffracted beams, respectively. Because of the \sin^2 dependence of η , the diffraction efficiency η_p in Fig. 4 shows a maximum at $70 \text{ V}/\mu\text{m}$, which corresponds to 100% internal diffraction efficiency. Using Eq. (2), we determined the absolute value of Δn for each of the composites (Fig. 4, inset; Table 1). With a refractive-index modulation of $\Delta n_p = 0.011$ the system PSX-stilbene-TNF exhibits state-of-the-art performance. The response times of the polymers were determined by a single-exponential fit to the temporal decay of $\eta^{1/2}$ after blocking of one of the writing beams.

Table 1. Summary of Photorefractive Properties of the Investigated Guest–Host Systems^a

Property	Guest–Host System		
	PSX–Azo–TNF	PSX–Stilbene–TNF	PSX–Tolane–TNF
Mass ratio	53:46:1	51:48:1	78:21:1
Γ_p (cm ⁻¹)*	221	53	23
Γ_s (cm ⁻¹)*	-56	-7	-6
Δn_p (10 ⁻³)*	5.8	10.5	2.3
Δn_s (10 ⁻³)*	1.8	1.7	0.7
ϕ (°)*	21 ± 3	4 ± 2	11 ± 4
N_{eff} (10 ¹⁷ cm ⁻³)*	1.5 ± 0.2	8 ± 4	3 ± 1
τ_{min} (10 s)*	0.5	6	4
$A_{\text{BR}}/A_{\text{EO}}$	-5.5 ± 1.0	-2.2 ± 0.6	-4.2 ± 0.7

^aThe quantities marked with* refer to $E = 100$ V/ μm for the tolane and the stilbene and to $E = 80$ V/ μm for the azo composites. The intensity of the writing beams was 1.2 W/cm².

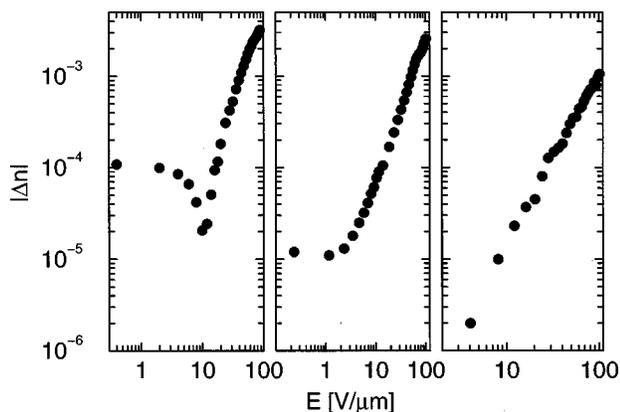


Fig. 3. Absolute value of refractive-index modulation Δn_s for the systems PSX–azo–TNF (left), PSX–stilbene–TNF (middle), and PSX–tolane–TNF (right).

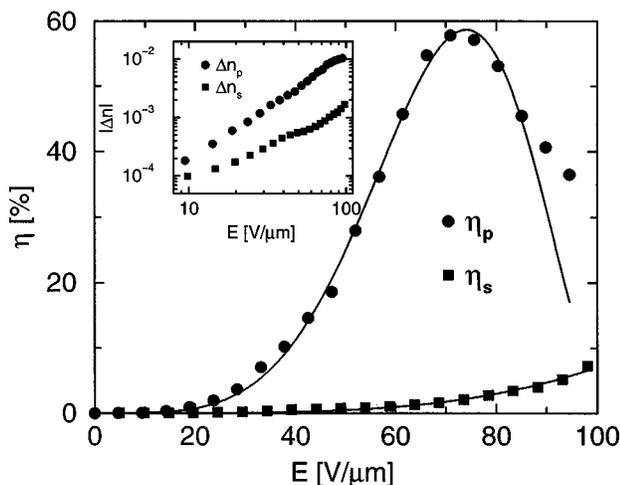


Fig. 4. External diffraction efficiency η for the system PSX–stilbene–TNF for s - and p -polarized reading beams (sample thickness, 40 μm). Inset, values of Δn as determined from Eq. (2). Curves indicate the corresponding fits.

The application of the theory of the orientational enhancement effect⁵ yields $A_{\text{BR}}/A_{\text{EO}}$, the ratio of Δn caused by birefringence and Δn owing to the electro-optic effect. We determined this ratio by using $\eta_s(E)/\eta_p(E)$ for the three systems. In each case the birefringent part of the system dominates (Table 1). Comparing $A_{\text{BR}}/A_{\text{EO}}$ with the size of the molecules, we can observe a correlation:

The smaller the size of the molecule, the larger is the contribution of the birefringence to Δn . This tendency is also visible for the holographic response times for which the smallest molecule—the azo dye—shows the fastest response. In the azo system the speed of the orientational effect is most likely also being catalyzed by the *trans*–*cis* photoisomerization cycles, which stimulate reorientation.

In summary, we have characterized a series of PR guest–host polymers with an azo, a stilbene, and a tolane chromophore. We measured the degree of the photoisomerization grating for each system and calculated the ratio $A_{\text{BR}}/A_{\text{EO}}$. The theory of the orientational enhancement effect was confirmed, and the influence of the chromophore size on the response time was determined. Measurements of the phase shift ϕ revealed a significant influence of the chromophores on the effective trap density in PR polymers.

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