Stabilization of the response time in photorefractive polymers

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The optical and photoconductive fatigue of fast photorefractive polymers have been studied in a family of C_{60}-sensitized polymer composites containing styrene-based chromophores with varying ionization potential. Changes in response time and in photoconductivity were studied for exposures up to 10^4 J/cm^2. Increasing the chromophore ionization potential beyond that of the polyvinylcarbazole host was found to stabilize the response time. Studies of the electric-field dependence of the steady-state diffraction efficiency in various samples confirm the role of C_{60} anions as possible traps. © *2000 American Institute of Physics.* [S0003-6951(00)02141-0]

Guest–host photorefractive polymer composites present the possibility of economical media for erasable holographic recording and real-time optical data processing. Soon after the first observation of photorefractivity in a polymer,[1] composites were doped with anisotropic chromophores, enhancing the index modulation through dipole reorientation by the photorefractive space-charge field and the applied field.[2] Subsequently, guest–host polymers with nearly 100% diffraction efficiency[3] could be demonstrated. In recent years, photorefractive polymers have been refined to produce improved dynamic range,[4] increased shelf life,[4] and ever-improving response times.[5,6] In contrast to these improvements, lesser consideration has been given to photoconductive fatigue and optical operating lifetime.

In this letter, we are concerned with the continuous-use stability of photorefractive polymer composites with short response times and large index modulations. We present a systematic study of the response times and the photoconductive properties as a function of optical exposure under applied field for a series of chromophores with various ionization potential (I_p) doped in a poly-N-vinylcarbazole (PVK)-based matrix sensitized with C_{60}. The value of the I_p of the chromophore relative to that of the photoconducting polymer host is found to impact the evolution of the response time for increased exposure. This increase of response time correlates with a decrease of the photoconductivity and with an increased accumulation of a population of C_{60} radical anions. Studies of the electric-field dependence of the steady-state diffraction efficiency performed in various samples for different exposures corroborates the recent proposal that the population of C_{60} radical anions acts as the main photorefractive hole trap.[7]

We studied four different composites, each comprising a photoconductive host doped with a sensitizer and an optically anisotropic chromophore. PVK provides a hole-transporting host with I_p of about 5.9 eV, and is plasticized with N-ethylcarbazole (ECZ) in a 2:1 mixture by weight. The composites are sensitized with C_{60}, providing the high photogeneration contributing to recent observations of fast photorefractive response.[5] The synthesis of the styrene chromophores and their measured I_p have been reported previously[8] (see Table I). Each composite is doped with 25 wt % of chromophores, 1 wt % of C_{60} and 74 wt % of the PVK/ECZ host. Samples were prepared by laminating a 105 μm thick layer of each composite between glass slides with indium–tin–oxide electrodes. In this letter, the samples containing chromophores with 0, 1, 2, and 4 fluorine atoms will be designated F0, F1, F2, and F4, respectively, as shown in Table I.

In all samples, steady-state diffraction-efficiency, grating buildup response time, and photocurrent were measured under a precisely controlled sequence of exposures described below. For each sample, transient evaluation began with simultaneous observation of diffraction efficiency and photocurrent until steady-state conditions occurred with a moderate applied field of $E_a = 38$ V/μm. Then, one of the writing beams and the reading beams were blocked, leaving the sample exposed to the uniform illumination of one writing beam for a controlled dwell time. During this exposure time the applied field was set to $E_a = 76$ V/μm. The bias was then reduced to the nominal value and the second writing beam and reading beam restored to conduct the next measurement. This sequence was repeated in a progression of dwell times. For each exposure, steady-state four-wave mixing measurements of the field dependence of the index modulation were conducted by sweeping E_a from 0 to 76 V/μm over a period of 2 min. For the four-wave mixing experiments, two s-polarized 633 nm writing beams, providing equal fluences of 0.25 W/cm^2 in the sample, formed an angle of 20.5° in air. The sample surface normal was rotated 60° with respect to the bisector of these beams in the plane of incidence. The grating period in the sample was 3.1 μm, given a refractive index of 1.7. A p-polarized beam of 1 mW/cm^2 counter propagating with respect to the writing beam nearer the surface normal probed the diffraction of the gratings. The transient four-wave mixing data were fitted using a sine-squared biexponential function to allow comparison to previous results.[6]

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TABLE I. Sample numbering scheme. Ionization potential (I_p) of the dopant chromophore. Summary of initial steady-state diffraction efficiency (η_0), transient response time (τ_0), and photoconductivity (σ_0) measured at an applied field of 38 V/μm.

Sample	I_p (eV)	η_0 (%)	τ_0 (ms)	σ_0 (pS/cm)	fluorine positions
F0	5.9	15	19	230	none
F1	6.0	12	27	250	2
F2	6.1	4.1	58	100	2,5
F4	6.3	1.0	50	180	2,3,5,6
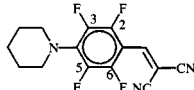
The initial diffraction efficiency η_0, the first response time constant τ_0, and the initial photoconductivity σ_0, measured for each sample at $E_a = 38$ V/μm are shown in Table I. We observe that the initial steady-state diffraction efficiency decreases with increasing of the ionization potential I_p of the chromophore. Note that for all the samples the response time is fast considering the low fluence of the writing beams and moderate value of the applied field. Figure 1 shows the evolution of the response time versus exposure in all four samples. For each composite, the response time is normalized to the initial value shown in Table I. For all samples, the buildup time of the photorefractive grating slows down moderately for exposures up to 100 J/cm^2. But beyond that exposure, a drastic change is observed for composites F0 and F1 leading to a tenfold increase in time constant. We observe a clear trend between the threshold at which the strong increase in response time is observed and the value of the I_p of the chromophore. Increasing the ionization potential through fluorine substitution of the phenyl ring in the styrene chromophore clearly stabilized the dynamics for exposures over 10^4 J/cm^2. To clarify the origin of the degradation of the response time we measured the photoconductivity of all samples *in situ* during the four-wave mixing experiments. The inset of Fig. 1 clearly shows that the evolution of the response time in different samples correlates with a decrease in photoconductivity. This result is consistent with the recent observation that the response time in these fast photorefractive polymers is mainly limited by the photoconducting properties of the sample rather than the orientational diffusion of the chromophore.[5,6] We attribute this evolution to the buildup of a population of C$_{60}$ radical anions in photorefrac-
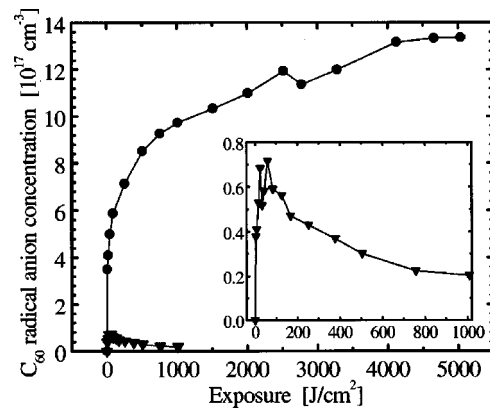
FIG. 2. C$_{60}$ radical anion concentration determined spectroscopically in samples F0 (●) and F4 (▼) as a function of exposure. Inset: closeup of the C$_{60}$ radical anion concentration as a function of exposure in sample F4.

tive polymer films under applied field and illumination as reported in PVK/C$_{60}$-based materials.[7,8] This population was found to correlate with the ionization potential of the chromophore for values of I_p near to, or less than, that of the host.[7] Here we show that this behavior is also observed for chromophores with I_p substantially higher than that of PVK.

To determine the exposure dependence of C$_{60}$ anion formation, absorbance readings in the spectral region of the known C$_{60}^-$ absorption peak at 1080 nm[7,8] were taken using a Cary 5G spectrophotometer with a 1 mm aperture. Each sample was exposed to a 633 nm beam at a fluence of 140 mW/cm^2 with $E_a = 80$ V/μm. In each cycle, the sample was removed from exposure, its absorbance measured with a delay of about 2 min, then returned to the exposure condition. The concentration of C$_{60}^-$ was calculated from the absorbance at 1080 nm, given[7,9] the extinction coefficient of 12000 L mol^{-1} cm^{-1}. As shown in Fig. 2, the evolution of the C$_{60}^-$ population following illumination under an applied field is quite different in samples F4 and F0. In sample F0, we observe a continuous increase with exposure as reported previously in Ref. 7. In contrast, when the ionization potential of the chromophore is significantly higher than that of PVK (sample F4), the C$_{60}^-$ population reaches a maximum for exposures of 100 J/cm^2 that is followed by a continuous decrease for longer exposures.

We note that the measured concentration of C$_{60}^-$ is in the range of 10^{16}–10^{18} per cm^3. In this range, and for our experimental conditions, the Kukhtarev model of photorefractivity predicts a transition from a trap-limited regime (for trap concentrations $< 10^{17}$ cm^{-3}) when the concentration of traps is insufficient to saturate the space-charge field, to a regime ($> 10^{18}$ cm^{-3}) where the space-charge field is equal to the component of the applied field along the grating spacing.[10] In orientational photorefractivity, the refractive index modulation amplitude Δn is proportional to the product $E_{sc}E_0$, where E_0 is the projection of the applied field E_a along the grating vector[2] and E_{sc} is the amplitude of the space-charge field. Consequently, Δn should exhibit a quadratic dependence on applied field ($\Delta n \propto E_a^2$) for high trap concentrations. For lower concentrations when the space-charge field is no longer saturated, the field dependence of Δn is more complex but can be fitted by a power dependence $\Delta n \propto E_a^P$ with $P < 2$. Thus, to assess whether or not the mea-
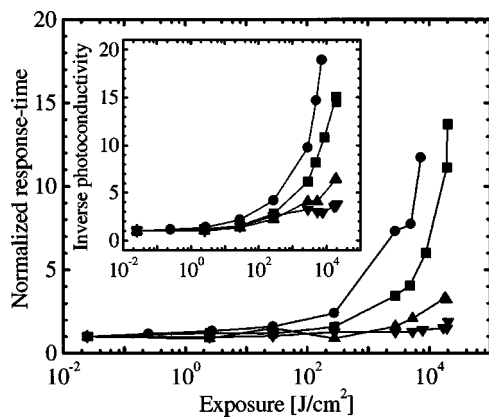

FIG. 1. Normalized response time as a function of exposure measured in four different samples: F0 (●), F1 (■), F2 (▲), F4 (▼). Inset: Inverse normalized photoconductivity as a function of exposure measured in the same samples.
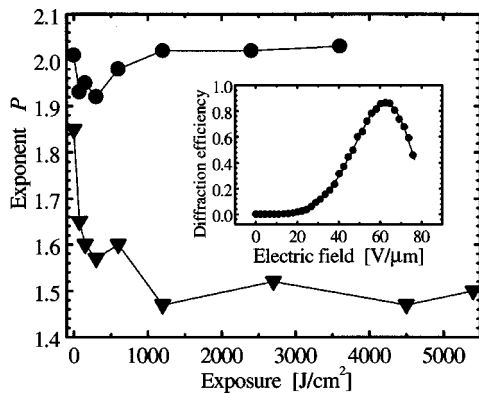
FIG. 3. Value of the exponent P of the field dependence of the refractive index modulation amplitude obtained by fitting the field dependence of the diffraction efficiency with Eq. (1) in samples F0 (●) and F4 (▼). Inset: Field dependence of the diffraction efficiency measured in sample F0 for an exposure of 3500 J/cm^2 (●) and the fit according to Eq. (1) (solid line).

sured population of C_{60}^- is the photorefractive trap, we measured the field dependence of the steady-state diffraction efficiency. Figure 3 shows the value of the exponent P as a function of exposure in samples F0 and F4 derived by fitting the field dependence of the steady-state diffraction efficiency (shown in the inset of Fig. 3) with the following simplified Kogelnik formula:[11]

$$\eta = A \sin^2(BE_a^P), \tag{1}$$

where η is the diffraction efficiency, E_a is the applied electric field, and A, B, and P are fitting parameters. In sample F0, $P > 1.9$ for all exposures and is consistent with the measured high concentration of C_{60}^-. In contrast, the clear decrease of P to values about 1.5 in sample F4, for prolonged exposures, is consistent with the decrease of the concentration of C_{60}^- to values for which the space-charge field is no longer saturated.

In conclusion, we showed that PVK-based photorefractive polymers sensitized with C_{60} and doped with styrene chromophores with various ionization potentials undergo a fatigue of the response time upon prolonged optical exposure with a strong continuous bias field. This change in dynamics was found to correlate with a decrease in photoconductivity that in turn was attributed to the accumulation of C_{60} radical anions. We show that the concentration of C_{60}^- can be controlled by adjusting the chromophore's I_p. Stabilization of the response time was demonstrated by increasing its value. Our studies corroborate the earlier proposal[7] that the radical anion of C_{60} acts as the photorefractive trap or directly controls its concentration. This letter clearly establishes that the photorefractive properties including diffraction efficiency and response time depend on the sample's exposure history and that great care should be taken when comparing the relative performance of different materials. We showed that the relative values of the energies of the frontier orbitals of the different components in a photorefractive polymer (sensitizer, photoconductor, and chromophore) play a major role in both the steady-state performance and its evolution under exposure. To fully validate the proposed structure–property relationships proposed here, further studies on different chromophore series will be required.

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