During the last decades much effort has been devoted to the investigation of photorefractive (PR) materials, mainly motivated by the wide range of potential applications for which they can be used (e.g., optical processing, phase conjugation, optical storage, and many others).1–3 One of the most investigated PR organic materials are the polymer composites that are based on a photoconducting polymer doped with a nonlinear optical (NLO) chromophore to provide the properties needed for photorefractivity, i.e., photoinduced charge generation, transport, trapping, and electro-optical activity. 4 In order to increase the charge generation efficiency, a sensitizer is generally added. In addition, after the discovery of the orientational enhancement effects in low glass transition temperature ($T_g$) systems,4 a plasticizer is often included to obtain composites with a $T_g$ close to room temperature.

One of the best-performing polymer composites, that has been extensively investigated, is the one based on the hole transporting polymer poly($n$-vinyl carbazole) (PVK), doped with the dicyanostyrene derivative 4-piperidinobenzylidene-malonitrile (PDCST) as nonlinear optical chromophore and the liquid plasticizer butyl benzyl phthalate (BBP), without the presence of sensitizer. The PR-effect is observed only when samples are previously subjected to an electric field (i.e., 20 V/$\mu$m for 10 min). Photoconductivity and birefringence of the composite become significant when the electric field treatment is performed at temperatures higher than room temperature (24 °C). Gain coefficient and PR speed, determined from two-beam coupling experiments, are compared to those obtained with the PVK/PDCST/BBP/C$_{60}$ standard sensitized composite. © 2005 American Institute of Physics. [DOI: 10.1063/1.2158032]
TABLE I. Photoconductive and birefringence properties (at 20 V/µm and 50 mW/cm²) and photorefractive properties (from 2BC experiments at 60 V/µm and 200 mW/cm²) at 633 nm and at room temperature (24°C) of sensitized (with C₆₀) and unsensitized (without C₆₀) PVK/PDCST/BBP composites. Conditioned samples have been subjected (prior to these experiments) to an electric field of 20 V/µm for 10 min at temperature of 32°C.

<table>
<thead>
<tr>
<th>Composite</th>
<th>σ_{dark} (pS/cm)</th>
<th>σ_{ph} (pS/cm)</th>
<th>M</th>
<th>(nₑ−nₒ)</th>
<th>Γ</th>
<th>Γ_{nl} (cm⁻¹)</th>
<th>τ (ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitized unconditioned (standard)</td>
<td>0.33±0.3</td>
<td>2.4±0.3</td>
<td>0.9±1</td>
<td>1.2±0.1</td>
<td>140±20</td>
<td>110±20</td>
<td>27±4</td>
</tr>
<tr>
<td>Sensitized conditioned</td>
<td>0.13±0.01</td>
<td>2.8±0.3</td>
<td>1.0±1</td>
<td>1.5±0.2</td>
<td>170±20</td>
<td>140±20</td>
<td>22±3</td>
</tr>
<tr>
<td>Unsensitized unconditioned</td>
<td>0.60±0.06</td>
<td>0</td>
<td>0</td>
<td>1.2±0.1</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Unsensitized conditioned</td>
<td>0.11±0.01</td>
<td>0.04±0.02</td>
<td>0.26±0.08</td>
<td>3.6±0.4</td>
<td>120±10</td>
<td>110±10</td>
<td>1000±100</td>
</tr>
</tbody>
</table>

unsensitized and sensitized composites, respectively). At present, the physical interpretation of this observation is still unclear. Additional experiments that provide detailed information about the changes in structure and polarization of the different components of the sample under the dc field need to be done.

First, we studied the effect of the field treatment on photoconductivity and birefringence. The photoconductivity measurements were made by a simple dc technique. Current flowing through the sample at 20 V/µm was measured with a Keithley 600B electrometer in the dark and under illumination at 633 nm provided by a 35 mW Melles Griot He–Ne laser with an intensity of 50 mW/cm². Then, the dark conductivity (σ_{dark}), the conductivity in the presence of light (σ_{light}), and the photoconductivity (σ_{ph} = σ_{light}−σ_{dark}) were obtained. Concerning conductivity, we also obtained the conductivity contrast defined by

\[ M = \frac{σ_{ph}}{σ_{ph} + σ_{dark}} \]

because it is preferable than σ_{ph} for PR characterization since the modulation of the internal space charge field in PR experiments is proportional to this parameter. Birefringence was measured by a simple transmission ellipsometric technique. The measured transmission (T) due to birefringence is given by

\[ T = \sin^2(\piΔn l/\lambda), \]

where Δn is the induced birefringence, l is the optical path length inside the sample, and λ is the wavelength. Samples were tilted 30° (internal angle ϕ=18°) and the external field strength was 20 V/µm. The birefringence of the poled polymer, assuming uniaxial symmetry, is defined as the semiaxis difference (nₑ−nₒ) of the index ellipsoid and related to the birefringence experienced in the ellipsoid by the approximated equation

\[ nₑ − nₒ = \frac{Δn}{\sin^2 \psi}. \]

It should be noted that both experiments, photoconductivity and birefringence, were performed at room temperature (24 °C), below the electric-field treatment temperature.

Values of σ_{dark}, σ_{ph} and M for conditioned and unconditioned standard composites [PVK (49.5%)/PDCST (35%)/BBP (15%)/C₆₀ (0.5%)] are shown in Table I. It can be seen that the field treatment produces an increase of photoconductivity due to an increase of σ_{light} and a decrease of σ_{dark}. Several groups have studied the relation between σ_{dark} and T₉ in PVK-based composites and in organic glasses. In our case, a decrease of σ_{dark} with increasing T₉ has been measured, in accordance with results reported in Ref. 12. Detail studies of the temperature and electric field dependence of σ_{dark} and σ_{ph} will be reported in a more extended paper. As previously mentioned, the field treatment leads to an increase in T₉, that justifies the observed reduction in σ_{dark}. Finally, it should be noted that the relative increase in the conductivity contrast produced by the field treatment is small (about 10%) because the photoconductivity is primarily due to C₆₀ sensitizer.

In order to investigate the effect of the field treatment without the interference of C₆₀, we also measured σ_{dark} and σ_{light} for conditioned and unconditioned samples of the unsensitized PVK (50%)/PDCST (35%)/BBP (15%) composite (α=6.0 cm⁻¹ at 633 nm). Values of σ_{dark}, σ_{ph} and M corresponding to this composite are also included in Table I. As for sensitized composites, also in this case conditioned samples show a lower σ_{dark} value than unconditioned ones. In addition, σ_{dark} of unsensitized composites is larger than that of sensitized ones. This is due to the fact that T₉ is lower for unsensitized composites. It is also observed that σ_{ph} is null for the unconditioned composite, while a relatively high photoconductivity that leads to a value of the conductivity contrast about 0.26 is obtained for the conditioned composite. Figure 1 shows the conductivity contrast as a function of the field treatment temperature for unsensitized samples. It is observed that conductivity contrast increases with temperature. The treatment temperature of 32 °C seems to be a good choice because higher temperatures produce sample breakdown, while treatments at lower temperatures have less efficacy.

Birefringence measurements are also included in Table I. Samples were subjected to an electric field of 20 V/µm until
birefringence reached the steady state, 90 s for the unsensitized conditioned composite and 10 s for the others three cases. Results show that the field treatment increases birefringence and that this increase is significantly higher for the unsensitized conditioned composite. The fact that \( n_e - n_o \) is lower for sensitized composites suggests that \( C_{60} \) would inhibit chromophore orientation. Local distortions in the electric field produced by \( C_{60} \) ions would affect chromophore orientation. Very recently, similar results were reported in other composites also sensitized with \( C_{60} \). In addition, for unsensitized composites, \( n_e - n_o \) gets larger only when samples have been conditioned. This indicates that the field treatment affects the PDCC in such a way that they have a better facility to get aligned when an electric field is applied again.

The PR properties were studied by performing 2BC experiments at room temperature (24 °C). We used a 35 mW He–Ne laser operating at 633 nm and the same geometry configuration of previous works.\(^6\)\(^,\)\(^7\)\(^,\)\(^14\) It consists of two \( p \)-polarized beams of equal intensity (100 mW/cm\(^2\) per beam) intersecting the sample with external angles of 30° and 60° with respect to the sample normal, that generate a grating spacing of 1.6 \( \mu \)m. The experiments were performed under the application of an external electric field of 60 V/\( \mu \)m perpendicular to the sample. A typical 2BC run consisted of the following steps. First, in the presence of the 30° beam, the electric field was applied to the sample. Then, the pump (60° beam) was turned on and the transmitted output powers of both beams were monitored until steady-state energy transfer was reached. No gain coupling was observed in unsensitized unconditioned samples. After steady state energy transfer was achieved, the gain (\( \gamma \)) was measured to determine the gain coefficients (\( \Gamma \)). Net gain coefficients were calculated by subtracting the absorption coefficient of the sample at 633 nm (\( \Gamma_{\text{net}} = \Gamma - \alpha \)). As in previous works,\(^6\)\(^,\)\(^7\)\(^,\)\(^14\) the speed of the PR effect was quantified by fitting the 2BC gain with a double exponential function and considering only the short time constant \( \tau_1 \) obtained from the fit.

\[ \Gamma, \Gamma_{\text{net}}, \text{and} \tau_1 \text{values are given in Table I. For standard samples (sensitized and unconditioned) these results are different than those already reported in literature}^{5} (\Gamma = 73 \text{ cm}^{-1} \text{ and} \tau = 230 \text{ ms at 50 V/\( \mu \)m and} 647 \text{ nm), due to the different excitation wavelength and applied voltage used in the experiments. Concerning the conditioned composite with} C_{60}, \text{as expected, it presents a slightly higher gain and a shorter response time than those obtained for the standard composite. The most interesting results were obtained for unsensitized composites: the conditioning treatment led to PR net gain coefficients (at 60 V/\( \mu \)m) similar to those of the standard composite. Preliminary studies of the electric field dependence of the photoconductivity, the birefringence and the PR properties is presently being performed and will be reported elsewhere.

Concerning the speed of the PR process, as observed in Table I the response time of the unsensitized conditioned composite is significantly longer than those of sensitized one. Previous works\(^6\)\(^,\)\(^7\) have reported that for standard composites, the PR speed is limited by the photoconductivity, that is by the formation of the internal electric field, rather than by the orientation of the NLO chromophores. If the same is assumed for unsensitized and conditioned samples, the longer response time measured might be explained by the reduced photoconductivity this type of composite shows.

In conclusion, we have shown that the PVK (50%)/PDCST (35%)/BBP (15%) composite has a significant PR response after conditioning in a 20 V/\( \mu \)m electric field for about 10 min at a temperature of 32 °C. The 2BC net gain coefficient (117 cm\(^{-1}\) at 60 V/\( \mu \)m) is similar to that obtained for the standard composite with 0.5% of \( C_{60} \) sensitizer at the same field strength. We have also shown that this result is due to an increase of photoconductivity and birefringence of the composite during conditioning under the electric field. PR response times (1.0 s for 60 V/\( \mu \)m) are longer than those of the standard composite (27 ms for 60 V/\( \mu \)m).

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