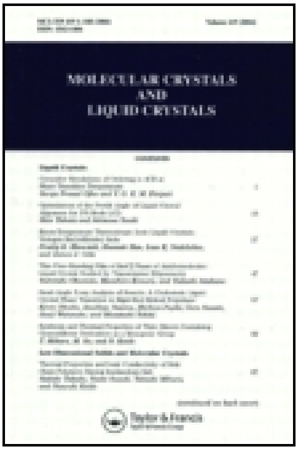

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PHOTOREFRACTIVE POLYMERS AND THEIR APPLICATIONS

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Abstract We review the basic properties of photorefractive polymer composites and discuss the performance of low glass-transition guest/host type polymers. Examples of applications using these new materials are presented.

INTRODUCTION

First discovered as a detrimental effect in inorganic crystals, the photorefractive (PR) effect has been rapidly recognized as a powerful mechanism for recording and processing of optical information. It is based on the photogeneration of charge carriers followed by charge separation through carrier migration, and trapping. These steps lead to the build-up of an internal spatially varying electric field that modulates the optical properties of the material. In electro-optic crystals such as Lithium Niobate, the space-charge field modulates the refractive index through the Pockels effect (or linear electro-optic effect). Hence, this process can be used to record a phase replica of an incident light distribution, such as a hologram, with low power laser sources, and in addition, the information is erasable. The basic properties for photorefractivity include photosensitivity, photoconductivity, and electro-optic activity. Half a decade ago, photorefractivity was achieved for the first time in a polymer composite by combining all these functionalities.[1] This first polymer had low performance but it laid the foundation of a rapidly growing field. Within a few years, the performance of photorefractive polymers has been improved by more than four-orders of magnitude.[2-6] Recently, we reported near 100% four-wave mixing diffraction efficiency in 105 µm-thick films and net gain coefficients in excess of 200 cm^{-1} at an applied field of 90 V/µm in a PVK-based photoconductor doped with the DMNPAA nonlinear optical molecule.[2] The rapid progress in this field has been made possible by combining the knowledge generated separately over the last two decades in the fields of organic electro-optic materials, photoconducting polymers, and inorganic photorefractive crystals. At this level of performance, photorefractive polymers compete with inorganic crystals and in some respect are superior to them. Due to their structural flexibility, these new materials can be easily modified and their properties can be further optimized. The ease of processing, the low cost, and the low weight of polymers generate a strong technological interest for their use in real-time optical processing and holographic storage applications. In this paper, we review the different design strategies that have been used to combine all the required functionalities for photorefractivity into a polymer. Then, we discuss the properties and performance of the guest/host polymers we developed recently, and give some examples of applications already demonstrated with these highly efficient materials.

PHOTOREFRACTIVE POLYMER DESIGNS

A big advantage of polymers over inorganic crystals is their structural flexibility, offering several design strategies to incorporate all the functionalities required for photorefractivity. In addition, photosensitivity, photoconductivity, and/or electro-optic properties can be adjusted nearly independently by mixing together different functional moieties into a polymer. Photorefractive polymers can be divided into two main classes: (*i*) guest/host composites[2-6] and (*ii*) fully functionalized polymers.[7,8] These approaches are illustrated in Figure 1. For each class, several design options are possible and we give only a few examples. In the guest/host approach, low-molecular weight compounds are blended into a polymer matrix. The matrix can be inert, as illustrated in Figure 1a, or have one of the functionalities such as electro-optic activity or photoconductivity as shown in Figure 1b. Some of the moieties that are mixed into the polymer can also have dual functionalities such as electro-optic activity and photoconductivity. This way, an increase in concentration of this dopant optimizes both nonlinear optical and transport properties but offers less flexibility for the optimization of the mechanical and dielectric properties of the composite. It is, however, not desired to combine electro-optic activity with photosensitivity in the same dopant since photoexcitation of the chromophore can also lead to non-photorefractive effects such as photoisomerization effects for instance.[9] In the fully functionalized approach, all the functional moieties are incorporated into the polymer structure. They can be attached as side chains to the polymer backbone as illustrated in Figure 1c or be incorporated into the main chain of the polymer. This approach can lead to polymers with a high glass transition temperature that can exhibit

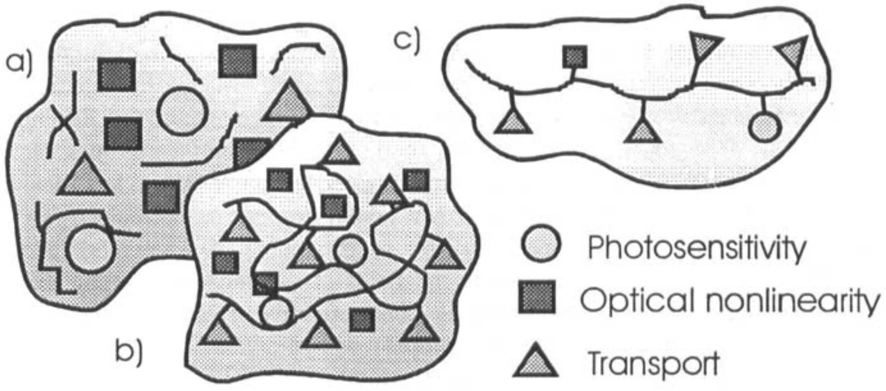

FIGURE 1 Illustration of different design approaches for photorefractive polymers. a) and b) are guest/host approaches, c) is a fully functionalized one.

quasi-permanent electro-optic properties. This second approach is generally more challenging from a synthetic point of view than the guest/host approach but leads to polymers that are more stable than guest/host systems where phase separation of the different compounds can limit the long term shelf-life. Nevertheless, good control of the processing of guest/host polymers can lead to samples with a lifetime of several months at high doping levels (50% wt. of chromophores)[2] or even years if the dye concentration is reduced. The unique properties of low glass-transition temperature (T*g*) polymers arising from their orientational mobility at room temperature can also be achieved in the fully functionalized approach by designing low T*g* polymer backbones, or by using dyes that do not crystallize. In the following sections, we restrict our discussion to guest/host polymer composites with a T*g* close to or even below room temperature.

PHYSICS AND PERFORMANCE

The physics of photorefractive polymers is significantly different from the one of inorganic photorefractive crystals. While the photogeneration efficiency is usually assumed close to unity in crystals, it shows a strong electric field dependence in polymers. This behavior can be explained by the strong Coulomb interaction in organics and resulting in strong geminate recombination rate that prevents the carriers from migration after photogeneration unless an electric field is applied to compensate for this effect. The field-dependence of the photogeneration efficiency, defined as the number of carriers that participate in charge transport per absorbed photon, can be described reasonably well by the Onsager theory.[7] We showed in a PVK-based polymer doped with DR1 (Disperse Red1) that this efficiency can be as low as 10^{-5} with low applied field and can be increased to a value of 1% at field values of 100 V/μm.[10] As a result, photorefractive polymers are sandwiched between two transparent ITO-coated glass electrodes. In contrast to inorganic crystals where transport of carriers can be due to either diffusion, drift, or both, in amorphous organic photoconductors, transport is mainly due to drift. In other words, charge migration through multiple hopping of carriers between adjacent transport moieties such as the carbazole moieties in PVK [poly-(N-vinylcarbazole)] leads to field-dependent mobilities of the form $\mu(E) \propto \exp(E^{1/2})$ in a variety of photoconducting polymers investigated so far. The applied electric field is also necessary in order to orient the nonlinear optical chromophores in the material and to break the centrosymmetry to induce second-order nonlinear optical properties. The optically active chromophores are generally push-pull molecules with a general structure of an electron accepting group and an electron donating group connected by a π-conjugated system. The orientation of the chromophores by the poling field leads to electro-optic properties that, for low poling field values ($E < 100$ V/μm), can be described in the oriented gas model by the following largest second-order susceptibility tensor elements:

$$\chi^{(2)}_{zzz}(-\omega;\omega,0) = NF^{(2)}\beta\,\frac{\tilde{\mu}E}{5kT} \qquad (1)$$

where the subscript z refers to the poling axis, N is the density of chromophores, $F^{(2)}$ is a local field correction factor that accounts for the dielectric effects of the surrounding matrix, β and $\tilde{\mu}$ are the first hyperpolarizability and permanent dipole moment of the chromophores, respectively, and kT the thermal energy. Due to their rod like shape, the chromophores have a strong polarizability anisotropy $\Delta\alpha$ in directions perpendicular and parallel to their molecular axis. As a result, their degree of orientation changes the birefringence of the sample. In the oriented gas model, the change in electric field of the first-order susceptibility tensor elements are given by:

$$\Delta\chi_{zz}^{(1)}(-\omega;\omega)=\frac{2}{45}NF^{(1)}\,\Delta\alpha\left(\frac{\tilde{\mu}E}{kT}\right)^{2} \qquad (2)$$

where $F^{(1)}$ is a local field correction factor. Note the quadratic dependence on electric field and permanent dipole moment on the right hand side of Equation (2). In purely electro-optic polymers or high T*g* photorefractive polymers, samples are pre-poled at elevated temperatures and tested for photorefractivity afterwards at room temperature. Pre-poling results in a quasi-permanent orientation of the chromophores resulting in quasi-constant spatially uniform birefringence and electro-optic activity in the sample.

On the other hand, in low T*g* photorefractive polymers the situation is quite different: the applied electric field leads to photogeneration, transport and orientation of the chromophores, resulting in the build-up of an internal space-charge field in the sample during illumination by the two writing beams. This internal field is responsible for the formation of a phase hologram that is generally phase shifted with respect to the initial light distribution but with the same spatial periodicity. As a result, the total electric field which is the superposition of the internal modulated field and the externally applied field, poles the molecules in real time. At steady-state, after photorefractive hologram formation, the molecules have no longer a uniform orientation but have an orientation that is spatially modulated both in magnitude and in direction as shown in Figure 2. The trap density in photorefractive polymers can be substantially high because structural anomalies such as impurities, defects of the monomeric units, or chain irregularities can act as traps. Consequently, the value of the space-charge field can be high and close to the value of the applied field along the grating spacing of the hologram. As a result, the periodic orientation of the chromophores can be significant and can result in a strong *orientational enhancement* effect[11] that simultaneously doubles the effect of the electro-optic contribution and, more important, leads to a modulated birefringence that adds to the total refractive index modulation.

Recently, we developed[2] a guest/host photorefractive polymer composite where the matrix is the photoconductor PVK (33% wt.). This polymer is doped with a small amount of 2,4,7-trinitrofluorenone (TNF) (1% wt.) to provide photosensitivity to visible light, and a large amount (50% wt.) of the chromophore 2,5-dimethyl-4-(p-nitrophenylazo)anisole (2,5DMNPAA). To lower the glass transition temperature of the composite close to room temperature we added the plasticizer N-ethylcarbazole (16% wt.). We characterized the photorefractive performance of 105 μm-thick samples

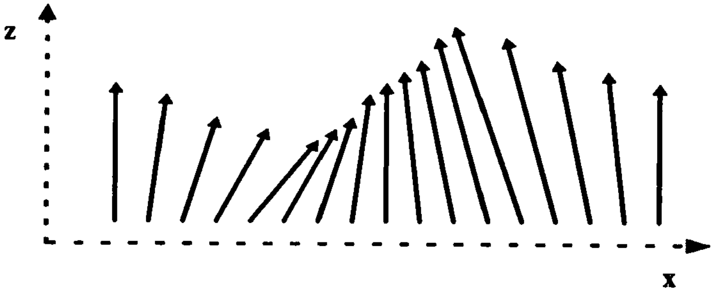

FIGURE 2 Periodic orientational distribution of the chromophores.

by four-wave mixing and two-beam coupling experiments in a slanted configuration with low power laser diodes emitting at 675 nm, and also at 633 nm with a He:Ne laser. These experiments are described elsewhere.[2,4,12] The properties of these polymers are summarized in Table I. Independent characterization of the chromophore by EFISH measurements, frequency-dependent dielectric measurements, and frequency-dependent ellipsometric experiments clearly show that the electro-optic effect alone is not responsible for the high refractive index modulation of $\Delta n = 0.007$ deduced from four-wave mixing data at 675 nm, at 1 W/cm^2, at an applied field of 90 V/μm and a grating spacing of 3 μm. Our results show that the strong orientational birefringence of the 2,5DMNPAA chromophore is largely responsible for the high efficiency of our materials.

Consequently, a new figure of merit F for chromophores for photorefractive applications can be defined by:

$$F = (\tilde{\mu}^2 \Delta\alpha + \tilde{\mu}\beta) / M \tag{3}$$

where M is the molecular weight. This result opens new horizons for the use of a variety of molecules with moderate hyperpolarizability but with high polarizability anisotropy $\Delta\alpha$ and dipole moment $\tilde{\mu}$, such as mesogens used in nematic liquid crystals.

TABLE I Performance of 2,5DMNPAA:PVK:ECZ:TNF polymers at 633 nm and applied field of 80 V/μm

α (cm^{-1})	Λ (μm)	Δn	τ (s)	S (cm^3/J)
25	3	0.0056	0.5	0.003

α: linear absorption, Λ: grating spacing, τ: response time, $S = \Delta n / \alpha / \tau$ sensitivity.

CONCLUSION AND OUTLOOK

Due to their high efficiency and good sensitivity, we used recently these photorefractive polymers in a variety of applications: (i) holographic storage of entire images and their retrieval with good efficiency was achieved[12] with a 675 nm low power laser diode in a transmission geometry; (ii) we demonstrated optical pattern recognition;[13] (iii) we performed dynamic holographic interferometry[12] and could visualize via real-time four-wave mixing, the mode patterns of a membrane excited by a loudspeaker. Holographic storage is an attractive application for this polymers because wavelength or angular multiplexing of several holograms on the same spot of the sample can lead to high storage densities. However, at this stage, polymers have not reached a level of performance required for this technology where issues such as non-destructive read-out, increased thickness, longer storage times and hologram fixing capabilities have to be addressed. For real-time optical processing applications including optical correlation and non-destructive testing, the performance of state of the art photorefractive polymers has reached a higher maturity. We believe that these new materials are expected to play an important role in such devices in a near future. Due to the flexibility of these materials, further improvements in their performance and a better control of their processing can be achieved.

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