Photorefractive polymers—A status report

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Abstract: A photorefractive system is one which is simultaneously
photoconductive and electrooptic.   Diffraction gratings or holograms can be
produced in a photorefractive material by the photogeneration, drift or diffusion
and subsequent trapping of mobile charges. The grating is produced by the internal
space charge field set-up by these charges which, via the electrooptic effect,
produces an index of refraction grating.   Until 1990 all photorefractive systems
were inorganic crystals such as $LiNbO_3$, $BaTiO_3$, $B_{12}SiO_{20}$, InP:Fe, GaAs, or
multiple quantum well materials.   In 1990, the first observation of the
photorefractive effect in an organic material, a carefully grown, doped molecular
crystal was described.   This was followed in short time by the discovery of
photorefractive polymers. The early photorefractive systems, polymeric and
crystalline, were inefficient compared to inorganic systems but in recent years the
efficiency and sensitivity of photorefractive polymers have become equal to
inorganic crystals. This paper describes the origins of the photorefractive effect
and the design, synthesis and characterization of photorefractive polymers. In
addition an orientational enhancement of the photorefractive diffraction efficiency
is discussed. This orientational enhancement does not occur in crystalline systems,
since it relies on the ability of the optically nonlinear chromophores to be aligned
not only by an externally applied field, but also by the sinusoidally varying space
charge field produced during photorefractive grating formation.

INTRODUCTION

Many mechanisms exist by which the index of refraction of a material can be modified in response to an incident optical beam, including photochromism, thermochromism, thermorefraction, and excited state generation.   None of these mechanisms result in index gratings with the critical property of spatial nonlocality that defines the photorefractive effect. Nonlocal character arises in a photorefractive material from the physical motion of photogenerated charges, usually over distances of a few microns. When interfering light beams are used to generate the charges, the charge transport gives rise to a charge distribution in the material that is in phase with the intensity pattern of the light. If the material is also electrooptic, that is if the index of refraction changes with an applied external electric field, then a phase shift between the incident light intensity pattern and the refractive index modulation is produced.   In conventional photorefractivity based on the linear electrooptic effect and in the limit that drift-induced charge transport dominates over carrier diffusion, this phase shift is $90°$. An important consequence of such a phase shift is the possibility of energy transfer between light beams interfering in the photorefractive medium, a phenomenon called asymmetric two beam coupling (2BC). Many of the most interesting

photorefractive applications are a consequence of 2BC, including coherent image amplification, novelty filtering, self-phase conjugation, beam fanning limiters and simulations of neural networks and associative memories[1]. Another potential application of photorefractive materials which has received increased recent interest is in holographic optical storage[2]. This application makes use, not of the phase shift, but of the significant refractive index modulation that can be induced at relatively low light intensities.

The photorefractive effect was first observed in $LiNbO_3$ more than 25 years ago[3]. Since that time a variety of inorganic photorefractive systems have been investigated. In 1990 the first organic photorefractive system was described[4]. The material was a carefully grown electrooptic organic crystal, 2-cyclooctylamino-5-nitropyridine (COANP) doped with the charge transporting molecule 7,7,8,8-tetracyanoquinodimethane (TCNQ). The growth of high optical quality, doped organic crystals containing reasonably large dopant concentrations is difficult because most dopants are expelled during crystal growth. Consequently, the strength of the photorefractive effect observed in this doped crystal was small. Polymeric materials, on the other hand, can be doped with various molecules at high concentrations with relative ease.

An isotropic polymer is not electrooptic. It can be made so by electric field induced orientation of dipolar molecules that are either dissolved in or chemically attached to the polymer backbone. In principal, all photoconducting polymers containing dipolar subunits can be made photorefractive in this way. By comparison only the relatively rare set of noncentrosymmetric crystal structures will be electrooptic. A polymer is not photorefractive simply because it is simultaneously photoconducting, electrooptic and contains sufficient carrier traps. One must also demonstrate a nonzero phase shift between light intensity and refractive index gratings by, for example, a 2BC experiment[5].

There are many reasons for pursuing the development of photorefractive polymers[6]. Polymers are easily processible into thin films of high optical quality, can be modified easily by chemical doping, and are compatible with integrated circuit processing techniques, making them potentially useful in integrated optical device applications. Polymer photorefractive systems can potentially yield larger maximum refractive index changes for equal densities of grating forming trapped charges when compared with inorganic crystals. This is because inorganic photorefractive crystals with large electrooptic coefficients also have large dc dielectric constants. A large dielectric constant screens the Coulomb field produced by trapped charges thus reducing the internal space charge field. For organic nonlinear materials, the nonlinearity is a molecular property arising from the asymmetry of the electronic charge distributions in the ground and excited states of the individual molecules. For this reason large electrooptic coefficients are not accompanied by large dielectric constants and a potential improvement in performance of up to a factor of ten is possible.

The first polymer to be shown to be photorefractive was composed of the electric field poled nonlinear epoxy polymer bisphenol-A-diglycidylether 4-nitro-1,2-phenylenediamine made photoconductive by doping with the hole transport agent diethylaminobenzaldeydediphenylhydrazone[7]. This material was slow and had a small steady-state diffraction efficiency but it did serve to demonstrate that the simultaneous requirements of optical nonlinearity, charge generation, transport, trapping and absence of interfering photochromic effects could be combined in a single polymeric material to produce photorefractivity.

A TYPICAL PHOTOREFRACTIVE POLYMER

From the above discussion it can easily be seen that the necessary, but not sufficient, elements for a material to be considered photorefractive are photoinduced charge generation, charge transport, trapping and electrooptical nonlinearity. A polymeric material can be made photorefractive either by incorporating these properties directly into the polymer itself or by doping guest molecules into the polymer to produce these properties. It is usually desirable to incorporate at least some of the photorefractive properties into the polymeric host itself to minimize the amount of inert volume in the material. In Fig. 1, a photorefractive polymer system is shown in which photoconductivity is provided by the polymer and optical nonlinearity by a guest molecule[8]. The polymer is poly(N-vinylcarbazole) (PVK) and the

electrooptic guest molecule is 3-fluoro-4-(diethylamino)-(E)-β-nitrostyrene (FDEANST). A small amount of 2,4,7-trinitro-9-fluorenone (TNF) is added as a long wavelength absorption sensitizer. The fluorinated DEANST has reduced absorption in the red relative to the unfluorinated analog[9] and therefore only the charge transfer complex PVK:TNF absorbs in the red and infrared region of the spectrum. The PVK:TNF:FDEANST system has a glass transition temperature T_g of 40°C; low enough so that it can be made electrooptic by electric field poling at room temperature. The low T_g also means that when the poling field is removed, the dipolar molecules relax to a random configuration and the photorefractive grating disappears, only to reappear again when the external bias field is turned back on. This material shows diffraction efficiencies in a four-wave mixing(4WM) experiment greater than 1% in 125μm thick samples with grating growth times near 100ms at 1W/cm^2.
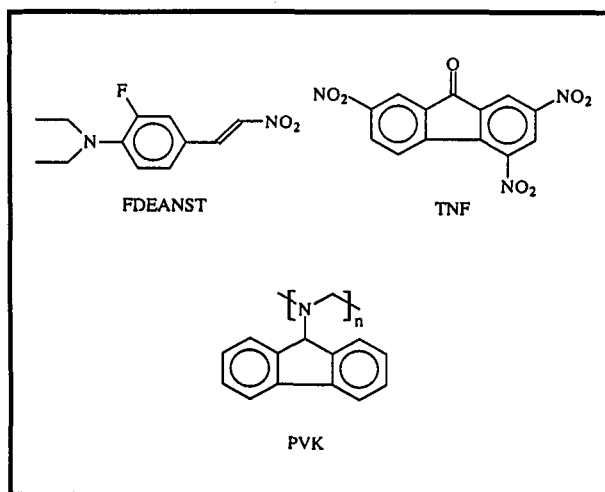

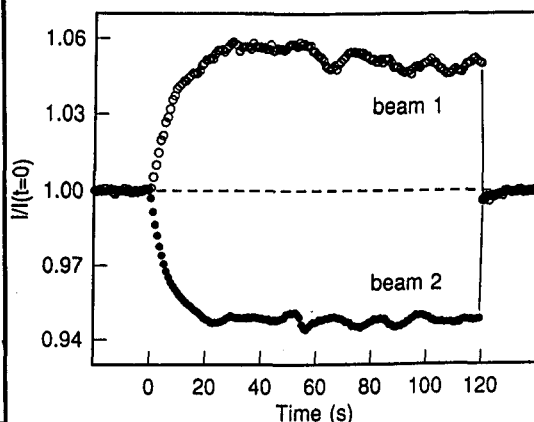Fig. 1 Components of a typical photorefractive polymer.

Fig. 2 Two beam coupling experiment. The intensity of beam 1 monitored as beam 2 is switched on at t = 0 and off at t = 120s (open circles) and the intensity of beam 2 monitored as beam 1 is turned on and off.

In a 4WM experiment, a diffraction grating is produced in the material by the interference of two light beams, while a third beam is used to interrogate the index of refraction grating so produced. By this technique one can measure the steady state diffraction efficiency η, as well as follow the growth in time of the diffraction grating. The presence of a 4WM grating does not, by itself, prove that the material is photorefractive. A variety of spatially local process like photochemistry can produce gratings. A definitive experiment demonstrating that a material is photorefractive is 2BC. The results of a two beam coupling experiment are shown in Fig. 2. In the upper trace the intensity of beam 1 is monitored as beam 2 is switched on at t=0 and off at t=120s. In the lower trace the intensity of beam 2 is monitored as beam 1 is turned on and off. The asymmetric transfer of energy between the two beams is proof of the photorefractive origin of the grating. The two beam coupling gain can be defined by the quantity Γ where:

$$I/I_o = \exp(\Gamma - \alpha)x \qquad (1)$$

and α is the absorption coefficient. I is the diffracted intensity, I_o the incident intensity and x the distance through the sample. If Γ > α then net gain has been achieved. The system PVK:TNF:FDEANST was the first polymeric system in which net gain was observed

Peyghambarian and co-workers have been able to increase the maximum 4WM efficiency and 2BC gain by using a more optically nonlinear chromophores than FDEANST. These results are summarized in Table 1[10][11]. In fact these authors have achieved efficiencies of 86% using an external electric field of 60V/μm. This efficiency is limited only be reflection losses at the polymer interfaces. They have also observed a net gain Γ–α = 207cm^{-1} with fields of 90V/μm.

Table 1. Comparison of properties of photorefractive polymers at an external applied field of 40V/μm.

	λ (nm)	d (μm)	α (cm⁻¹)	η (%)	Γ (cm⁻¹)
PVK:TNF:FDEANST[8]	647	125	32	0.85	11
	676	125	17	1.3	9.9
	753	125	1.4	0.1	8.6
PVK:TNF:ECZ:DMNPAA[10]	674	105	24	5	30

ENHANCEMENT MECHANISM

It is possible to calculate the magnitude of the internal space charge field E_I produced by the photogenerated charges in a photorefractive system from the measured value of the 2BC gain Γ using the following expression:

$$\Gamma = \frac{\pi n^3 r_{eff}|E_1|}{\lambda \cos \theta} \tag{2}$$

where n is the index of refraction, λ the optical wavelength and θ the incident angle. The effective electrooptic coefficient r_{eff} depends on the magnitude of the applied external electric field but is small, around 2pm/V[8]. If one carries out the calculation using Eq.(2) for the systems listed in Table 1, it becomes clear that the calculated internal space charge field is greater than the external electric field, a physical impossibility. An enhancement mechanism must be present. The enhancement arises from the ability of the dipolar chromophores to be aligned, not only by the externally applied poling field, but also by the internal sinusoidally varying space charge field produced by the photogenerated charges[12]. The resulting spatially periodic poling of the sample leads to a modulation of the birefringence of the material and to a modulation of the electrooptic response, the combination of which can substantially enhance the measured photorefractive gain and efficiency.

This alignment mechanism is illustrated in Fig. 3. The left hand part of the figure shows the situation when the external electric field $E_0 \neq 0$ and the right hand part where $E_0 = 0$. For simplicity both E_0 and the space charge field are assumed to be directed along the z axis and the z axis is given in units of the fringe spacing Λ. The interfering light beams are assumed to produce a sinusoidally varying space charge field. The externally applied electric field will add to this field to produce a total field E_T. Since the dipolar chromophores have orientational mobility due to the low T_g of the polymer or to their small molecular size, a spatially periodic orientational pattern is produced. This is shown in the middle two panels of the figure. The effect of the periodic orientation is to produce a modulated birefringence and a modulated electrooptic coefficient, both of which can contribute to the production of a modulated refractive index grating as shown in the bottom panel. For these two effects, the nonlinear response of the material is quadratic in the total electric field. This can be simply seen in the case of the electrooptic coefficient modulation from the relationship:

$$\Delta n = -\tfrac{1}{2} n^3 r_{eff} E_T \tag{3}$$

Since r_{eff} depends on the total electric field, Δn in Eq. (3) must depend quadratically on E_T. As the bottom panel of the figure indicates, when no dc electric field is present, the modulation is at twice the frequency of the interference grating produced by the incident light. This means that there will be no first order diffracted beam. When a dc field is applied, since the total field now consists of the sum of this field and the modulated field, the quadratic response now yields a component at the spatial frequency of the light produced grating. This modulation of poling produces a contribution to the diffraction efficiency even if the modulation of the electrooptic coefficient is ignored and only the modulation of birefringence is present. Hence, chromophores with zero or negligible hyperpolarizability but large ground state dipole moment and large birefringence are potentially useful in the formulation of photorefractive polymers, if such chromophores exist.
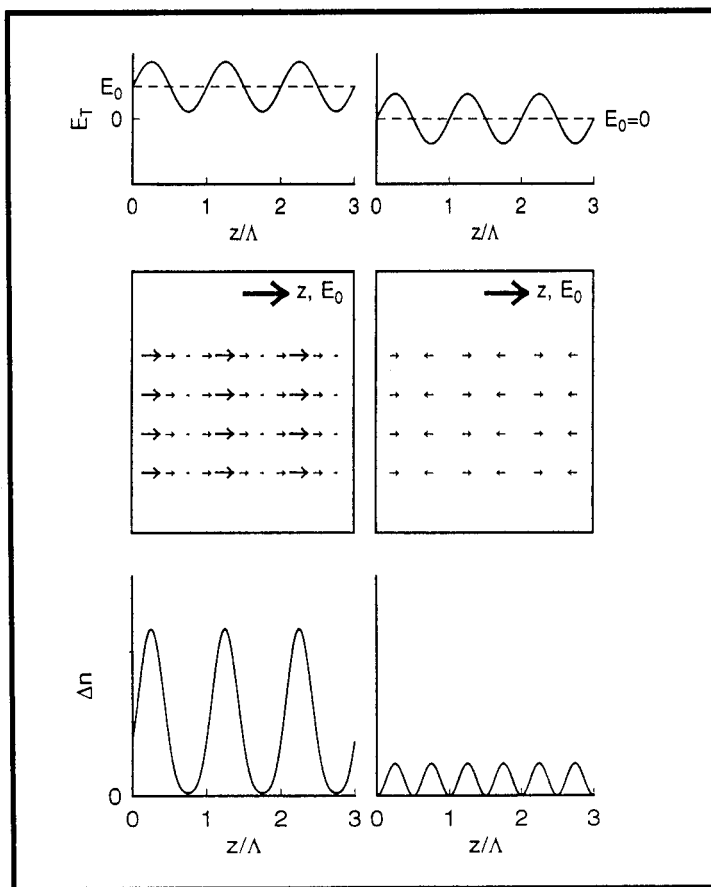
Fig. 3. Schematic illustration of the periodic poling responsible for the orientational enhancement effect.
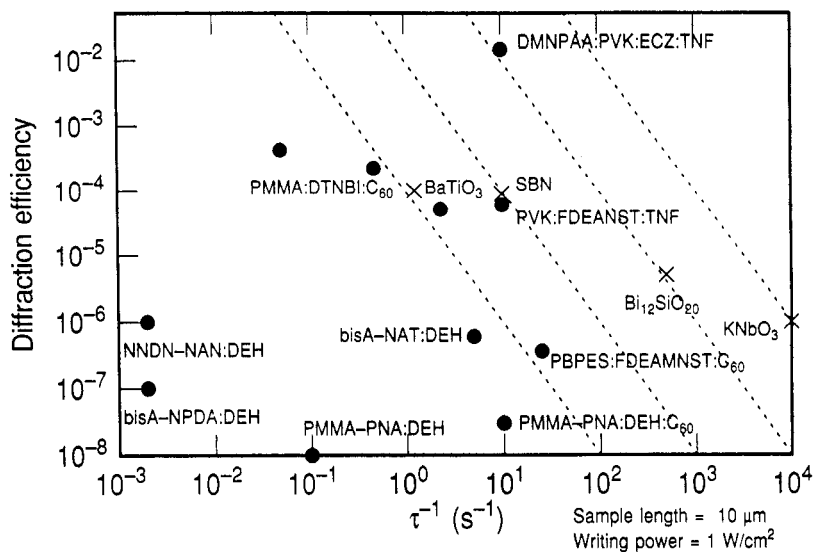

Fig. 4. Comparison of several inorganic photorefractive crystals and a selection of photorefractive polymers. Saturation diffraction efficiency η vs. growth rate τ^{-1}, scaled to 10μm thickness and 1 W/cm² writing intensity. The dashed lines are lines of constant sensitivity.

CURRENT STATUS

Fig. 4 is a comparison of the saturation diffraction efficiency and the growth rate τ^{-1} for a variety of inorganic crystals (crosses) and organic polymers (filled circles). Also shown by dotted lines are contours of constant sensitivity S defined by:

$$S = (1/d)(\partial \eta^{\frac{1}{2}}/\partial W) \qquad (4)$$

where d is the sample thickness and W the incident fluence. All points are scaled to a sample length of 10 μm and a grating writing power of $1W/cm^2$. Despite the fact that photorefractive polymers were first identified only four years ago, their performance at present is comparable to that of some of the well known and much more extensively studied inorganic crystalline photorefractive materials. The very fact that such a large number of new photorefractive polymers have appeared in such a short time is a measure of the flexibility of polymers in accepting multiple dopants in large concentrations. It is quite clear that the ultimate limitations of these materials have not been reached and that much interesting work remains to be done both in identifying new systems and in developing an understanding of the underlying physical mechanisms responsible for the magnitude and speed of growth of photorefractive gratings in such systems.

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