

ARTICLES

Multifunctional Polymers Exhibiting Photorefractive Effects

LUPING YU,* WAI KIN CHAN, ZHONGHUA PENG, AND ALI GHARAVI

Department of Chemistry and James Frank Institute, The University of Chicago, 5735 South Ellis Avenue, Chicago, Illinois 60637

Received June 27, 1995

Photorefractive (PR) materials are multifunctional materials which combine photoconductivity and an electro-optic (E-O) response to manifest a photorefractive effect.¹ In these materials, the indices of refraction can be modulated by a light via their E-O effect (Pockel effect) and a photoinduced space charge field. It is generally believed that there are four basic processes involved in the photorefractive effect: the photogeneration of charge carriers upon absorbing photons, the transport of the generated charge carriers either by thermal diffusion or by electric drifting, the trap of the charge carriers in the trapping centers which results in the charge separation and the formation of the space charge field, and the formation of a phase grating due to the space charge field modulation of the refractive index via the linear electro-optical effect.¹ Figure 1 illustrates these basic processes. Notice that two light beams are needed to generate the oscillating space charge field. A unique feature of the space charge field is that it has a phase shift from the interference pattern. This feature results in a special property for photorefractive materials: the optical energy of the two incident beams can exchange in an asymmetric way; one of the beams will lose energy, and the other beam will gain energy.

The driving force behind the study of the photorefractive materials is their potential application, such as in three-dimensional holographic light processing, phase conjugation, and the handling of large quantities of information in real time.¹ Photorefractive phenomena have been studied for almost 30 years since its discovery in ferroelectric single crystals (LiNbO₃) in 1966.² Since then, research on photorefractive effects has focused exclusively on inorganic materials, such as ferroelectric crystals (LiNbO₃, LiTaO₃, BaTiO₃), semiconductors (GaAs, InP, CdF₂) and sillenites (Bi₁₂SiO₂₀).^{1,2} Recently, organic single

Luping Yu was born in Zhejiang Province, People's Republic of China (1959), and received his B.S. (1982) and M.S. (1984) in chemistry from Zhejiang University and his Ph.D. from the University of Southern California (1989). Following postdoctoral work at USC (1989–1991), he joined the Department of Chemistry at the University of Chicago and is currently an associate professor.

Wai Kin Chan was born in Hong Kong in 1969 and received his B.S. (1991) in chemistry from the Chinese University of Hong Kong and his Ph.D. from the University of Chicago (1995). He is a faculty member in the Department of Chemistry, the University of Hong Kong, Pokfulam Road, Hong Kong.

Zhonghua Peng was born in Hubei Province, People's Republic of China (1966), and received his B.Sc. (1989) in Chemistry and M.S. (1991) in materials science from the University of Science and Technology of China, People's Republic of China. He is currently a doctoral candidate in chemistry at the University of Chicago.

Ali Gharavi was born in Iran (1957) and received his B.Sc. (1985) and M.S. (1988) in applied physics from the University of New Orleans and his Ph.D. from Tulane University (1994). He is currently a postdoctoral associate with Dr. Luping Yu.

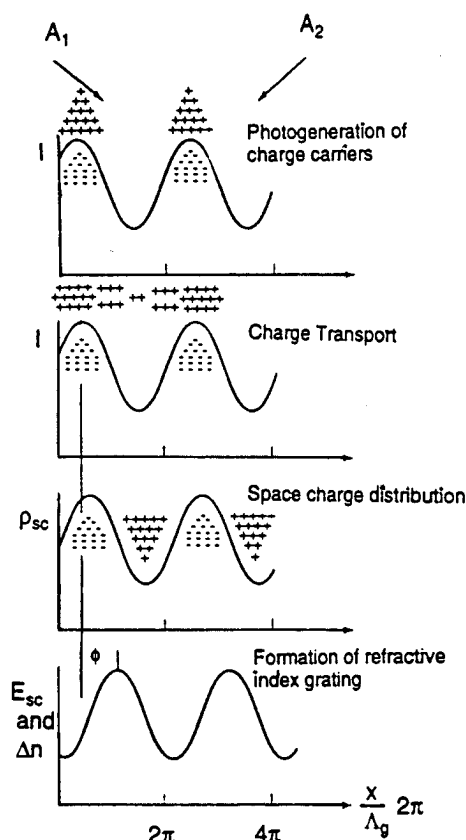


Figure 1. Schematic view of the processes involved in the photorefractive effect. Two laser beams were applied.

crystal and photorefractive polymers have emerged as new kinds of optical materials.^{3,4} It is expected that PR polymers will possess unique properties supplemental to those of their inorganic counterparts: properties such as ease of preparation for large-area samples, a low dielectric constant, high optical performance, and low cost.⁵

(1) (a) Gunter, P., Huignard, J. P., Eds. *Photorefractive Materials and their Applications*; Springer-Verlag: Berlin, 1988; Vols. 1 and 2. (b) Yariv, A. *Optical Electronics*, 4th ed.; Harcourt Brace Jovanovich: Orlando, FL, 1991.

(2) (a) Ashkin, A.; Boyd, G. D.; Dziedzic, J. M.; Smith, R. G.; Ballmann, A. A.; Nassau, K. *Appl. Phys. Lett.* **1966**, *9*, 72. (b) Chen, F. S. *J. Appl. Phys.* **1967**, *38*, 3418. (c) Chen, F. S.; LaMacchia, J. T.; Fraser, D. B. *Appl. Phys. Lett.* **1968**, *13*, 223. (d) Chen, F. S. *J. Appl. Phys.* **1969**, *40*, 3389.

(3) (a) Sutter, K.; Hulliger, J.; Gunter, P. *Solid State Commun.* **1990**, *74*, 867. (b) Sutter, K.; Gunter, P. *J. Opt. Soc. Am. B* **1990**, *7*, 2274.

(4) Ducharme, S.; Scott, J. C.; Tweig, R. J.; Moerner, W. E. *Phys. Rev. Lett.* **1991**, *66*, 1846.

(5) Moerner, W. E.; Silence, S. M. *Chem. Rev.* **1994**, *94*, 127.

In the past several years, two approaches have been developed to prepare or synthesize photorefractive polymeric materials, namely, the composite material approach and the fully functionalized polymer approach.⁵⁻²² Composite materials are composed of polymer hosts (electro-optic polymers, photoconductive polymers, or inert polymers) doped with different functional molecules necessary for the photorefractive effect. Fully functionalized polymers are single-chain polymers which contain all of the functionality necessary for the photorefractive effect. Both approaches have enjoyed success in identifying photorefractive polymers. The materials performances have been greatly enhanced; for example, a nearly 85% diffraction efficiency and 200 cm⁻¹ optical net gain was observed in a composite material.²³ Prototype devices based on these materials were also attempted.²⁴

Composite systems exhibit a major advantage. They make it easier to prepare different materials and to survey different compositions quickly. However, composite systems also exhibit several serious problems, such as intrinsic instability due to phase separation and low glass transition temperature. Although fully functionalized polymer systems exhibit several disadvantages, such as time-consuming chemical synthesis and difficulty in rational design, these polymers offer advantages that the composite materials do not possess, such as the long-term stability of photorefractive effect and minimized phase separation. Therefore both approaches are necessary for the development of photorefractive polymers. However, judging from the development history of second-order nonlinear optical (NLO) polymers, the functionalized polymer approach will be the preferred one.^{25,26}

Our research group has been mainly involved in synthesizing fully functionalized PR polymers. Three

polymer systems have been developed: functionalized polyurethanes, functionalized conjugated polymers, and polyimides containing porphyrin and NLO chromophore units.⁶⁻²⁰ The main focus of this Account is on the progress in rational design, synthesis, and characterization of fully functionalized photorefractive polymers. Significant progress in composite materials will be briefly mentioned. An excellent review of composite photorefractive polymeric materials can be found in ref 5.

Despite the exciting progress, we must emphasize that photorefractive polymer studies are still in their infancy. There are numerous issues which prevent these materials from practical application. The Concluding Remarks will discuss the problems existing in this area.

Functionalized Polyurethanes^{6-8,10,13}

Design and Syntheses. Our initial idea to synthesize fully functionalized photorefractive polymers was simple: attaching four different species onto the polymer backbone. The design principle was based on the general view that, in a photorefractive material, four functional species exist simultaneously: a photocharge generator, a charge transporter, charge-trapping centers, and a second-order nonlinear optical moiety. In the first such polymer, we intentionally did not incorporate the charge-trapping center. Trapping centers naturally exist in the polymer sample due to defects and conformational disorders. Thus, only the NLO chromophore, the charge generator, and the transporting compound were covalently linked to the polyurethane backbone. There are numerous compounds which can be chosen to play these three roles. When different species are selected, an important consideration is the absorption windows of different species. We chose the charge generator absorbing at long wavelengths (above 500 nm) so that a continuous diode laser could be used to excite the species. However, we chose the charge-transporting compound and the NLO chromophore to absorb at short wavelength. The purpose of this design is to avoid the excitation of the other species when the charge generator was excited, so that the physical properties of the charge transporter and NLO chromophore would not change. Figure 2 shows the monomer structures and their absorption maximum wavelengths.

The synthesis of polyurethanes was straightforward, and the structures of the resulting polymers were fully characterized (see Figure 2 for polymers' compositions). After polymerization, the maximum absorption wavelength of the charge generators did not change significantly, which indicated that there were no charge transfer complexes formed between the charge generator and the various other species. The absorptions of the NLO chromophore and the transporting compound were similar to those of the corresponding monomers.

Photoconductive Studies. In order to manifest the photorefractive effect, a polymer must possess two properties: photoconductivity and electro-optical activity. The photoconductivity is required to achieve charge separation, and the electro-optic response is needed to modify the index of refraction of the materi-

(6) Yu, L. P.; Chan, W. K.; Bao, Z. N.; Cao, S. *Polym. Prepr.* **1992**, 33 (2), 398.

(7) Yu, L. P.; Chan, W. K.; Bao, Z. N.; Cao, S. *J. Chem. Soc., Chem. Commun.* **1992**, 1735.

(8) Yu, L. P.; Chan, W. K.; Bao, Z. N.; Cao, S. *Macromolecules* **1993**, 26, 2216.

(9) Yu, L. P.; Chan, W. K.; Chen, Y. M.; Peng, Z. H.; Bao, Z. N. *Polym. Prepr.* **1993**, 34 (2), 536.

(10) Chen, Y. M.; Chan, W. K.; Peng, Z. H.; Yu, D.; Yu, L. P. *Polym. Prepr.* **1993**, 34 (2), 430.

(11) Chan, W. K.; Chen, Y. M.; Peng, Z. H.; Yu, L. P. *J. Am. Chem. Soc.* **1993**, 115, 11735.

(12) Yu, L. P.; Chan, W. K.; Chen, Y. M.; Peng, Z. H.; Bao, Z. N.; Yu, D. *Proc. SPIE-Int. Soc. Opt. Eng.* **1993**, 2025, 268.

(13) Chen, Y. M.; Peng, Z. H.; Chan, W. K.; Yu, L. P. *Appl. Phys. Lett.* **1994**, 64, 1195.

(14) Yu, L. P.; Chen, Y. M.; Chan, W. K.; Peng, Z. H. *Appl. Phys. Lett.* **1994**, 64, 2489.

(15) Peng, Z. H.; Bao, Z. N.; Chen, Y. M.; Yu, L. P. *J. Am. Chem. Soc.* **1994**, 116, 6003.

(16) Yu, L. P.; Chan, W. K.; Chen, Y. M.; Peng, Z. H. *Mater. Res. Soc. Symp. Proc.* **1994**, 328, 63.

(17) Yu, L. P.; Peng, Z. H. *Polym. Mater. Sci. Eng.* **1994**, 71, 441.

(18) Chan, W. K.; Yu, L. P. *Polym. Prepr.* **1994**, 35 (2), 98.

(19) Yu, L. P.; Chen, Y. M.; Chan, W. K. *J. Phys. Chem.* **1995**, 99, 2797.

(20) Chan, W. K.; Yu, L. P. *Macromolecules*, submitted.

(21) (a) Kippelen, B.; Tamura, K.; Peyghambarian, N.; Padias, A. B.; Hall, K. H. Jr. *J. Appl. Phys.* **1993**, 74, 3617. (b) Kippelen, B.; Tamura, K.; Peyghambarian, N.; Padias, A. B.; Hall, K. H., Jr. *Phys. Rev. B* **1993**, 48, 10710.

(22) Sansone, M. J.; Teng, C. C.; East, A. J.; Kwiatek, M. S. *Opt. Lett.* **1993**, 18, 1400.

(23) Meerholz, K.; Volodn, B. L.; Sandalphon; Klppelen, B.; Peyghambarian, N. *Nature* **1994**, 371, 497.

(24) Stankus, J. J.; Silence, S. M.; Moerner, W. E.; Bjorklund, G. C. *Opt. Lett.* **1994**, 19, 1480.

(25) Burland, D. M.; Miller, R. D.; Walsh, C. A. *Chem. Rev.* **1994**, 94, 31.

(26) Marks, T. J.; Ratner, M. A. *Angew. Chem., Int. Ed. Engl.* **1995**, 34, 155.

(27) Mort, J.; Pfister, G., Eds. *Electronic Properties of Polymers*; John Wiley and Sons: New York, 1982.

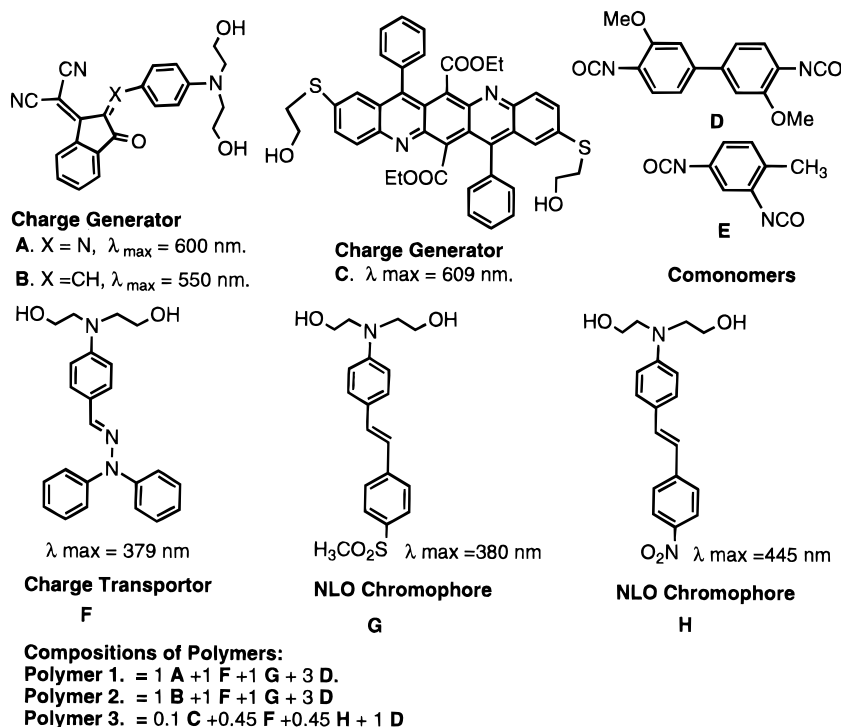


Figure 2. Structures and absorption wavelengths of monomers and the compositions of polymers 1–3.

als. All of the polymers 1–3 were found to be photoconductive. A maximum photocurrent of $1.5 \mu\text{A}$ was observed for polymers 1 and 2 with an applied electric field of 1000 kV/cm and a laser intensity of 400 mW/cm^2 (at 632 nm). A photoconductivity of $1.3 \times 10^{-13} \Omega^{-1} \text{ cm}^{-1}$ for polymer 3 was obtained under a field strength of 290 kV/cm and a laser intensity of 270 mW/cm^2 (at 690 nm), corresponding to a quantum efficiency of charge generation, ca. 4.3×10^{-7} . Just like other photoconductive polymers, the photocurrents of these polymers were both field and intensity dependent; as the field increased, the photoconductivity increased.²⁷ A linear relationship between the photocurrent and the incident laser intensity was found, indicating that bimolecular recombination of the charge carrier was absent in this polymer system.

Electro-optic Effect. The pristine polymer thin film has a random dipole orientation and exhibits no electro-optic response. However, if the dipoles of the NLO chromophores are aligned under an external electric field, the materials become asymmetric and thus electro-optically active. The most frequently used method is the corona discharging to electrically pole the polymer film when it is heated near the glass transition temperature. After that, the electro-optic effect in the polymer can be studied using a continuous laser source.²⁸ Electro-optic coefficients, r_{33} , of 12.2 and 13.0 pm/V were detected for polymers 1 and 2, respectively, at 632 nm . The linear E-O coefficient r_{33} of polymer 3 was determined to be 4.0 pm/V (thickness: $0.8 \mu\text{m}$) at 690 nm . One of the advantages of these polymers is that their E-O coefficients are quite stable due to hydrogen bonding. For example, a r_{33} value of 11.6 pm/V was detected 3 months after poling for polymer 1.

Two-Beam Coupling Experiments. Possession of two necessary properties does not ensure the materials to be photorefractive. In order to confirm

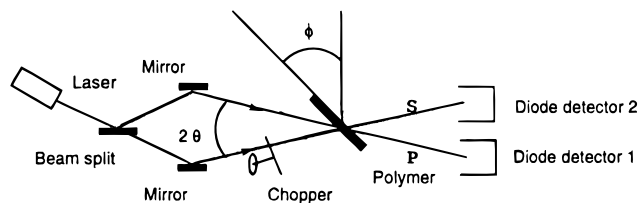


Figure 3. Experimental setup for two-beam coupling, where S and P are signal and pump beams.

the photorefractive effect, a distinctive experiment, two-beam coupling, should be performed. As shown in Figure 1, when two coherent laser beams intersect upon the photorefractive polymers, an index grating can be generated, which can diffract these very two beams into each other, leading to an asymmetric energy exchange characterized by the beam-coupling coefficient, Γ .¹ By monitoring this optical energy exchange, one can deduce the optical gain coefficient from the equation¹

$$\Gamma = \frac{1}{L} \ln \left(\frac{1+a}{1-\beta a} \right) \quad (1)$$

where $a = \Delta I_s(L)/I_s(L)$, $\Delta I_s(L)$ is the intensity change of the signal beam, $I_s(L)$ is the total signal beam intensity emerging from the sample, L is the path length of the writing beam, and $\beta = I_s(0)/I_p(0)$, is the ratio of the incident beam intensities.

The two-beam-coupling experiments are performed in a setup shown in Figure 3 where the polymer film is tilted by an angle of ϕ in order to have a nonzero effective E-O coefficient value, r_{eff} . For example, polymer 3 was studied by using a diode laser (690 nm , s polarized) as the light source with the sample being tilted 30° . The effect of the asymmetric optical energy exchange between the two beams is clearly demonstrated (see the inset of Figure 4). When the two writing beams, beam S (signal beam) and beam P

(pump beam), were overlapped in the sample, beam S (curve a) lost optical energy and beam P (curve b) gained optical energy. After the sample was rotated 180° around the rotation axis in the sample plate, the phenomena became reversed: beam S (curve c) gained optical energy and beam P (curve d) lost energy. Unpoled samples showed no such phenomena. This experimental result indicated that this polymer was indeed photorefractive.

The optical gain results were measured as a function of the grating period ($\Lambda = \lambda/(2 \sin \theta)$, Figure 4). Two parameters characterizing the PR polymer, the effective density of the empty trap centers (N_e) and the maximum refractive index change (Δn), can be extracted. According to the band transport theory, the value of grating spacing corresponding to the maximum optical gain is equal to the Debye screening length $L_t = (4\pi^2 \epsilon_0 \epsilon k_B T / e^2 N_e)^{1/2}$, where k_B is Boltzmann's constant.²⁹ Thus, from the results of Figure 4, a N_e value of ca $2.3 \times 10^{14} \text{ cm}^{-3}$ was obtained. It is known that the maximum optical gain is related to Δn by $\Gamma_{\text{max}} = 4\pi \Delta n / (\lambda \cos \theta)$, where θ is the half interaction angle between the two writing beams.¹ The value of Γ_{max} , 0.88 cm^{-1} , from Figure 4, leads to a Δn of 1×10^{-5} .

For polymers 1 and 2, the two-beam-coupling experiments were carried out in a waveguide structure using a HeNe laser. In this experiment, the E-O coefficient tensor component r_{51} was utilized.^{1b} The largest optical gain coefficient under a zero external field is 2.3 cm^{-1} at a grating wavenumber of $0.6 \times 10^5 \text{ cm}^{-1}$.

It is worth mentioning that although these polymers are indeed photorefractive, the observed optical gain under zero field conditions is not a net gain because of the strong absorption. There are also several common features in those functionalized polyurethanes.^{6–8, 10, 13} First, a comonomer (diisocyanate in this case) was used to link the different species; therefore, the density of the different species is limited to a low level. To optimize the PR effect, the densities of the charge transporter and the NLO chromophore should be optimized. In the above polymer systems, this could not be done simultaneously. Second, the polymer backbones were polyurethanes which cannot effectively transport the photocharge carriers. Third, since it is a copolymer with three functional species, their molecular weight is very difficult to optimize. Any impurities or weighing errors in monomers can lead to the miss-match of the monomers' stoichiometry which will lower the molecular weight. These are the reasons that the second type of PR polymers were designed, which contain a conjugated backbone and a second order NLO chromophore.^{9,11,12,14,16,18,19}

Functionalized Conjugated Polymers

Design Ideas and Syntheses. The rationale for designing these new materials was that the conjugated backbone absorbs photons in the visible region and plays the triple role of charge generator, charge transporter, and backbone. It is known that conjugated polymers have relatively high photogenerated

(29) Kukhtarev, N. V.; Markov, V. B.; Odulov, S. G.; Vinetskii, M. S. *Ferroelectrics* **1979**, *22*, 949.

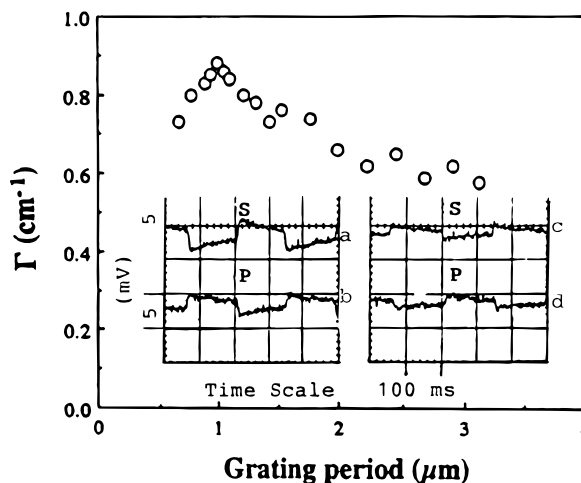


Figure 4. Optical gain coefficient, Γ , as a function of the grating period for polymer 3. The inset depicts the asymmetric energy exchange signals.

carrier mobilities (10^{-3} – $10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$).³⁰ Thus, the four functions necessary to manifest the PR effect exist simultaneously in a single polymer. Furthermore, the use of conjugated backbones enhances the density of the NLO chromophores.

However, in order to synthesize these polymers, a new polymerization approach needs to be developed because these polymers contain many functional groups which may not be tolerated in many polymerization processes, such as Ziegler–Natta polymerization,³¹ electrochemical polymerization and the oxidative coupling reaction.³² Fortunately, we have found that the Stille coupling reaction, a palladium-catalyzed reaction between organic halides (or triflate) and organotin compounds, offers the solution to this problem.^{33–35} The reaction requires very mild conditions and can tolerate different substituents of monomers, such as amines, esters, ethers, etc., allowing us to introduce different functionality into the polymer backbone. The structure of the conjugated photorefractive polymers synthesized is shown in Scheme 1 (polymers 4–7). We introduced the dihydropyrrolopyrroledione (DPPD) compound as the photosensitizer to extend the photosensitive region into a longer wavelength.³⁶ These types of compounds have strong absorptions in the visible region.

The polymerization went smoothly when a typical Stille catalyst system was used. Either $\text{Pd}(\text{PPh}_3)_4$ with LiCl or $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ alone can be used as the catalyst. Four polymers were synthesized with various compositions. These polymers were fully characterized by various spectroscopic and other techniques. The results were all consistent with the proposed polymer structures.

As the composition changed, the UV/vis spectral features of the polymers also changed. It can be noted that polymer 7 has an absorption at ca. 390 nm, mainly due to the absorption of the NLO chromophore. Polymers 4 and 6, however, show absorptions at 573

(30) Peng, X.; Horowitz, G.; Fichou, D.; Garnier, F. *Appl. Phys. Lett.* **1990**, *57*, 2013.

(31) Ordian, G. *Principles of Polymerization*, 2nd ed.; John Wiley & Sons: New York, 1981.

(32) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.

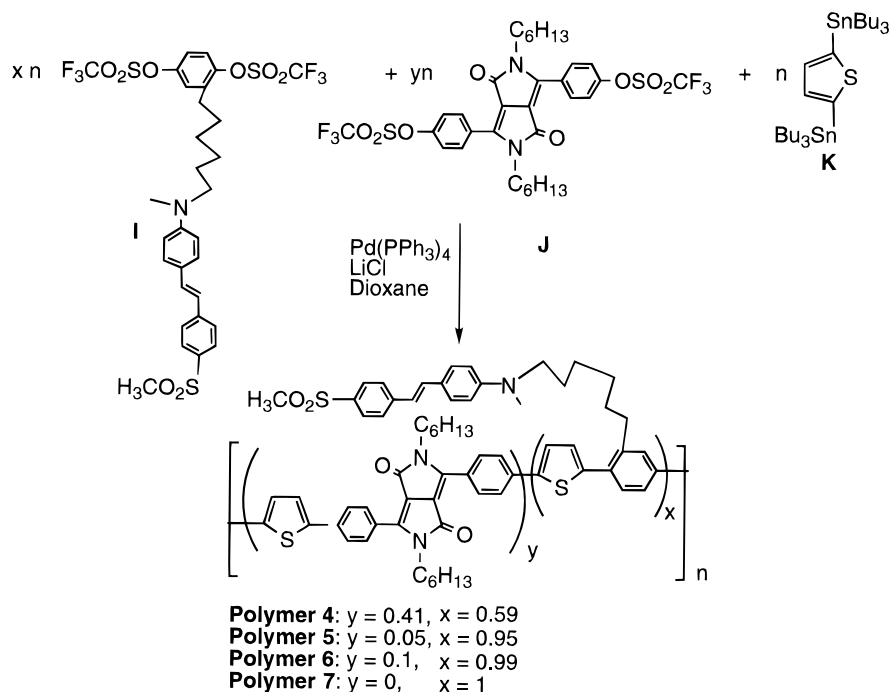
(33) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.

(34) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478.

(35) Bao, Z. N.; Chan, W. K.; Yu, L. P. *Chem. Mater.* **1993**, *6*, 2.

(36) Potrawa, T.; Langhals, H. *Chem. Ber.* **1987**, *120*, 1075.

Scheme 1. Synthetic Scheme of Polymers 4–7 Utilizing the Stille Coupling Reaction



nm, which is dramatically shifted from the absorption of monomer **J** (483 nm). This illustrates clear evidence for the incorporation of the DPPD unit into the polymers. The absorption strength correlates well with the concentration of the DPPD units (Figure 5). These results indicate that we can control the absorption strength of polymers at specific regions. This is very important for the design of photorefractive polymers. In order to demonstrate the photorefractive effect, the materials must have certain but small absorptions at the wavelength of a working laser; otherwise, either charge carrier cannot be generated or the materials are too absorbing. For this reason, polymer **5** has been studied in detail.

As we pointed out at the beginning, there are four processes involved in the photorefractive effect, namely, charge generation, charge transporting, charge trapping, and grating formation. In the present polymer system, the role of charge trapping is played by the defects existing in the polymer. Detailed studies about the trapping were very difficult before the exact nature of the trapping centers was known.

Charge Generation. Photoconductivity studies of these polymers showed a strong dependence on the external field strength. As the electrical field was increased, the photocurrent initially increased linearly (Ohmic behavior) and then almost quadratically. A typical photocurrent response time of ca. 100 ms was estimated. A photoconductivity of $1.8 \times 10^{-11} \Omega^{-1} \text{cm}^{-1}$ was obtained for polymer **5** under a field strength of 1500 kV/cm and a laser intensity of 311 mW/cm². The photoconductivities for polymers **4** and **6** were found to be ca. 8×10^{-11} and $4 \times 10^{-11} \Omega^{-1} \text{cm}^{-1}$, respectively. These values are comparable to those of well-known conjugated polymers, such as poly(phenylene/vinylene).^{37,38} The photocurrent of polymer

5 was also measured as a function of several wavelengths of excitation at the same laser intensity (48 mW/cm²) and electric field (400 kV/cm). It was found that the spectral dependence of the photocurrent had a similar shape to the absorption spectrum of the conjugated PR polymer. This seemed to indicate that the optical excitation of the conjugated backbone was the origin of the photocharge generation.

The quantum yields of the photogeneration of charge carriers evaluated from the photocurrent results are listed in Table 1. These yields are much larger than those in the polyurethane system. They showed the

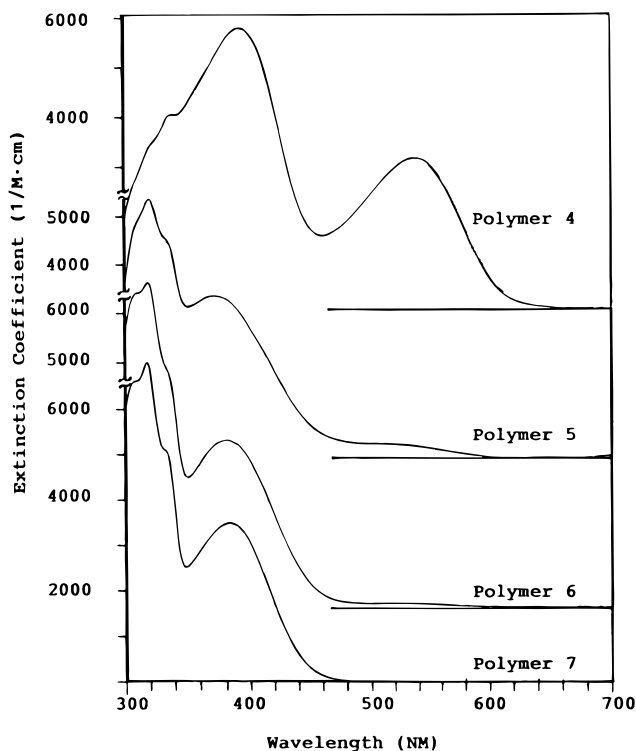


Figure 5. UV/vis spectra of polymers 4–7 in THF.

(37) (a) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Marcel Dekker Inc.: Basel, 1989. (b) *Electroresponsive Molecular and Polymeric Systems*; Skotheim, T. A., Ed.; Marcel Dekker Inc.: Basel, 1991; Vol. 2.

(38) Gailberger, M.; Bassler, H. *Phys. Rev.* **1991**, *B 44*, 8643.

Table 1. Summary of the Physical Properties of Polymers 4–6

polymers	α (cm^{-1})	d_{33} (pm/V)	r_{33} (pm/V)	Φ (at 400 kV/cm)
4	242	54	4	7×10^{-4}
5	201	89	10	3×10^{-4}
6	137	90	10	1.5×10^{-4}

electric field dependence which can be theoretically simulated by Onsager's model of the geminate-pair dissociation.³⁹ The simulation results generated the two parameters from the best fitting, η_0 (the yield of the thermalized bound pairs, independent of field), and r_0 ($=e^2/4\pi\epsilon_0 kT$, the Onsager distance), which were 0.02 and 15 Å, comparable to the values for the known conjugated polymers and the photoconductive polymers.^{27,37} The r_0 was also known to relate to the activation energy E_A at low-field conditions.³⁸

$$r_0 = e^2/4\pi\epsilon_0\epsilon E_A \quad (2)$$

Temperature-dependent measurements of the carrier mobility indicated an activation energy of 0.16 eV for this polymer. The r_0 was then calculated to be 18 Å, in agreement with experimental fitting results.

Charge Transporting. The charge carrier mobility (μ) is an important parameter for characterizing the charge-transporting process. We used the time-of-flight (TOF) technique to determine the charge carrier mobility. The results showed a dispersive charge transport as indicated by the initial decay and the tail of the transient signals. The temperature-dependent measurements of the charge carrier's mobility indicated that the charge-transporting process is thermally activated with Arrhenius activation energies of 0.16 and 0.23 eV for polymers **5** and **4**, respectively. The field dependence of the carrier mobility was anomalous; as the field was increased, the mobility decreased. Similar phenomena were observed in the poly(2-phenyl-1,4-phenylenevinylene) systems³⁸ and in a few composite photoconductive systems.⁴⁰ It was attributed to the random walk of the charge carrier within a random potential field.³⁸ The randomness of the potential field in this polymer was manifested by the broadened absorption spectrum (Figure 5).

Electro-optic Effect. The E-O coefficients were measured according to the method described in ref 28. The results are shown in Table 1. Compared to the polyurethane systems, these polymers are less stable in E-O response; a gradual decay (to 80% of initial value after 100 h) was observed for all of these polymers.

Optical Gain and Photorefractive Grating. Two-beam-coupling experiments were performed to characterize the photorefractivity of the polymers. The asymmetric optical energy exchange is shown in the inset of Figure 6. The resulting Γ values for polymer **5** are plotted as a function of the grating wavenumber ($K = 4\pi \sin \theta/\lambda$) in Figure 6. Similar results were obtained for polymers **4** and **6**. Two parameters characterizing the PR polymer **5**, the effective density of the empty trap centers (N_e) and the maximum

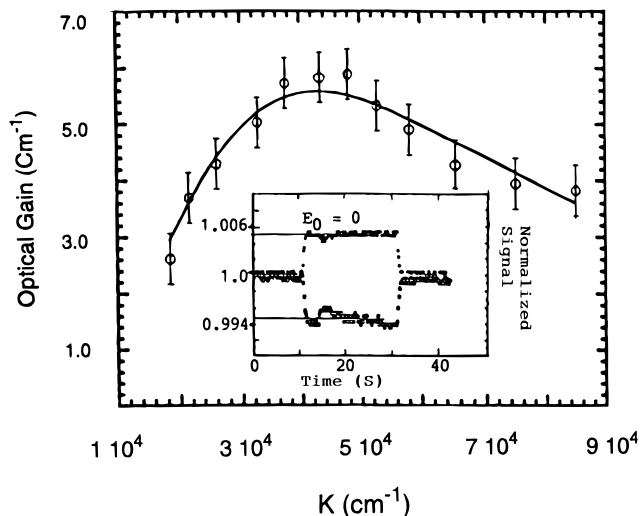


Figure 6. Optical gain coefficient, Γ , as a function of the grating wavenumber for polymer **5**. The inset depicts the asymmetric energy exchange signals under a zero field.

refractive index change (Δn), extracted from Figure 6, are ca. $2 \times 10^{14} \text{ cm}^{-3}$ and 4×10^{-5} , respectively. For polymer **4**, a N_e of ca. $1.9 \times 10^{15} \text{ cm}^{-3}$ and a Δn of 3×10^{-5} were deduced.

The refractive index change is related to the space-charge field by $\Delta n = n^3 r_{\text{eff}} E_d^2$, where r_{eff} is the effective electro-optic coefficient. The large index change ($\Delta n \approx 7.1 \times 10^{-5}$) under zero-field conditions implied either a large space-charge field ($\sim 100 \text{ kV/cm}$) or a large electro-optical coefficient (200 pm/V). Both implications are in contrast with theoretical expectation and with the results obtained by independent measurements. According to the photorefractive theory based on the band transport model, the largest space-charge field which can be achieved under zero-field conditions is the thermal diffusion field $E_d = k_B T K / e$ ($\sim 1.37 \text{ kV/cm}$).¹ The experimental value of the E-O coefficient for this polymer was about 2–4 pm/V (electrode poling). These discrepancies implied that there are other factors responsible for such a large optical gain. A reasonable assumption is that an internal field exists which assisted the charge separation and enhanced the photorefractivity under a zero field. This assumption has a solid base because of the orientation of the dipoles of the nonlinear optical chromophore after electric poling.

Further evidence was obtained from the field-dependent studies of the optical gain. It was found that the optical gain decreased when the field was increased in the region of 0–100 kV/cm, and there existed a flat valley near the field of 10^2 kV/cm (Figure 7). The optical gain increased as the field further increased. The results indicated that the internal field was about 10^2 kV/cm opposite of the direction to the poling field. Many further measurements gave results with more clear trends which are consistent with the suggested internal field.

Theoretical fitting was carried out based on the relationship between the optical gain and the space-charge field (E_{sc}):¹

(39) (a) Onsager, L. *Phys. Rev.* **1938**, *54*, 554. (b) Mozumder, A. J. *Chem. Phys.* **1974**, *60*, 4300.

(40) Borsenberger, P. M.; Pautmeier, L.; Bassler, H. *J. Chem. Phys.* **1991**, *94*, 5447.

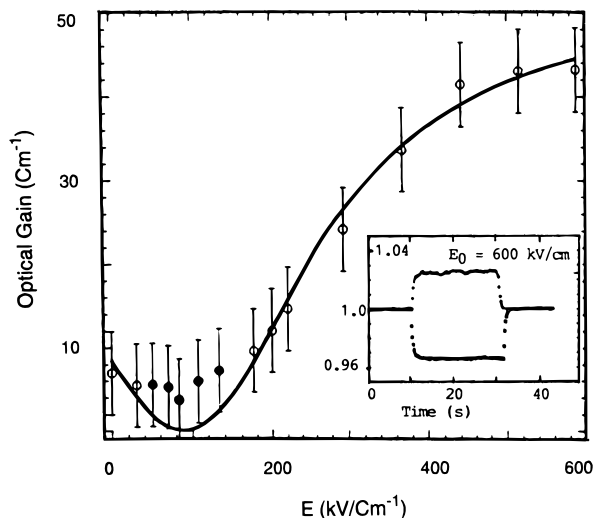


Figure 7. Optical gain coefficient, Γ , as a function of the external electric field for polymer 5. The inset depicts the asymmetric energy exchange signals under an electric field of 600 kV/cm.

$$\Gamma = \frac{\pi n^3 \sin \phi r_{\text{eff}} E_{\text{sc}}}{\lambda m \cos \theta} = \frac{\pi n^3}{\lambda \cos \theta} \sin \phi r_{\text{eff}} E_q \sqrt{\frac{E_0^2 + E_d^2}{E_0^2 + (E_d + E_q)^2}} \quad (3)$$

with

$$\phi = \tan^{-1} \left[\frac{E_d}{E_0} \left(1 + \frac{E_d}{E_q} + \frac{E_0^2}{E_d E_q} \right) \right] \quad (4)$$

where ϕ is the phase shift between the interference pattern and the index grating, r_{eff} the effective E-O coefficient, $E_d = k_B TK/e$ is the diffusion field, $E_q = eN_e/\epsilon_0 \epsilon K$ is the limiting space-charge field, E_0 is the external electric field, ϵ is the dielectric constant (4.85), and N_e is the effective density of the empty trap centers. By incorporating the internal field term, the E_0 term in the above equation becomes $(\sin \theta)(E^* + E_i)$, where θ is the angle between the grating wave vector and the sample plane (30°), E^* is an applied field (0–588 kV/cm), and E_i is an internal field. The simulation of the field-dependent data yielded $E_q = 1.0 \times 10^2$ kV/cm, $E_i = 8.8 \times 10^2$ kV/cm, and $r_{\text{eff}} = 1.0$ pm/V. The extracted value of E_i from the fitting was very interesting and was in reasonable agreement with the value evaluated theoretically in other polar polymer systems.⁴¹

It is known that there are many different types of conjugated polymers which can be explored for photorefractive studies. An obvious extension is to utilize other conjugated polymer backbones, such as poly(phenylenevinylene) (PPV), which exhibits high photoconductivity. Studies by us and other groups also indicate that PPV backbones are easy to functionalize by utilizing the Heck coupling reaction.⁴² Two dibromobenzene derivatives substituted with a NLO chromophore and an alkoxy group were used as monomers. These monomers were copolymerized with *p*-divinylbenzene to give the resulting copolymers (Scheme 2). However, detailed photorefractive studies revealed

that although the copolymer possessed both photoconductivity and electro-optic response, the polymer systems exhibited no positive result of photorefractive phenomena. This is one example which shows the complication in designing PR polymers; the existence of two necessary physical properties in a single polymer does not sufficiently ensure that the polymer will be photorefractive. A similar phenomenon was observed in a composite PR material (polyvinylcarbazole:2,4,7-trinitro-9-fluorenone:2-(4-nitrophenyl)-4,5-bis(4-methoxyphenyl)imidazole).⁴³

Functionalized Polyimides^{15,17}

The third type of PR polymers contain NLO chromophores and porphyrin-electron acceptor (quinones or imide) moieties. This PR system was designed on the basis of the fact that porphyrin-electron acceptor (quinones or imide moieties) systems are well-known model compounds for photosynthetic processes and exhibit very interesting charge transfer properties.⁴⁴ A high quantum yield of charge separation can be achieved in these systems. Polyimides were found to be photoconductive and to allow charge transport.⁴⁵ Furthermore, polyimides possess high glass transition temperatures and therefore their electric-field-induced dipole orientations can be fixed after imidization.⁴⁶

As shown in Scheme 3, polymerization was carried out in aprotic polar solvents, such as DMAC or NMP under room temperature conditions. Spectroscopic studies supported the structure of the polymer. The DSC studies showed that the polyamic acid had a glass transition temperature at ca. 90 °C and started to imidize around 160 °C; the polyimide exhibited a much higher glass transition temperature (250 °C). The absorption coefficient at 690 nm was determined to be 1260 cm⁻¹.

This polyimide was photoconductive and second-order nonlinear-optically active. The photoconductivity of the polyimide was determined to be 1.1×10^{-12} Ω^{-1} cm⁻¹ under an external field of 1500 kV/cm using a diode laser ($\lambda = 690$ nm) as the light source ($I = 5.9$ mW/cm²). After the sample was poled using a corona poling technique (poling field, 2 mV/cm), second harmonic generation measurements revealed a sizable d_{33} value (ca. 110 pm/V at 1064 nm). This photorefractive polyimide exhibited very high temporal stability in dipole orientation at elevated temperatures. There was no significant decay in the d_{33} value at 90 and 150 °C. Long-term stability was observed even at 170 °C; the initial d_{33} value of 80% was retained after 120 h.

This polyimide demonstrated interesting photorefractive effects. For instance, an asymmetric optical energy exchange in the two-beam-coupling experiment has been observed. For an unpoled sample, no such phenomena were observed. A very large optical gain

(42) Heck, R. F. *Org. React. (N.Y.)* **1982**, *27*, 345. Examples of Heck coupling reaction utilized in polymer synthesis: (a) Heitz, W.; Brugging, W.; Freund, L.; Gailberger, M.; Greiner, A.; Jung, H.; Kampschulte, U.; Niebner, N.; Osan, F. *Makromol. Chem.* **1988**, *189*, 119. (b) Martelock, H.; Greiner, A.; Heitz, W. *Makromol. Chem.* **1991**, *192*, 967. (c) Weitzel, H. P.; Mullen, K. *Makromol. Chem.* **1990**, *191*, 2837. (d) Bao, Z.; Chen, Y.; Cai, R.; Yu, L. *Macromolecules* **1993**, *26*, 5281.

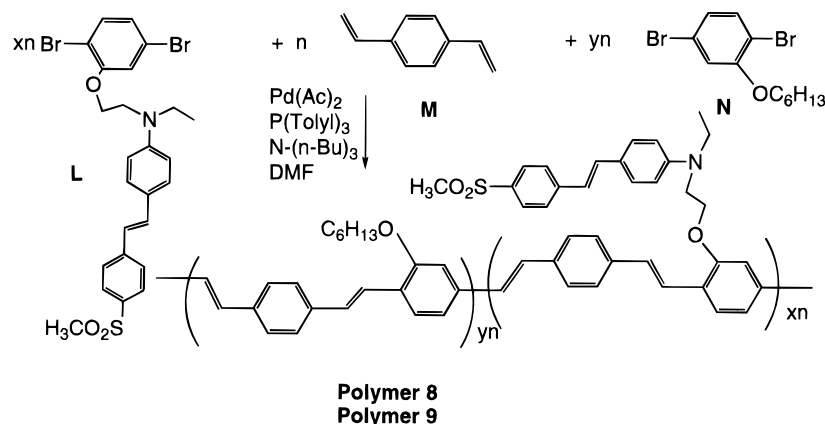
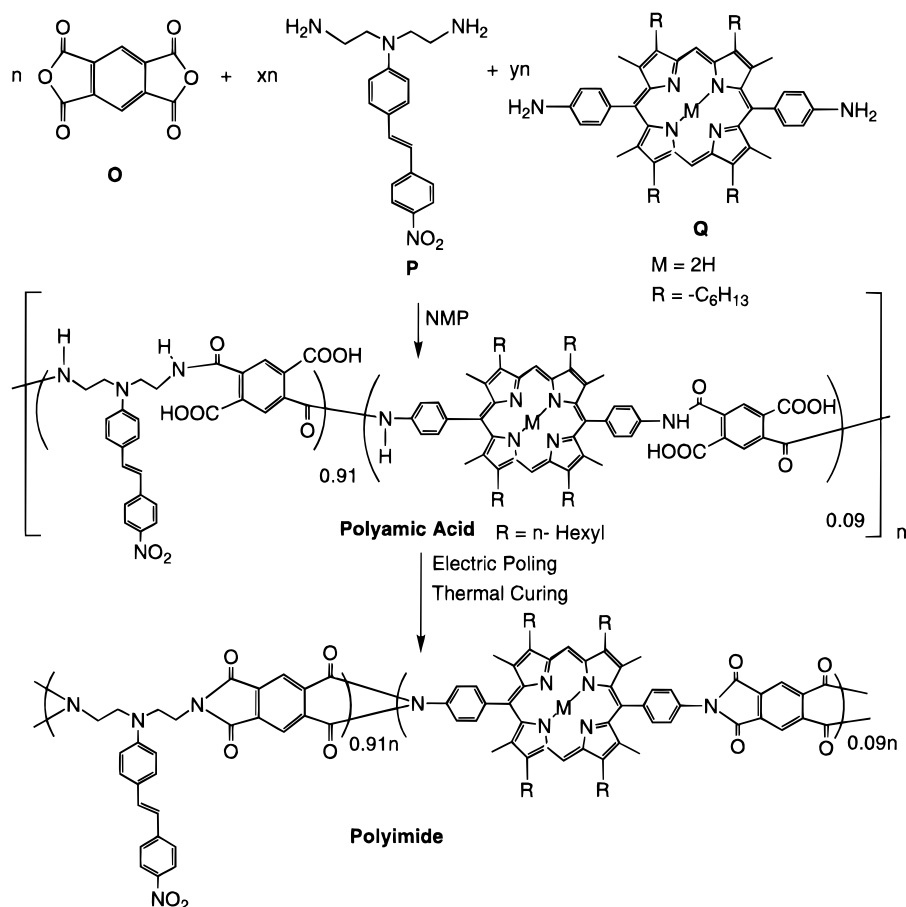
(43) Silence, S. M.; Donkers, M. C. J. M.; Walsh, C. A.; Burland, D. M.; Moerner, W. E.; and Twieg, R. J. *Appl. Phys. Lett.* **1994**, *64*, 712.

(44) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.

(45) Iida, K.; Nohara, T.; Nakamura, S.; Sawa, G. *Jpn. J. Appl. Phys.* **1989**, *28*, 1390.

(46) Peng, Z. H.; Yu, L. P. *Macromolecules*, **1994**, *27*, 2638.

(41) Minami, N.; Sasaki, K.; Tsuda, K. *J. Appl. Phys.* **1983**, *54*, 6764.

Scheme 2. Synthetic Scheme of Functionalized Poly(phenylenevinylene) (Polymers 8 and 9) Utilizing the Heck Coupling Reaction

Scheme 3. Synthesis of Photorefractive Polyimide Containing Porphyrin Moieties


coefficient (22.2 cm^{-1}) under zero-field conditions was detected. This unusually large optical gain originated from the existence of an internal field in the poled polymer samples.

Other Functionalized Photorefractive Polymers

Several examples of functional PR polymers have appeared in literature other than those discussed above. Peyghambarian²¹ *et al.* prepared a copolymer of polyacrylate which contained carbazole and (tricyanovinyl)carbazole groups as the side chain. A plasticizer (benzylbutylphthalate) was added to lower the glass transition temperature so that the polymer film

could be poled at room temperature. A small E-O coefficient (0.25 pm/V) under an external electric poling field (260 kV/cm) was detected. Four-wave-mixing experiments revealed a small diffraction efficiency, 3×10^{-7} , with an applied field of 450 kV/cm .

Another example was reported by Sansone²² *et al.* A PMMA polymer backbone was functionalized with (dialkylamino)nitrostilbene. The NLO chromophores in these polymers served as both the charge sensitizers and the charge transporters. Four-wave-mixing experiments indicated a diffraction efficiency on the order of 10^{-4} . However, since the physical studies were carried out at a wavelength of 633 nm , which is in the absorptive region of the NLO chromophore, photoinduced cis–trans isomerization of the stilbene

likely occurred. This photochemical transformation certainly affected the NLO properties and refractive index of the polymer. The grating observed probably originated from the photochromic effect, as pointed out correctly by these authors. In both papers, only the field dependent diffraction efficiencies and electro-optic activities were studied. No information about the two-beam-coupling experiment was given. Therefore, the evidence is not conclusive to support the photorefractive nature of these polymers.

Concluding Remarks

Synthesis and studies on the photorefractive effects of multifunctional polymers are a new research area which is filled with surprises and challenges. The past five years have witnessed a rapid growth in this area, especially in composite polymer systems.⁵ Some of the characteristic parameters in these systems, such as optical gain and diffraction efficiency, have reached extraordinarily high values. However, the challenges we are facing are also overwhelming: very little understanding has been gained on the mechanism for these photorefractive materials. Photoconductive polymers have been studied for many decades, but their mechanism for photoconduction is still not well understood. In a photorefractive polymer, the introduction of electro-optic species makes the system tremendously more complicated. Further complications in composite systems arise from the fact that they suffer from phase separation and low glass transition temperatures. So far, only those composite systems with glass transition temperatures below room temperature give rise to net optical gains. Our fully functionalized polymers exhibiting higher glass transition temperatures did not show any net optical gains although the

two necessary physical properties are comparable to or even better than those of some composite systems. This raises a question about the true mechanism of the photorefractivity in polymeric materials. Theoretical studies on the photorefractive effect in organic polymer systems are extremely difficult due to both their complication and the lack of data. At the present stage, the band transport theory developed for inorganic single crystals was applied in interpreting the experimental results.²⁹ Although this theory worked well so far, its validation is not justified. For example, it is not proper to describe the energetic structure of the amorphous polymer according to the band theory. The charge transport in polymeric materials is dispersive with a wide distribution of the charge carrier's mobility; it most probably occurs via the hopping mechanism. A wide range of trapping centers exist in polymeric materials as evidenced by the long tail in the absorption spectrum. However, despite the complication in these polymeric materials, the potential application in photonic devices, the advantages of these materials over their inorganic counterparts, and the challenge in synthesis, physical studies, and fundamental understanding justify the pursuit of research in this area. From the chemistry point of view, the synthetic approaches developed will be very useful in the design and synthesis of other types of functional and multifunctional polymers.

This work was supported by the Air Force Office of Scientific Research and by the National Science Foundation. Support from the National Science Foundation Young Investigator program and the Arnold and Mabel Beckman Foundation (Beckman Young Investigator Award) is gratefully acknowledged.

AR9501176