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Large Photorefractivity in an Exceptionally Thermostable Multifunctional Polyimide

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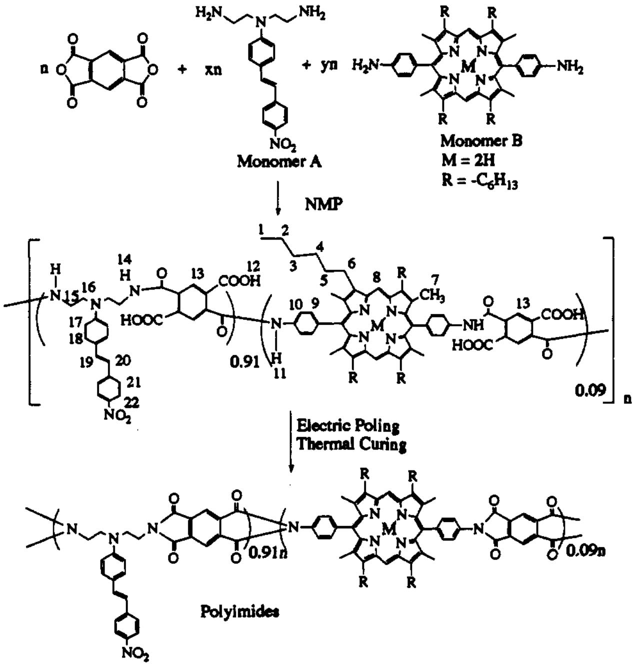
The driving force to pursue research on photorefractive polymers comes from both fundamental interests and practical expectations. It is known that photorefractive materials are multifunctional materials which combine the electrooptic (EO) effect and photoconductivity to manifest a new property: photorefractivity.[1] Fundamentally, it is interesting to design and synthesize such multifunctional polymers.[2-5] It is believed that polymeric materials possess several advantages over their inorganic counterparts, such as low dielectric constants, large EO coefficients, ease in processing, and versatility in structural modification.[6] However, to be truly competitive with or even superior to inorganic photorefractive materials, several important issues in organic systems have to be addressed: (1) the low quantum yield in photocharge generation, (2) the low charge carrier mobility, (3) the dispersion of the charge carrier's mobility, and (4) the instability of second-order NLO activities (or dipole orientation). Some of these issues are inherent to the known organic materials, rendering a tremendous challenge to both chemists and physicists.

In the past two years, our research has evolved from the synthesis of multifunctional polyurethane to the synthesis of conjugated photorefractive polymers.[2-5] Significant progress has been made in solving the above issues. More recently, we have designed new polymers with the structure as shown in Scheme 1. We expected this polymer to be photorefractive (PR) and to possess improved performance and enhanced stability in photorefractive effects. The rationale to design this PR system is that porphyrin–electron acceptor (quinones or imide moieties) systems are well-known model compounds for photosynthetic processes and exhibit very interesting charge-transfer properties.[7] A high quantum yield of charge separation could be achieved in these systems. It was found that polyimides were photoconductive and that charge transporting was possible.[8] Furthermore, polyimides possess high glass transition temperature and therefore the electric field induced dipole orientation can be fixed after imidization.[9] The experimental results confirmed our expectation. In this paper, we report the results on the synthesis and characterization of this new photorefractive polymer system.

Scheme 1. Synthesis of Polyamic Acid and Polyimide



As shown in Scheme 1, the key step is the synthesis of two amino monomers, monomers A and B. Monomer A was synthesized by the approach developed in our laboratory by utilizing the Mitsunobu reaction starting from the corresponding dihydroxy compounds.[9] Monomer B was synthesized from the corresponding dipyrromethane and 4-nitrobenzaldehyde followed by the reduction of dinitroporphyrin with $SnCl_2$.[10] All of these monomers were carefully purified, and their structures were confirmed by microanalysis and by spectroscopic methods.[11]

Polymerization was carried out in aprotic polar solvents, such as DMAC or NMP under room temperature. The polymer was separated by precpitation in acetone, and the yield was quantitative. An intrinsic viscosity of 0.3 dL/g was obtained in DAMC at 30 °C. Optical quality films with a thickness around 10 μm were cast from the DMAC solution.

Spectroscopic studies supported the structure of the polymer. The ^{1}H NMR spectrum of polyamic acid indicated that the porphyrin moieties were incorporated into the polymer. The assignments and the integrations of different peaks in the NMR spectrum of the polyamic acid were consistent with the structure.[12]

The FTIR spectra of the polyamic acid and the polyimide exhibited the corresponding features. The polyamic acid exhibited bands at 1720 cm^{-1} due to a carbonyl group in an amide linkage and at 1651 cm^{-1} due to a carbonyl group in a carboxylic acid. Two strong absorption bands due to the nitro group in the NLO chromophore appeared at 1339 and 1516 cm^{-1}. The polyimide showed new bands at 1773 (carbonyl asymmetric stretching), 1389, 1154, and 725 cm^{-1}. The band at 1651 cm^{-1} completely disappeared after the polymer film was cured at 190 °C for 2 h. However, the bands due to the nitro group in the NLO chromophore did not change appreciably in intensity, indicating that the NLO chromophore survived during the curing process.

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(11) Monomer A (recrystallized from MeOH/H_2O): dark red plate crystal, yield 46%, mp 160.2 °C (DSC result). Anal. Calcd: C, 66.23; H, 6.80; N, 17.17. Found: C, 66.04; H, 6.75; N, 17.06. Monomer B (recrystallized from CH_2Cl_2/MeOH): purple needle crystals, yield 77% mp 293–294 °C. ^{1}H NMR (DMSO-d_6, ppm): δ, –2.575 (s, inner ring H, 2 H), 0.859 (t, J = 7.15 Hz, H_1, 12 H), 1.295–1.338 (m, H_2, 8H), 1.402–1.444 (m, H_3, 8 H), 1.648–1.689 (m, H_4, 8 H), 2.070–2.096 (m, H_5, 8 H), 2.559 (s, H_7, 12 H), 3.870 (t, J = 6.46 Hz, H_6, 8 H), 5.501 (s, NH_2, 4 H), 6.936 (d, J = 7.56 Hz, H_{10}, 4 H), 7.535 (d, J = 7.49 Hz, H_9, 4 H), 10.033 (s, H_8, 2 H). Anal. Calcd: C, 81.40; H, 9.11; N, 9.49. Found: C, 81.36; H, 9.05; N, 9.47.

(12) **Polymer**: ^{1}H NMR (DMSO-d_6, ppm, see Scheme 1 for labeling): δ, –2.50 (inner ring H of porphyrin), 0.869 (H_1), 1.346 (H_2), 1.470 (H_3), 1.732 (H_4), 2.136 (H_5), 2.582 (H_7), 3.454 (H_{15}), 3.533 (H_{16}), 3.774 (H_6), 6.934 (H_{17}), 7.064 (H_{19}), 7.332, 7.735, 8.120 (cis trans H_{13}), 7.355 (H_{20}), 7.461 (H_{18}), 7.683 (H_{21}), 8.096 (H_{22}), 8.286 (H_9), 8.578–8.668 (d, H_{14}), 8.760 (H_{10}), 10.180 (H_8), 10.90–11.10 (H_{11}), 13.50 (b, H_{12}). Anal. Calcd: C, 64.20; H, 4.96; N, 9.82. Found: C, 62.36; H, 5.23; N, 9.30.

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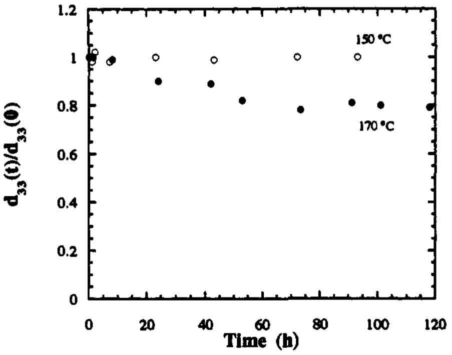

Figure 1. Temporal stability of the second harmonic signals at 150 and 170 °C.

The UV/vis spectrum of the polyamic acid in solution showed a strong Soret band of porphyrin moieties at 412 nm. Fairly weak Q bands from the porphyrin rings were also noticeable at ca. 510, 540, 575, and 630 nm. The absorption due to the NLO chromophore appeared at 458 nm, which was partially overlapped with that of the porphyrin Soret band. However, the NLO chromophore absorption and the Soret band smeared together in the solid state (thin films). The absorption maximum appeared at ca. 435 nm. The imidization process did not significantly change the absorption spectrum. The corona poling process (poling field strength, 2×10^6 V/cm) led to a decrease in the absorption at 435 nm due to the birefringence induced by the dipole orientation of the NLO chromophore. The absorption coefficient at 690 nm was determined to be 1260 cm^{-1}.

The polyamic acid had a glass transition temperature at ca. 90 °C and started to imidize around 160 °C as shown by the DSC studies. The polyimide exhibited a much higher glass transition temperature (at 250 °C). TGA studies indicated that three weight loss processes for the polyamic acid started at 160, 345 and 420 °C, respectively, under nitrogen atmosphere. Only the latter two processes existed in the polyimide.

The polyimide was photoconductive and second-order nonlinear-optically active. The photoconductivity of the polyimide was determined to be $1.1 \times 10^{-12}\ \Omega^{-1}\ cm^{-1}$ under an external field of 1500 kV/cm using a diode laser ($\lambda = 690$ nm) as the light source ($I = 5.9$ mW/cm^2). After the sample was poled using a corona poling technique (poling field 2 mV/cm), second harmonic generation measurement revealed a sizeable d_{33} value (ca. 110 pm/V at 1064 nm). This photorefractive polyimide exhibited unusual 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, and the initial d_{33} value of 80% was retained after 120 h (Figure 1). This remarkable stability offer us the unique opportunity to study the photorefractive mechanisms. For example, it is possible to study the temperature effect on photorefractivity at the temperature range below 170 °C.

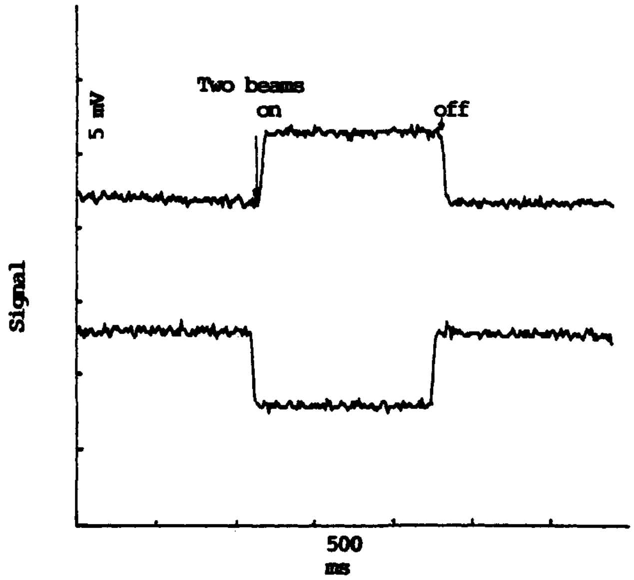

Figure 2. The oscilloscope traces of the asymmetric two beam coupling signals. The data were taken using a digitized oscilloscope (Tektronix Model TDS 540).

This polyimide demonstrated very interesting photorefractive effects. An asymmetric optical energy exchange in the two beam coupling experiment has been observed. Figure 2 shows such a phenomena where one beam gained energy and another beam lost energy. After the sample was rotated 180°, the situation was reversed. For an unpoled sample, no such phenomenon was observed. This is unambiguous evidence for the photorefractivity.[1] A very large optical gain 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. We have found firm evidence for the role of the internal field.[13] Detailed physical studies about this polymer system will be reported separately.

In summary, we have demonstrated a new idea to synthesize novel photorefractive polymer systems by utilizing the principles for the design of photosynthetic charge transfer model compounds. Remarkable thermal and temporal stability of the second-order NLO effect was observed. An asymmetric optical energy exchange was observed, indicating the photorefractive nature of the polymer. A very large, zero external field optical gain was detected.

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