Photoinduced electron transfer and its applications–Study on photochemical solar energy storage and polymeric photorefractive materials

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Abstract. The applications of photoinduced electron transfer, one in solar energy storage and the other in polymeric photorefractive materials are reported. In the former case, two new kinds of polymers containing norbornadiene and carbazole pendants were synthesized. The photoisomerization of norbornadiene pendants were achieved by irradiation with the light above the wavelength of 350 nm and a photoinduced electron transfer mechanism was proposed via fluorescence quenching, chemically induced dynamic nuclear polarization and thermodynamic discussion. In the latter case, a fast photorefractive response time of a polymer film composed of poly(N-vinylcarbazole), 2,4,7-trinitro-9-fluorenone and 4-(dicyanovinyl)-N,N-diethylaniline was observed by four-wave mixing diffraction measurement and the function of photoinduced electron transfer process in this photorefractive polymer film was also illustrated.

Keywords. Photoinduced electron transfer; norbornadiene pendants; carbazole pendants; valence isomerization, photorefractive effect.

1. Introduction

Over the past three decades, the photoinduced electron transfer and charge separation has been an area of great interest to physicists and chemists, not only because it plays an important role in photothesis [1], but also because it is usually one of the key steps to achieve some required properties in variant photoelectronic devices, such as photoconductivity materials [2] and photorefractive (PR) materials [3]. In this paper, two applications of photoinduced electron transfer and charge separation are reported, one in solar energy storage and the other in PR materials.

It is well known that photoinduced electron transfer processes have been widely applied to solar energy conversion and storage, for example, photosensitization of photochemical energy storage reactions [4] as well as preparation of hydrogen by photolysis of water [5] and photo-electrochemical cells [6]. Among many photochemical energy storage reactions, valence isomerization of norbornadiene to quadricyclane is one of the most promising systems [7]. Since norbornadiene itself and lots of norbornadiene derivatives cannot harvest sunlight (its major energy distributes in the region 300–700 nm) directly or effectively, photosensitizations including via electron transfer

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P_1

P_2

P_3

P_{1-2}

Ia X=CN
IIa X=COOH
IIIa X=COOCH$_3$

Ib X=CN
IIb X=COOH
IIIb X=COOCH$_3$
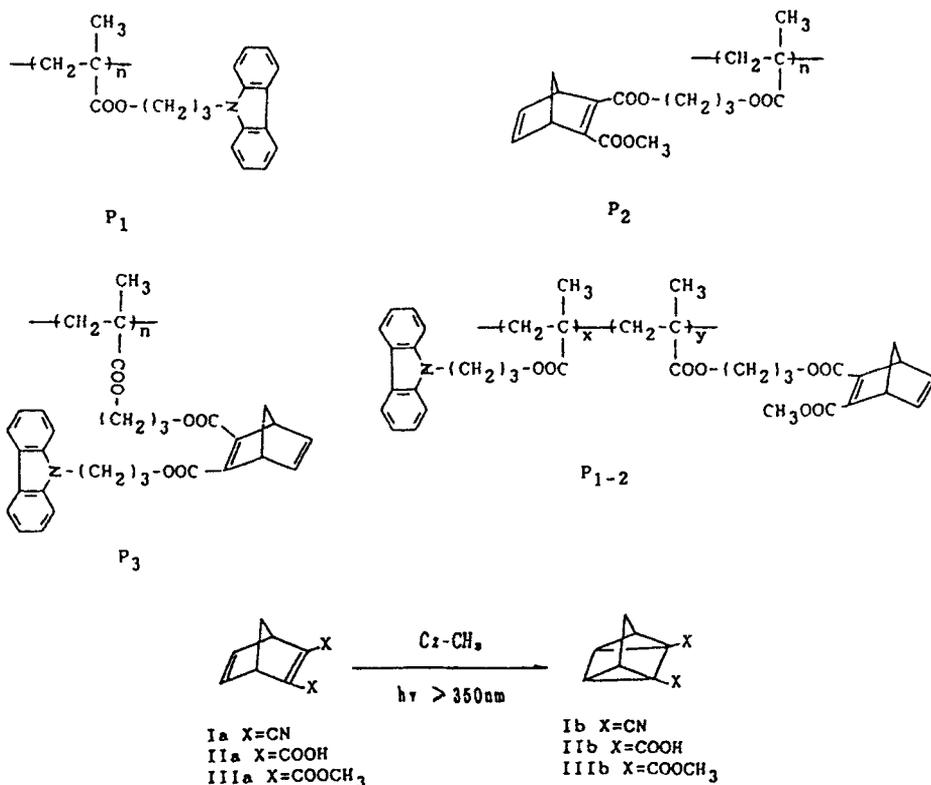
Scheme 1.

and triplet-triplet energy transfer mechanisms received much attention [4,7]. However, photosensitized isomerization of norbornadienes were mainly performed in small molecular systems, even though polymeric sensitizers taking effect by way of energy transfer mechanism [8] and polymers bearing norbornadiene pendants were investigated by several research groups [9].

In this work, two new kinds of polymers P_3 and P_{1-2} (scheme 1) containing norbornadiene and carbazole pendants were designed and synthesized. The valence isomerization of norbornadiene pendants were smoothly achieved by irradiation with the light above the wavelength of 350 nm and a mechanism involving electron transfer was proposed. To our knowledge, the photosensitized valence isomerization of norbornadienes not only via electron transfer mechanism but also in polymer systems like P_3 and P_{1-2} have not been reported by other researchers. There is no doubt this work is a good example to elucidate how photoinduced electron transfer reactions are applied to store solar energy.

After detailed studies on inorganic PR crystals for nearly three decades, it has been definitely confirmed that the PR effect results from three consecutive and cooperative processes [3] (i) Generation of free charge carriers (holes or electrons) owing to the absorption of photons, or in another words, photoinduced electron transfer and charge separation; (ii) formation of space charge field due to the diffusion or drift of photocarriers over a distance on the order of micrometers; (iii) electro-optic

response of nonlinear optical chromophore on space charge field. Thus, polymers which possess photoconductivity and electro-optic effect simultaneously will be candidates of PR materials.

There are several reasons for pursuing the development of polymeric PR materials [3] (i) High figure-of-merit for PR effect is probably obtained in PR polymers arising from the low dielectric constant and high electro-optic response. The latter is due to the high second-order nonlinearity of organic molecules in polymers, (ii) variable operation wavelength region due to the high flexibility of polymers in terms of doping and modifying the molecular structures, (iii) ease of processing into various forms such as films and waveguides of different shapes, (iv) low cost.

The first observation of PR effect in polymer films was reported in 1991 [10]. Up to now, diffraction efficiencies near 100% [11] and response times as short as 39 ms at a writing intensity of 1 W/cm^2 have been observed in different polymers [12].

One possible limitation of PR polymers is the relatively slow speed of response, especially relative to the semiconductor materials. Moerner [3] pointed out "the route to even faster PR polymers lies in increasing the quantum efficiency of charge generation, either through higher applied electric fields or intrinsically more efficient sensitizers".

In this paper, a polymer composed of poly(*N*-vinylcarbazole)(PVK), 2, 4, 7-trinitro-9-fluorenone (TNF) and 4-(dicyanovinyl)-N,N-diethylaniline (DCVDEA) (scheme 2) was also prepared. Four-wave mixing (FWM) diffraction measurements indicate it is a PR polymer with fast response. The play of photoinduced electron transfer and charge separation between PVK and TNF in this PR polymer was also illustrated.

2. Experimental

2.1 *Materials*

N-methylcarbazole, various norbornadiene derivatives (I a, II a and III a), P_1, P_2, P_3, P_{1-2} (see scheme 1), TNF, DCVDEA (see scheme 2) were all synthesized in our laboratory. PVK (Aldrich, secondary standard, average molecular weight is 200,000) was used as supplied. Acetonitrile (E Merck, Darmstadt; analytic grade reagent) was dried on KOH before the experiments. Toluene and cyclohexanone (analytic grade reagent) were redistilled before use.

2.2 *Apparatus*

The absorption spectra were taken with a Hewlett–Packard 8451A spectrophotometer. IR spectra were run on a Perkin–Elmer 983G grating spectrophotometer using

PVK   TNF   DCVDEA
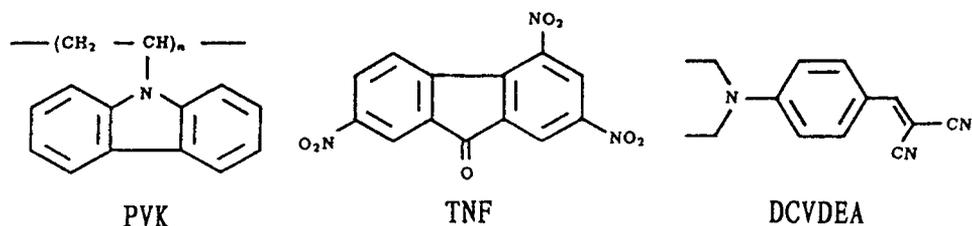
Scheme 2.

KBr pellets. Fluorescence spectra were recorded on a Hitachi MPF-4 spectrofluoro-meter. Fluorescence lifetimes were measured on a Horiba NASE-1100 single-photon-counting nanosecond fluorescence spectrometer. Chemically induced dynamic nuclear polarization (CIDNP) experiments were carried out with a slightly modified Bruker ^{1}HNMR spectrometer (operating at 80 MHz).

In FWM measurements, the light source is a He–He laser at 632·8 nm. It has a total output power of about 40 mW. The two coherent writing beams (beams 1 and 2 as shown in the inset of figure 4) were _s_-polarized and crossed at an angle of 30°. In order to have a non-zero component of the external electric field along the grating wave vector K, the experiments were performed in a tilted geometry. The incident angles of beams 1 and 2 are, $\alpha = 23°$ and $\beta = 53°$ respectively. The two writing beams are let to have equal powers. The total intensity of the two beams can be varied from 15 to 170 mW/cm^2. The reading beam(beam 3), which has a low intensity of 1 mW/cm^2, propagates contradirectionally to beam 1. The diffracted signal (beam 4) was measured by using a photo-multiplier tube connected to a Model 4203 signal averager.

2.3 *Irradiation*

The irradiations of polymer P_{1-2}, P_3 and P_2 were carried out at a distance of 5 cm from a 400 W medium pressure mercury lamp under a nitrogen atmosphere. Light with a wavelength greater than 350 nm was obtained by setting a filter (Corning 0–52) in front of the lamp.

2.4 *Preparation of PR polymer film*

PVK was dissolved in a 4:1 toluene/cyclohexanone mixture together with 30·4 wt% DCVDEA and 1·5 wt% TNF. From this viscous solution, films were cast on two indium tin oxide (ITO)-coated substrates. After drying at ambient temperature and pressure for 24 h and at 60°C and in vacuum for another 24 h, the two coated ITO plates were sandwiched together at 120°C.

3. Results and discussion

3.1 *Photoisomerization of polymers*

UV spectrum of P_3 film and the change in IR spectrum of P_3 by irradiation with the light above the wavelength of 350 nm are shown in figures 1 and 2 respectively. Figure 2(a) shows the IR spectrum of P_1 in the range 1700–1500 cm^{-1}; and the absorption peaks at 1622 and 1595 cm^{-1} are ascribed to the skeletal vibration absorption of carbazole pendants. Because there are double bonds of norbornadiene in P_3, the intensity of the absorption at 1622 cm^{-1} is higher than that at 1595 cm^{-1} as shown in figure 2(b). After irradiation by light above the wavelength of 350 nm (in film state or in solution), the intensity of the absorption at 1622 cm^{-1} is distinctly decreased as shown in figure 2(c), which indicated that the irradiation caused the disappearance of double bonds and the norbornadiene pendants had been converted into corresponding quadricyclane pendants. Although the photoisomerization of P_{1-2} can also take place under the same irradiation condition, the difference between the reaction rates of P_3 and P_{1-2} is distinct. If the photoisomerization quantum yield of P_3 is assumed to be one unit, the photoisomerization quantum yield of P_{1-2} is only 0·41.
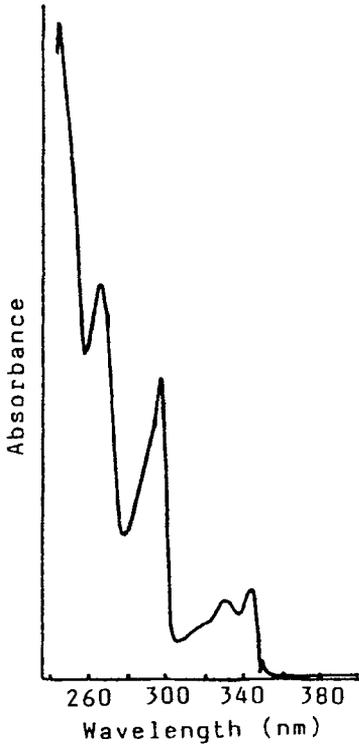
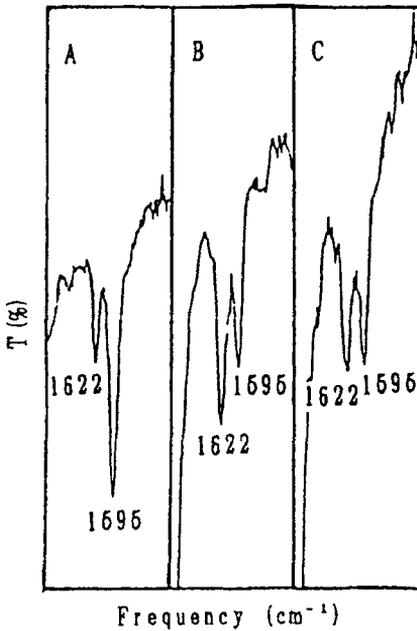**Figure 1.** UV spectrum of P_3 film.

Figure 2. Change in IR spectrum of P_3 after irradiation with the light of wavelength greater than 350 nm: (a) IR spectrum of P_1; (b) IR spectrum of P_3; (c) IR spectrum of P_3 after irradiation.

Under the same irradiation condition (wavelength, greater than 350 nm), there were no changes in the IR spectrum of P_2 which has only norbornadiene as pendant, either in the film state or in solution. Thus, it is confirmed that the valence isomerization of norbornadiene pendants in P_3 and P_{1-2} proceeded under the sensitization of carbazole pendants.

3.2 *The mechanism for photosensitized isomerization of norbornadiene*

3.2a *Fluorescence quenching*

In order to clarify the mechanism for the photosensitized isomerization of norbornadiene pendants in P_3 and P_{1-2}, several norbornadiene derivatives (Ia, IIa and IIIa), which serve as electron acceptors, were selected for quenching study of N-methylcarbazole. The fluorescence intensity I and fluorescence lifetime τ are related to the quenching rate constant K_q and the concentration of quencher $[Q]$ by the Stern–Volmer equation [19],

$$I_0/I = \tau_0/\tau = 1 + kq\tau_0[Q],$$

where I_0 and τ_0 are the fluorescence intensity and fluorescence lifetime respectively, in the absence of quencher. In the quenching experiments mentioned above, all data followed the Stern–Volmer equation and gave straight lines with intercept of unity. From the slopes $K_q\tau_0$ of these straight lines and the lifetime of N-methylcarbazole (14·8 ns), the fluorescence quenching rate constants K_q obtained are in the order of $10^{10}\,M^{-1}\,s^{-1}$ magnitude (shown in table 1), approaching the diffusion-controlled limit, as expected for efficient (exothermic) electron transfer.

The fluorescence lifetimes of N-methylcarbazole in the presence of quenchers with different concentrations have been measured. The plots of τ_0/τ vs $[Q]$ are also predicted to yield a straight line of slope equal to $K_q\tau_0$ and intercept equal to 1. The K_q values obtained from τ_0/τ are consistent with those from I_0/I. This implies that the fluorescence quenching of sensitizer by quencher is a dynamic process, i.e. there is no interaction in ground states between fluoromophore and its quencher.

The efficiencies of fluorescence quenching of carbazole unit (electron donor D) by norbornadiene unit (electron acceptor A) in P_{1-2} and P_3 were 79·4% and 98·8% respectively. The electron transfer rate constants K_{et} in P_{1-2} and P_3 calculated from the following equation were $2·60 \times 10^8\,s^{-1}$ and $5·56 \times 10^9\,s^{-1}$ respectively,

$$K_{et} = 1/\tau - 1/\tau_0$$

where, τ_0 (14·8 ns) is the lifetime of the model compound (N-methylcarbazole) in which no electron transfer occurs, and τ is the lifetime of carbazole chromophore in

Table 1. Quenching rate constants k_q

	$k_q \times 10^{-10}\,(1\,mol^{-1}\,s^{-1})$	
	From I_0/I	From τ_0/τ
Ia	2·40	2·30
IIa	4·00	
IIIa	1·30	1·20
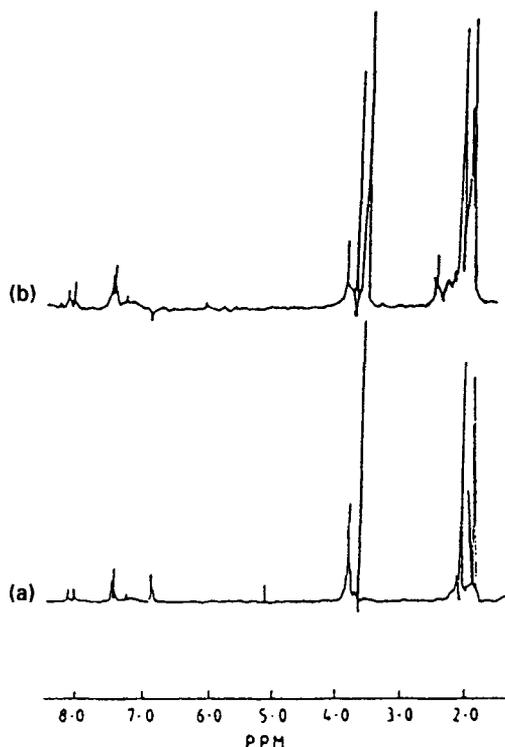
Figure 3. ^{1}HNMR spectra (80 MHz) of CH_3Cz (7×10^{-3} M) and IIIa (2×10^{-2} M) in acetonitrile-d_3 (a) before irradiation and (b) during irradiation.

P_{1-2} (3·05 ns) or P_3 (0·18 ns) where photoinduced electron transfer takes place. The fluorescence quenching efficiency, the electron transfer rate constant and the photoisomerization quantum yield of P_3 are all greater than those of P_{1-2}. Therefore, it can be deduced that the isomerization is through an electron transfer reaction and it is more favourable in the polymer with covalently bonded *D-A* as pendants (P_3) than in that with separate *D* and *A* as pendants (P_{1-2})

3.2b *Chemically induced dynamic nuclear polarization experiments*

The CIDNP method has proved to be a valuable tool for the investigation of photoinduced isomerizations that proceed via electron transfer and radical-ion intermediates.

The solution of IIIa (2×10^{-2} M in CD_3CN) was irradiated in the probe of a ^{1}HNMR spectrometer in the presence of N-methylcarbazole (7×10^{-3} M). A characteristic CIDNP signal was observed. Olefinic protons of norbornadiene (IIIa) were observed in emission. The corresponding protons of the quadricyclane isomer exhibited a complementary polarization, namely enhanced absorption (figure 3).

No nuclear polarization could be detected for the protons of either IIIa or IIIb or for the protons of N-methylcarbazole. Irradiation of IIIa in the absence of N-methylcarbazole resulted in slow photoisomerization but no CIDNP was observed. Photolysis in the presence of typical triplet photosensitizers (such as benzophenone) brought about efficient isomerization, but no nuclear polarization was observed.

The results of CIDNP experiments are consistent with the existence of intermediates of radical-ion pairs and a triplet recombination mechanism. According to the well-known Kaptein rules [13]

$$\Gamma \text{ (net polarization)} = \mu\varepsilon\Delta g^a H = + A \text{ (enhanced absorption)}$$
$$= - E \text{ (emission)}.$$

The net polarization effect depends on four parameters: the initial spin multiplicity μ of the radical pair, the mode ε of product formation, the sign of the difference Δg between isotropic factors of the individual radicals and the sign of the hyperfine coupling constant (HPC) $^a H$ for the magnetic nucleus under observation.

In our reactions, all products are expected to be formed within the cage ($\varepsilon > 0$). The factors for the hydrocarbon radical cations are to be smaller than the value for norbornadiene anion which bears electron-withdrawing substitutes ($\Delta g > 0$). The signs for the proton HPC of the radical anion of norbornadiene are not known, but all seem to have the same signs and must therefore be positive ($^a H > 0$) [14]. Thus $\mu < 0$ implies singlet radical-ion pair recombination which favours norbornadiene; $\mu > 0$ implies triplet radical-ion pair recombination which favours quadricyclane.

3.2c   *Thermodynamic discussion*

The free-energy change involved in an electron transfer process can be calculated by the Relm–Weller equation [15]

$$\Delta G = 23 \cdot 06 [E(D/D^+) - E(A^-/A) - e_0^2/\varepsilon r - \Delta E_{0,0}].$$

Table 2 indicates the redox potentials and excitation energies for N-methylcarbazole and its quenchers, ΔG values and the radical-ion pair energies for carbazole-norbornadiene ($S^+ - N^-$). The all negative ΔG values suggest the electron transfers from the N-methyl-carbazole to norbornadienes are exothermic or efficient. Energetic parameters show that the radical-ion pair energies are all higher than that of N-methylcarbazole. Thus, norbornadiene triplet could only be directly formed via recombination of radical ion pairs.

From fluorescence quenching, CIDNP experiment and thermodynamic discussion, the mechanism of valence isomerization for P_{1-2} and P_3 can be deduced to be as follows (N denotes norbornadiene pendants and S denotes carbazole pendants),
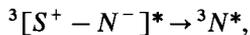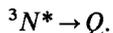
(a) electron transfer

$$^1 S^* + N \rightarrow {}^1 [S^+ - N^-]^*,$$
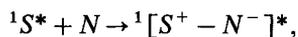
(b) intersystem crossing

$$^1 [S^+ - N^-]^* \rightarrow {}^3 [S^+ - N^-]^*,$$
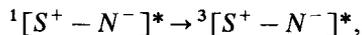
(c) recombination

$$^3 [S^+ - N^-]^* \rightarrow {}^3 N^*,$$

(d) valence isomerization

$$^3 N^* \rightarrow Q.$$

3.3   *Four-wave mixing measurements in PVK:TNF:DCVDEA film*

In PVK:TNF:DCVDEA film, PVK is a well-known charge transporting polymer which provides the host matrix for the PR polymeric mixtures. TNF is a long

Table 2. Redox potentials, excitation energies, ΔG values and ion pair energy

	$E(D - D^+)(V)$	$E(A^- - A)(V)$	E_s (kcal mol⁻¹)	E_T (kcal mol⁻¹)	ΔG (kcal mol⁻¹)	$G(S^+ \cdots N^-)^a$ (kcal mol⁻¹)
CH₃Cz	1·10	—	83·2	71·5	—	—
Ia	—	−1·40	—	53	−26·98	56·3
IIa	—	−1·25	—	53	−30·44	52·8
IIIa	—	−1·67	—	53	−20·75	62·5

[a] Ion pair energies were calculated from $G = 23·06[E(D - D^+) - E(A^- - A)] - e^2/a\varepsilon$.
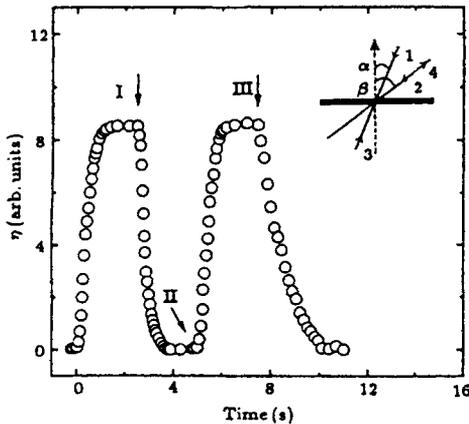
Figure 4. Dynamics of grating formation and decay. The total intensity of the two writing beams is $170\,mW\,cm^2$. The electric field applied on the sample is $19\,V/\mu m$. The writing beams are turned on at $t = 0$. Points I and II correspond, respectively, to the moments when one writing beam is turned off and turned on. Point III corresponds to the moment when the electric field is removed. Inset: experimental geometry.

wavelength photosensitizer [16]. The charge-transfer complex formed by PVK and TNF is known to have good photosensitivity and high efficiency for photocarrier generation in the visible region [17]. When this CT complex absorbs photons, electron transfer takes place at once and results in the formation of carbazole cation-TNF anion pairs. If an external electric field is applied at this moment, the transportation of hole along PVK chain begins immediately and as a result, a space charge field is built in material. In the polymer composite, DCVDEA is a nonlinear chromophore which establishes a linear electro-optic response to the polymer after poling. Thus, our polymer possesses the three indispensable properties required for PR effect as described above.

Typical experimental results about the grating formation and decay dynamics of our polymer are presented in figure 4. Two important points can be easily noticed. First, the growth as well as erasure (by a single writing beam) of the grating are fast and, in the case of erasure, complete. This means that there is no permanent grating formed in the polymer and the polymer has a fast response as will be discussed later. Second, the grating quickly decays and then disappears when the electric field is removed. This clearly demonstrates that the grating formed in the polymer is a photorefractive grating rather than a photoisomerization one or even other types of gratings that often exist in polymers. In our experiments, we have observed that in the absence of electric field, there is no diffracted signal and thus no grating formed in the polymer. The quick decay of the photorefractive grating after removing the electric field is due to the low glass-transition temperature of the polymer. That is to say, the poled polymer quickly loses its electro-optic property after the removal of electric field due to the relaxation of orientational alignment of the nonlinear optical chromophores.

In a PR polymer, the electric field plays three important roles [3,18]: (a) orienting the nonlinear optical chromophores; (b) aiding the photoexcited charge carrier generation and polymer; (c) facilitating the transport of charge carriers. Thus, the photorefractivity of a polymer should be a sensitive function of the electric field. This is indeed what we
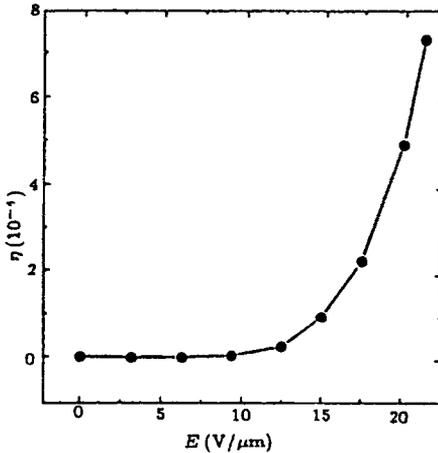
Figure 5. FWM diffraction efficiency η of the polymer as a function of the electric field E. The thickness of the polymer is about 80 μm.
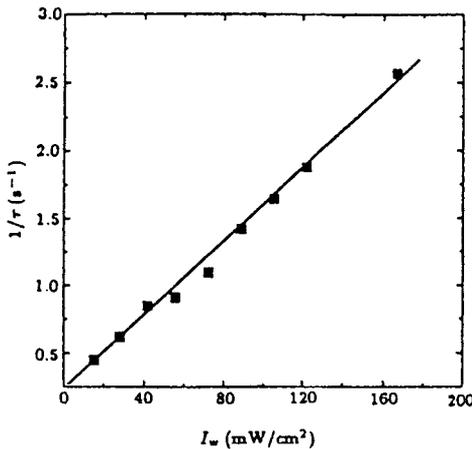

Figure 6. Response time of the polymer as a function of total writing intensity I_W. The electric field used is 19 V/μm.

have observed in our polymers. The FWM diffraction efficiency η of our polymer as a function of electric field E is shown in figure 5. It can be seen that η increases quickly with the increase of E. The largest value we obtained is $7 \cdot 4 \times 10^{-4}$, corresponding to an electric field of 21V/μm which is the highest that we can apply to the sample.

In the single-charge-carrier model for photorefractivity, the growth of η can be described by $\eta \propto [1 - \exp(-t/\tau)]^2$, where τ corresponds to the photorefractive response time of the polymer [18]. By using this expression, τ of our polymer has been determined at different writing intensities. One typical result is shown in figure 6, which shows that $1/\tau$ is linearly proportional to the total writing intensity I_W. The shortest response time that we experimentally obtained at our largest available writing intensity (170 mW/cm^2) is 400 ms. By using extrapolation, we can estimate that our polymer should have a response time of about 70 ms at 1W/cm^2, noting that the shortest

response time reported so far in a photorefractive polymer is 39 ms obtained at 1 W/cm². This means that the speed of response of our polymer is comparable to that of the fastest polymer presently available.

4. Conclusion

(1) Photosensitized valence isomerization of norbornadiene pendants in P_3 and P_{1-2} were carried out by irradiation with the light above the wavelength of 350 nm and a mechanism involving photoinduced electron transfer was proposed by way of fluorescence quenching, CIDNP and thermodynamic discussion.

(2) Photorefractive properties of PVK:TNF:DCVDEA film were characterized by FWM experiment and a fast photorefractive response time as short as 400 ms was observed at a writing intensity of 0·17 W/cm². Furthermore, the important effect of the charge transfer in ground state and electron transfer in excited state between PVK and TNF were also illustrated as an example of applications of photoinduced electron transfer in photoelectronic devices.

Acknowledgement

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