Photoinduced absorption and photoinduced reflectance in conducting polymer/methanofullerene films: Nonlinear-optical changes in the complex index of refraction

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We report photoinduced absorption (PIA) and photoinduced reflectance (PIR) spectra of poly(3-octyl thiophene)/methanofullerene films. As a result of the efficient photoinduced intermolecular charge transfer, the PIA and PIR spectra of the composite films are significantly enhanced in magnitude over those in either of the component materials. From the PIA and PIR spectra, the corresponding changes in the complex refractive index $\Delta N = \Delta n(\omega) + i\Delta\kappa(\omega)$ are obtained. The results indicate that the PIA spectra are dominated by $\Delta\kappa(\omega)$; the subgap electronic absorptions peak at approximately 0.1 and 1.6 eV. The PIR spectra are dominated mainly by $\Delta n(\omega)$, which exhibits a derivative spectral shape with zero crossing at 0.1 eV. The implications of these photoinduced changes in the index resulting from photoexcitations are discussed in terms of potential optoelectronic and nonlinear-optical applications of these materials. [S0163-1829(96)05439-2]

I. INTRODUCTION

The recent discovery of photoinduced charge transfer in composites of conjugated polymers and fullerenes (C_{60}) has attracted considerable interest.[1] Time-resolved measurements revealed that the photoinduced charge transfer is ultrafast (within 300 fs), with a quantum efficiency approaching unity. Although reversible, the charge-transferred state is metastable with the back-charge-transfer rate many orders of magnitude slower than the forward-charge-transfer rate.[1–3] Because of the high quantum efficiency and the metastability of photoinduced charge separation, the photoinduced charge-transfer mechanism could be a route to high-performance nonlinear optical (NLO) materials. Indeed, nonlinear absorption and optical limiting have been demonstrated.[4]

The mechanism responsible for the NLO response in the conjugated polymer/C_{60} blends is inherently different from that of conventional NLO materials.[3,4] The nonlinear response arises from efficient photoinduced charge transfer from conjugated polymers onto C_{60} followed by absorption from the charge-separated excited state, thereby leading to an enhanced density of photocarriers and to creation of additional excitation channels with high absorption cross sections. The retarded back electron transfer, arising from the metastability of the charge-transferred state, causes the excited-state absorption to persist to a longer time scale (even on the order of milliseconds).[5] Thus measurements of the photoexcitation spectral profile (the photoinduced absorption) over a wide range of time scales are of fundamental importance. A deeper understanding of the photophysical phenomena requires detailed studies of steady-state photoexcitation spectra to determine the corresponding changes in the frequency dependence of the complex index of refraction, $\Delta N = \Delta n(\omega) + i\Delta\kappa(\omega)$, where $n(\omega)$ and $\kappa(\omega)$ are the real and imaginary parts of the index, and $\Delta n(\omega)$ and $\Delta\kappa(\omega)$ are the corresponding photoinduced changes. The $\Delta n(\omega)$ and $\Delta\kappa(\omega)$ data provide information on the location of spectral windows appropriate for optoelectronic and NLO applications of these materials.

We have utilized steady-state infrared (IR) photoexcitation methods to measure the photoinduced absorption (PIA) and photoinduced reflectance (PIR) spectra of composite films of poly(3-octyl thiophene), P3OT, mixed with methanofullerene. The data allow direct evaluation of the corresponding changes in $\Delta n(\omega)$ and $\Delta\kappa(\omega)$. As a result of the efficient photoinduced intermolecular charge transfer, the magnitudes of $\Delta n(\omega)$ and $\Delta\kappa(\omega)$ are significantly enhanced over those in either of the component materials, with Δn and $\Delta\kappa \approx 10^{-2}$ in the IR (0.01–0.5 eV) at a laser pump intensity of only 50 mW/cm^2. Moreover, the photoinduced absorption shows features at 1.2 and 1.6 eV, both of which are associated with excited-state absorptions of the methanofullerene anion. The measured $\Delta n(\omega)$ and $\Delta\kappa(\omega)$ imply that conducting polymer/methanofullerene films are promising as high-performance nonlinear optical materials.

II. EXPERIMENTAL DETAILS

Reflectance (and photoinduced reflectance) measurements in the IR require films with sufficient thickness that transmission and/or reflectance from the back surface are negligible. In addition, optical quality surfaces are necessary. However, because of the tendency for C_{60} to phase separate and crystallize, it is difficult to process the conducting polymer–C_{60} composite into thick free-standing films. This limited processibility has been overcome by use of the recently developed methanofullerenes: i.e., soluble functionalized C_{60} derivatives.[6] Utilizing phenyl-C_{61}-butyric acid cholesteryl ester, denoted hereafter as (6,6)PCBCR, we obtained homogeneous, stable films with good optical quality containing 1:1 by weight methanofullerenes (approximately one acceptor for every five repeat units of P3OT). In addition solid films of pure (6,6)PCBCR and pure P3OT were prepared for comparative studies. Each material was dissolved in xylene. Films of proper thickness (6–7 μm) were cast from filtered solution onto proper IR substrates as described in previous publications.[5]

A comprehensive characterization of the composite films

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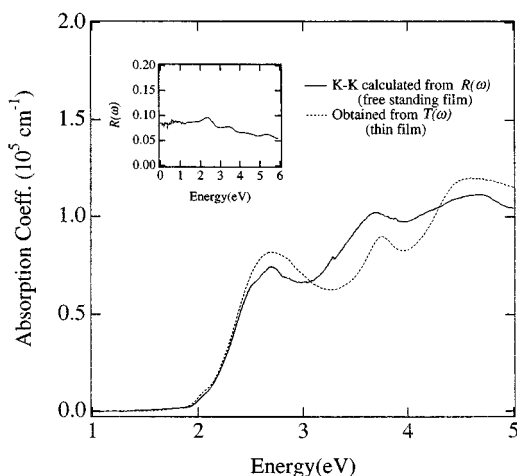
FIG. 1. Linear absorption spectrum of P3OT-(6,6)PCBCR composite film (solid line) obtained from KK analysis of $R(\omega)$. The absorption spectrum is compared with that obtained from transmittance through a spin-coated thin film (dashed line). The inset shows the $R(\omega)$ of composite film up to 6 eV.
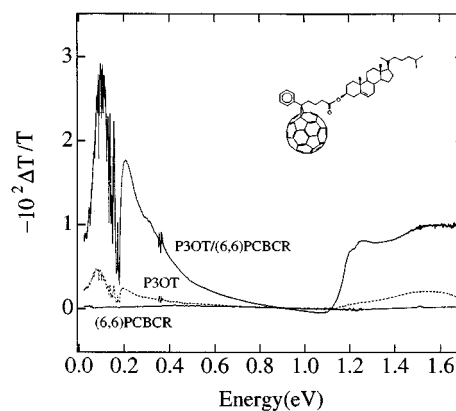

FIG. 2. PIA spectra of P3OT (dashed line) and P3OT/(6,6)PCBCR composite (solid line) films from 0.01 to 1.7 eV at 50 K obtained by pumping with an Ar^+ laser at 2.41 eV (514 nm) with 50 mW/cm^2. The PIA spectrum of a pure (6,6)PCBCR film is shown under the same experimental conditions. The molecular structure of (6,6)PCBCR is shown in the inset.

in the ground state was carried out through linear transmission (T) and reflectance (R) measurements over the wide spectral range from 0.01 to 6 eV. Because of the high optical density of the thick films, absorption spectra $\alpha(\omega)$ above 2 eV (a π-π^* gap of P3OT) cannot be obtained from transmission measurements. Therefore, $\alpha(\omega)$ of the composite films were determined from the Kramers-Kronig (KK) analysis of the reflectance spectra; details are described elsewhere.[7]

Photoinduced absorption (PIA) spectra were obtained by measuring spectral changes (ΔT) in the IR transmission between 0.01 and 1.7 eV in response to the external pumping source (2.41-eV line of an Ar^+-ion laser) incident on the sample. Photoinduced reflectance (PIR) spectra were determined by measuring the change in specular reflectance (ΔR) at near-normal incidence ($\approx 10°$) for incident photon energies from 0.05 to 0.5 eV. Identical laser pumping conditions were used for PIA and PIR measurements. A Nicolet Magna 750 Fourier transform infrared system was used for all measurements; ΔT (or ΔR) was measured by recording spectra for 10-s intervals with the excitation source on and then with the sample in the dark. By taking ratios, one obtains $-\Delta T/T$ (or $\Delta R/R$). All measurements were carried out with samples at 50 K in vacuum (10^{-6} Torr).

III. RESULTS AND DISCUSSION

Figure 1 shows the linear absorption spectrum of a composite film evaluated from the KK analysis of the reflectance spectrum (0.01–6 eV) shown in the inset. The absorption spectrum is compared with that obtained from a thin spin-cast film of the same composition; for the thin film, $\alpha(\omega)$ was determined directly by transmission measurements alone. The spectra are in satisfactory agreement, demonstrating the validity of characterization of films by reflectance measurements. The π-π^* absorption of P3OT is clearly observed with a peak at 2.6 eV along with the first dipole-allowed transition in (6,6)PCBCR at 3.75 eV. Consistent with previous studies,[5] the spectrum is a simple superposition of the two components without any indication of either a charge-

transfer band or states below the π-π^* gap (≤ 2 eV).

The PIA spectrum of a P3OT/(6,6)PCBCR composite is shown in Fig. 2, together with those of pure P3OT and (6,6)PCBCR films, in the energy range from 0.01 to 1.7 eV (photoexcitation with the 2.41-eV line of an Ar^+-ion laser at 50 mW/cm^2). The molecular structure of (6,6)PCBCR is also shown in Fig. 2.

Consistent with previous results using C_{60},[5] the PIA spectrum of the P3OT/methanofullerene film has two subgap electronic absorptions; a lower-energy feature [superposed on the enhanced IR-active vibrational (IRAV) modes] with a peak around 0.1 eV and a higher-energy feature which onsets at approximately 1.1 eV. The PIA is significantly enhanced in magnitude over that in either of the component materials.

In previous studies, the spectral signature associated with a C_{60} anion was observed as a prominent peak at 1.15 eV. The 1.15-eV absorption was assigned to the allowed highest-occupied-molecular-orbital–lowest-unoccupied-molecular-orbital [HOMO(T_{1u})-LUMO(T_{1g})] transitions of C_{60}^-. The corresponding absorption of the methanofullerene anion is observed as the relatively strong shoulder at 1.2 eV.

The photoinduced changes in the reflectance ($\Delta R/R$) of P3OT and P3OT/(6,6)PCBCR composite films are shown in Fig. 3 for the spectral range between 0.08 and 0.5 eV. The laser pumping conditions were identical to those used for the PIA measurements. The PIR signal of the P3OT-methanofullerene film is negative (decreased reflectance) above 0.11 eV, with a minimum around 0.15 eV. There is a zero crossing at 0.11 eV, with $\Delta R/R$ positive and increasing with decreasing frequency. As in the PIA spectra, the PIR spectra exhibit spectral features associated with the IRAV modes between 0.1 and 0.2 eV. The magnitude of the photoinduced reflectance of the composite film is significantly enhanced over that of the pure P3OT film, consistent with the PIA measurements.

The subgap spectral response resulting from photoexcitation (both PIA and PIR) arises from self-localized charged excitations typical of conjugated polymer systems. In conjugated polymers with a quasi-one-dimensional electronic structure, the dominant elementary excitations are strongly
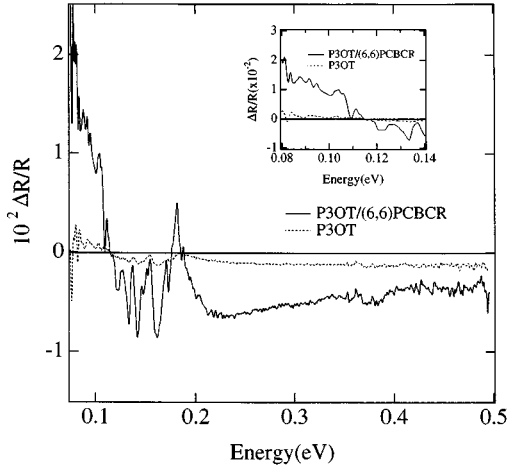
FIG. 3. PIR spectra of P3OT (dashed line) and P3OT/
(6,6)PCBCR composite (solid line) films in the IR range from 0.08
to 0.5 eV at 50 K with a laser pump intensity 50 mW/cm^2 at 2.41
eV. The inset shows details below 0.14 eV.

coupled to the molecular structure, creating local chain distortions around charge carriers.[8] As a result, the symmetrical (Raman-active) modes become IRAV modes, and electronic states are self-localized and split off into the energy gap, leading to photoinduced electronic absorption at photon energies less than the energy gap.[8]

The large increase in oscillator strength of the photoinduced signals and the appearance of the 1.2-eV feature associated with the (6,6)PCBCR anion in the composite film unambiguously prove the existence of photoinduced charge transfer from P3OT onto (6,6)PCBCR. The increase in oscillator strength arises from a combination of enhanced quantum efficiency for photogeneration of charge carriers and extended lifetime of excited states.

In principle, determining both PIA and PIR spectra enables one to obtain the corresponding changes in the real and imaginary components of the index of refraction, $\Delta n(\omega)$ and $\Delta\kappa(\omega)$, without any additional calculation (such as KK analysis). The modulated transmittance of a film (thickness d) can be expressed as[9]

$$\frac{-\Delta T}{T} = \left[\frac{2R}{(1-R)}\right]\left(\frac{\Delta R}{R}\right) + \frac{2d\omega\Delta\kappa}{c}. \quad (1)$$

Using Fresnel's equation for reflectance at normal incidence, the modulated reflectance can be expressed in terms of Δn and $\Delta\kappa$ as[10]

$$\frac{\Delta R}{R} = A(n,k)\Delta n + B(n,k)\Delta k, \quad (2)$$

where the $A(n,k)$ and $B(n,k)$ coefficients are functions of n and κ:

$$A(n,\kappa) = 4(n^2 - \kappa^2 - 1)/\{[(n+1)^2 + \kappa^2][(n-1)^2 + \kappa^2]\}, \quad (3a)$$

$$B(n,\kappa) = 8n\kappa/\{[(n+1)^2 + \kappa^2][(n-1)^2 + \kappa^2]\}. \quad (3b)$$

Therefore, Eqs. (1) and (2) allow direct evaluation of Δn and $\Delta\kappa$ from the PIA and PIR spectra, using $n(\omega)$ and $\kappa(\omega)$ as obtained from the linear spectra.
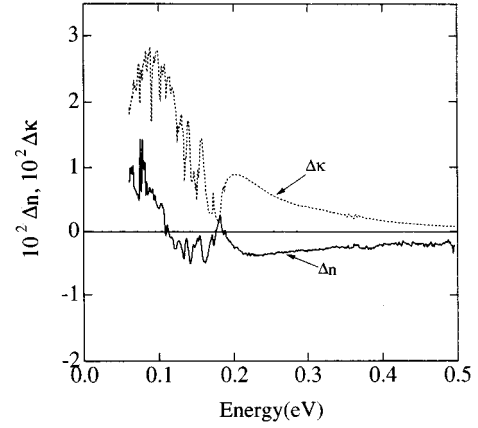

FIG. 4. Photoinduced changes of the components of the refractive index $\Delta n(\omega)$ (solid line) and $\Delta\kappa(\omega)$ (dashed line), for P3OT/ (6,6)PCBCR composite film as obtained directly from the PIA (Fig. 2) and PIR (Fig. 3) spectra through Eqs. (1) and (2).

Since R is quite small in the IR range ($R \approx 0.08$; see Fig. 1) for the semiconducting samples used in the PIA and PIR measurements, the PIA spectra are dominated by the absorption contribution (second term) rather than reflectance contribution (first term) in the Eq. (1). Thus Eq. (1) can be approximated as $-\Delta T/T \approx 2d\omega\,\Delta\kappa/c$. Also, in semiconducting materials with no contribution from free carriers in the ground state, the magnitude of n is much larger than that of κ in the IR (for the P3OT/methanofullerene film, $n \approx 1.8$, while $\kappa \approx 0.018$ for $\hbar\omega < 2$ eV), so that $A(n,k) \gg B(n,k)$. Thus the PIR response is dominated by Δn rather than $\Delta\kappa$, i.e., opposite to the PIA which is dominated by $\Delta\kappa$.

Figure 4 shows Δn and $\Delta\kappa$ obtained from the PIA and PIR spectra through Eqs. (1) and (2). As expected, the spectral response of $\Delta\kappa$ resembles the PIA spectrum, remaining positive over the energy range below 0.5 eV with a peak at 0.1 eV; whereas Δn has a derivativelike spectral shape with a zero crossing at 0.1 eV, similar to the PIR spectrum.

In general, $\Delta n(\omega)$ and $\Delta\kappa(\omega)$ are connected through the KK relation[10]

$$\Delta n(\omega) = \frac{2}{\pi}\int_0^\infty \frac{\omega'\Delta k(\omega')}{\omega^2 - \omega'^2}\,d\omega'. \quad (4)$$

Qualitatively, the spectral shapes of Δn and $\Delta\kappa$ are consistent with Eq. (4): $\Delta\kappa$ exhibits a resonance at $\omega_0 \approx 0.1$ eV, while Δn has a derivativelike shape in the vicinity of $\omega_0 = 0.1$ eV. To check the self-consistency of the data, we compared Δn measured directly by the PIR and PIA spectra with Δn_{KK} obtained from the KK transformation of $\Delta\kappa$ as obtained only from the PIA spectrum (0.01–1.7 eV) using $-\Delta T/T \approx 2d\omega\Delta\kappa/c$. In the KK calculation, the PIA spectrum above 1.7 eV was approximated using photomodulation spectroscopic results (0.6–2.5 eV) on the same sample. The two spectra are in good agreement, demonstrating explicitly that Δn and $\Delta\kappa$ are KK consistent. Even the details of the IRAV features at energies between 0.1 and 0.2 eV are consistent for Δn and Δn_{KK}.

The measured $\Delta\kappa$ and the KK calculated Δn_{KK} are shown in Fig. 5 through the near IR up to 1.7 eV. The spectral features in $\Delta\kappa$ are associated with the high-energy subgap
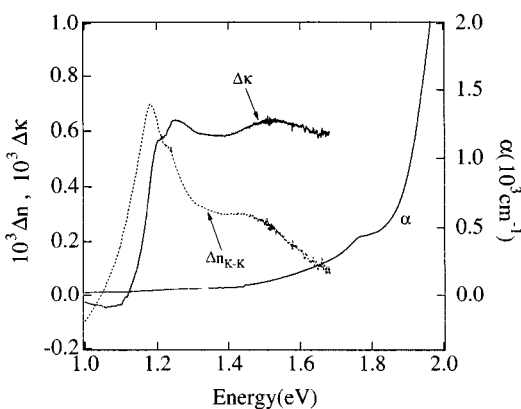
FIG. 5. Photoinduced $\Delta\kappa(\omega)$ (solid line) determined from the PIA spectrum of the composite film and the corresponding Δn_{KK} (dashed line) obtained by the KK transformation of the $\Delta\kappa(\omega)$ in the near IR are shown together with the linear $\alpha(\omega)$ of a composite film (right vertical axis).

electronic absorption of P3OT superimposed on the excited-state absorptions of the methanofullerene (the 1.2 and 1.6 eV features), consistent with the quantum-chemical calculations.[11]

The data in Fig. 5 imply that the energy range 1.1 eV$<\hbar\omega$ $<$1.2 eV will be a good spectral window for optoelectronic and NLO applications using P3OT-methanofullerene composites: Δn is large, $\Delta\kappa$ is small, and $\hbar\omega$ is less than the energy gap, so that there is reasonable transparency (T $>$80%). On the other hand, when nonlinear absorption is important, such as in optical limiting or photochromic gratings, the energy range around 1.6 eV (760 nm) is attractive because $\Delta\kappa$ is large, and Δn is small.

As inferred from third-harmonic-generation (THG) measurements on this system,[4] the THG spectra for P3OT and the composite films are essentially identical. Thus the photo-induced changes in the complex index do not arise from the third-order nonlinear optical susceptibility $\chi^{(3)}$. This conclusion is confirmed by the pump intensity (I) dependence of the photoinduced signals; we find an $I^{1/2}$ intensity dependence of the PIA signal over a wide range of intensities from 5 to 300 mW/cm^2, implying bimolecular recombination of the photoexcitations,[8] in contrast with a $\chi^{(3)}$ effect where a linear dependence on pump intensity would be expected.[12] In the P3OT/methanofullerene system, the NLO response is a consequence of efficient photoinduced charge transfer from the conjugated polymer onto the methanofullerene, followed by absorption in the charge-separated excited state.

Access to the long-lived excited state opens additional excited-state absorption channels which yield features at 1.2

and 1.6 eV. This is consistent with the resonantly enhanced nonlinear absorption at 1.63 eV (760 nm) reported by Cha *et al.*,[4] and observed in picosecond time-resolved measurements on this system.[2] The nonlinear absorption[4] is consistent with the results reported here. As shown in Fig. 5, $\Delta\kappa$ [$=c\Delta\alpha/(2\omega)$] is relatively large in the near IR while, for $\hbar\omega<1.7$ eV, the linear absorption remains sufficiently small to enable good transparency but large enough to initiate photoexcitation. Thus the spectral range from 1.2 to 1.7 eV is a promising energy range for optical limiting, as demonstrated by Cha *et al.*[4]

IV. SUMMARY AND CONCLUSION

In summary, photoinduced absorption and photoinduced reflectance spectra were obtained for P3OT/methanofullerene composite films in the IR. The data enable direct evaluation of the corresponding changes in the components of the complex refractive index, $\Delta n(\omega)$ and $\Delta\kappa(\omega)$. As a result of efficient photoinduced charge transfer and charge separation, the magnitude of index changes which result from photoexcitation are significantly enhanced, and additional absorption features associated with the methanofullerene anion are observed. The results are consistent with the nonlinear absorption and optical limiting observed in the same system, and they provide insight into the charge-transfer approach to enhanced optical limiting.[4] Generalization of the photoinduced absorption and photoinduced reflectance measurements to other charge-transfer systems can serve as an efficient method of determining spectral windows of potential interest for nonlinear absorption and for photoinduced changes in the real part of the index.

As a result of the efficient photoinduced intermolecular charge transfer, the magnitudes of $\Delta n(\omega)$ and $\Delta\kappa(\omega)$ are significantly enhanced in the P3OT/methanofullerene composites, with Δn and $\Delta\kappa\approx10^{-2}$ in the far IR at a laser pump intensity of only 50 mW/cm^2. With the much higher pumping powers available from pulsed lasers, Δn and $\Delta\kappa\gg1$ should be achievable in the far IR and perhaps even in the millimeter wave regime. Thus, the P3OT/methanofullerene composites offer potential as fast, optically driven ''switches'' for far-IR radiation.

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