Photoexcitation spectroscopy of conducting-polymer–C_{60} composites: Photoinduced electron transfer

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We present a comparative study of the steady-state photoinduced absorption and photoinduced electron-spin-resonance (ESR) spectra of conducting polymers mixed with the fullerene C_{60}. For conjugated polymers with nondegenerate ground states as donors, electron transfer takes place prior to either radiative or nonradiative recombination of π-electron photoexcitations on the conducting polymer. In the case of a conjugated polymer with a degenerate ground state as donor, the structural relaxation associated with the formation of charged solitons is faster; and no indications of photoinduced charge transfer are observed. Thus, composites using a derivative of poly(1,6-heptadyene) as donor do not exhibit long-lived charge separation, whereas charge transfer and charge separation are observed in composites using poly(p-phenylene vinylene) or polythiophene derivatives as donors. The relaxation (as a function of temperature) of the charge separated state is studied through photoinduced absorption spectroscopy (excitation spectroscopy) and photoinduced ESR. The results are discussed in terms of designing suitable donor-acceptor pairs for photoinduced electron transfer using conducting polymers and C_{60} as donor and acceptor, respectively.

I. INTRODUCTION

Recently, we reported the discovery of photoinduced electron transfer from the conducting polymer, poly[2-methoxy, 5-(2'-ethyl-hexyloxy)-p-phenylene vinylene], hereafter referred to as MEH-PPV, onto C_{60}.[1,2] The excellent acceptor properties[3] of C_{60} together with π-electron delocalization on the conjugated polymer were proposed to stabilize the photoinduced charge separated state.[1] This molecular level photoinduced electron transfer was subsequently utilized to fabricate conducting polymer (as donor-type semiconductor)-C_{60} (as acceptor-type semiconductor) heterojunction diodes, photodiodes, and solar cells.[4]

The discovery of conducting polymers and the ability to dope these polymers over the full range from insulator to metal has resulted in the creation of a class of materials that combines the electronic and optical properties of semiconductors and metals with the attractive mechanical properties and processing advantages of polymers.[5–8] Moreover, the ability to control the energy gap and electronegativity through molecular engineering has enabled the synthesis of conducting polymers with a range of ionization potentials and electron affinities.[9,10] Considering the breadth of opportunity associated with this class of materials, it is important to establish the generality of the photoinduced charge-transfer process from conjugated polymers to C_{60}.

Given a neutral donor-acceptor couple (i.e., a pair for which there is little or no mixing of the wave functions in the ground state), the question of whether or not charge transfer occurs depends on the energetics of the photoexcited state; electron transfer cannot occur unless $I_{D^*} - A_A - U_C < 0$, where I_{D^*} is the ionization potential of the excited state (D^*) of the donor, A_A is the electron affinity of the acceptor, and U_C is the Coulomb energy of the separated radicals (including polarization effects). Even in the case where this inequality is satisfied, however, photoinduced electron transfer can be "short-circuited" by a faster competitive process.

The phenomena associated with nonlinear excitations (solitons, polarons, and bipolarons) characteristic of these quasi-one-dimensional solids in which the electronic structure is strongly coupled to the lattice have been a focal point of interest in the physics of conducting polymers.[5–7,11] In conjugated polymers with a degenerate ground state, solitons are the lowest-energy charge storage configurations. The photogeneration of solitons has been studied in detail in polyacetylene;[6] transient spectroscopy measurements have demonstrated that soliton formation occurs at times less than 10^{-13} s following photoabsorption, in agreement with the predictions of Su and Schrieffer.[12] When the ground-state degeneracy is lifted, the solitons are confined, and the nonlinear excitations are polarons and/or bipolarons.[5–7,11] Thus, quite generally in conducting polymers, photoexcitation is rapidly (at times less than 10^{-13} s) followed by structural relaxation due to the electron-phonon coupling, thereby creating energy states within the π-π^* gap.

It is of interest to establish whether structural relaxation following photoexcitation of the conducting polymer donor can compete with and possibly prevent the photoinduced electron transfer to C_{60}. The structural relaxation in *trans*-polyacetylene is very large in magnitude (a bond-alternation reversal over a length of about fifteen carbon atoms) with excitations stabilized deep in the energy gap. The photoluminescence of *trans*-polyacetylene is completely quenched by the more rapid nonradiative recombination channel associated with soliton formation. MEH-PPV, on the other hand, exhibits high quantum

efficiency photoluminescence with a small Stokes shift, thereby demonstrating that the effects of structural relaxation are small compared to those in *trans*-polyacetylene (where the ground state is degenerate). Thus, the possible sensitivity of the photoinduced electron-transfer process (from D^* to A) to the excited state dynamics of the conducting polymer (as D) is an important issue. Does electron transfer occur even faster than soliton formation, or will the nonradiative recombination channel associated with soliton formation quench the electron transfer?

In this paper, we report the results of near steady-state photoinduced absorption (PIA) spectroscopy and steady-state light-induced electron-spin resonance (LESR) studies on conducting polymer-C_{60} composites using a series of conducting polymers as the donor; the molecular structures of the conducting polymers included in this study are displayed in Fig. 1. In each case, we have investigated the conducting polymer alone and in composites with C_{60}. The relaxation of the charge separated state, the temperature dependence of the relaxation, and the dependence on this excitation energy and intensity have been characterized. The results show the existence of long-lived charge separated configurations in composites of C_{60} with MEH-PPV and with poly(3-octylthiophene) (P3OT), whereas in composites of C_{60} with the degenerate ground-state soluble derivative of poly(1,6 heptadiene) (PHDK), no indication of charge transfer was observed. In the case of (MEH-PPV)/C_{60}

FIG. 1. Molecular structures of the conducting polymers investigated in this study.

and PHDK/C_{60} composites there was no mixing of the wave functions observable in the ground state. In contrast, P3OT/C_{60} composites showed relatively strong mixing in the absorption spectra, as observed earlier.[13] Complete charge separation upon photoexcitation is demonstrated by the observation of two LESR signals: one with a g value characteristic of positive polarons on the conducting polymer donor and the other with lower g value characteristic of the unpaired spin of C_{60}^-.

II. EXPERIMENT

The synthesis and properties of MEH-PPV have been described in earlier reports.[14] Pristine poly(3-octylthiophene) was obtained from Neste Oy with a mean molecular weight of $M_{av} \approx 9.6 \times 10^5$ and a molecular weight distribution $M_w/M_N \approx 3$, as determined by gel permeation chromatography (GPC). The polymer was dissolved in chloroform and passed through a preparative GPC column (ultrastyragel) in order to reduce the polydispersity of the sample. Fractions were subsequently traced with an aqueous solution of EDTA (disodium salt) and dried over $MgSO_4$. For the photoexcitation studies, fractions with $M_{av} \approx 1.1 \times 10^5$ and $M_w/M_N \approx 1.2$ were used. Films of P3OT were prepared by casting the solutions onto a glass surface and evaporating off the solvent under a nitrogen blanket. The resulting films contained less than 10-ppm iron as determined by ion flame analysis. For specific experiments, P3OT was doped by exposing the film to a $1M$ solution of hydrous $FeCl_3$ in nitromethane.

The diketone derivative of poly(1,6 heptadiene) was polymerized by molybdenum (V) chloride and tetrabutyltin in dioxane under N_2. The polymer was obtained as dark red solids in 71% yield. It is readily soluble in chloroform, dioxane, ethyl acetate, THF, DMF, and acetonitrile. Infrared bands of the polymer in a KBr pellet appear at 1697, 1356, 1022 cm^{-1}. The uv-visible spectrum of the polymer in THF showed the λ_{max} at 532 nm. The number average molecular weight (M_n) determined by GPC with polystyrene standards is between 6960 and 8110.[15]

C_{60} powder was purchased in high purity (99.99%) from Polygon Enterprises, Texas. All samples used in optical experiments were films, either drop cast or spin cast from solutions onto quartz or sapphire substrates. The composite films with C_{60} were obtained by dissolving conducting polymer and C_{60} (1:1 by weight) in toluene or xylene (typically 1% solutions). The composite films are not as uniform as the polymers alone due to segregation of the less soluble C_{60} component. For LESR experiments quartz tubes were filled with solutions and dried under dynamic vacuum before being flame sealed.

Optical spectra were taken using Perkin Elmer Lambda 9 spectrophotometer. Photoexcitation spectra were recorded using a tungsten-halogen white-light source, an argon-ion and dye laser, a monochromator and a two-color Si/PbS detector. For direct absorption, the probe beam was mechanically chopped, and the signal was detected with a lock-in amplifier. Photoinduced changes in the absorption were recorded by chopping the pump
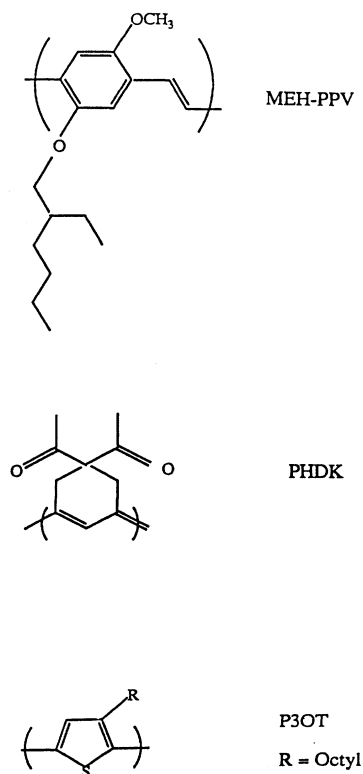
laser (argon-ion) beam and phase sensitively detecting the resulting change in absorption with the lock-in amplifier. The photoinduced absorption $\Delta\alpha$ was then directly calculated from the normalized changes $(-\Delta T/T \approx \Delta\alpha d)$ where d is the film thickness. The instrumental response (source and detector, etc.) is divided out with this method. In order to avoid contamination of the photoinduced signal by light emission from the sample, luminescence was checked in a separate experiment. Unless stated otherwise, all measurements were carried out at 80 K and at pressures on the order of 10^{-5} Torr.

LESR experiments used a BRUKER 200D ESR spectrometer equipped with a variable-temperature cryostat. The sample was illuminated using an optical fiber to bring the output beam from an argon-ion laser into the microwave cavity. Steady-state ESR spectra were recorded with the beam on and off, and compared.

III. RESULTS AND DISCUSSION

A. (MEH-PPV)/C$_{60}$ composites

Figure 2 shows the optical absorption spectrum of an (MEH-PPV)/C$_{60}$ composite film. The π-π^* absorption of MEH-PPV (peak at 2.5 eV) is clearly observed along with the first dipole-allowed transition in C$_{60}$ (at 3.75 eV). The spectrum is a simple superposition of the two components without any indication of states below the π-π^* gap of the conducting polymer due to interaction between the two materials in the ground state. The strong photoluminescence of MEH-PPV, however, is quenched by a factor in excess of 10^3, and the luminescence decay time is reduced from $\tau \approx 550$ ps to $\tau \ll 60$ ps (the instrumental resolution) indicating the existence of a rapid quenching process.[1,16] Assuming that the luminescence is quenched by rapid electron transfer from the polymer to the C$_{60}$, the electron-transfer rate is estimated to be in excess of 10^{12} s^{-1}.[1]

The photoexcitation spectrum of the (MEH-PPV)/C$_{60}$ composite is displayed and compared to that of MEH-PPV alone in Fig. 3. The spectra (with typical magni-
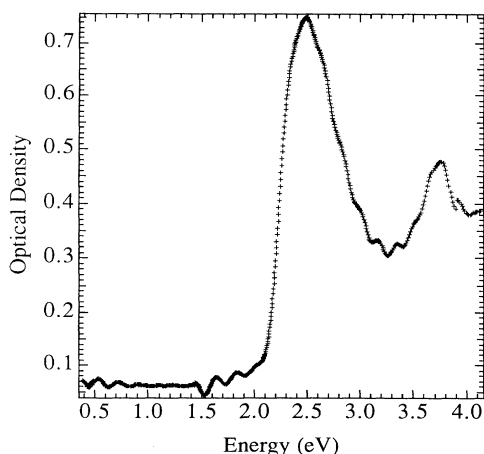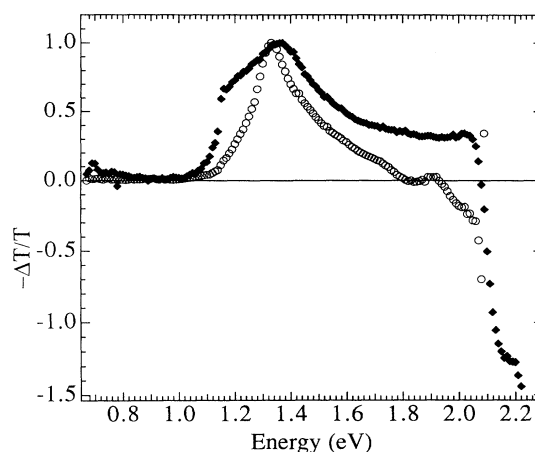

FIG. 3. Photoinduced absorption spectra of MEH-PPV (open circles) and the (MEH-PPV)/C$_{60}$ composite (solid diamonds) at 80 K obtained by pumping with argon-ion laser at 2.41 eV with 50 mW.

tudes of $\Delta T/T \sim 2 \times 10^{-3}$) are normalized to unity for comparison. The PIA of C$_{60}$ is neglected in this comparison because the magnitude is 10^2 times smaller when photoexcited with $\hbar\omega \approx 2.5$ eV as a result of the very low absorption of C$_{60}$ in that energy range. A sharp PIA edge at 1.1 eV and a plateau at 1.6–2.0 eV distinguish the composite PIA from that of MEH-PPV in which there is a single band at 1.35 eV. Bleaching of the MEH-PPV π-π^* absorption at 2.5 eV is observed in both the composite and reference, but the luminescence is quenched only in the composite.

The relaxation behavior of the PIA bands was measured by monitoring the dependence of the PIA band intensities on the chopping frequency. The results are displayed for comparison in Fig. 4. The relaxation of the PIA bands is similar for all PIA bands in the composite. We estimate the lifetime of the charge separated configuration to be of the order of milliseconds at 80 K. The intensity of the PIA bands in Fig. 3 increases with the laser pump intensity as $I^{0.59}$, as shown in Fig. 5. To perform a final check to show that all PIA bands in the composite originate from excitation of the MEH-PPV donor, we determined the excitation profile by recording the PIA spectrum with different excitation energies. The excitation profile displayed in Fig. 6 clearly shows the correlation of all the PIA bands in the composite with the π-π^* excitation of MEH-PPV component.

The photoinduced absorption experiments are consistent with rapid photoinduced charge transfer. Definitive evidence of charge transfer and charge separation is obtained from LESR experiments.[1] Figure 7 shows the ESR signal upon illuminating the (MEH-PPV)/C$_{60}$ composite with light of $\hbar\omega = E_{\pi\text{-}\pi^*}$, where $E_{\pi\text{-}\pi^*}$ is the energy gap of the MEH-PPV component. Two photoinduced ESR signals can be resolved: one at $g = 2.0000$ with full width at half maximum linewidth $\Delta H_{\text{FWHM}} \approx 7.2$ G and the other at $g = 1.9955$ with $\Delta H_{\text{FWHM}} \approx 6$ G.[1] The higher g-value line is assigned to
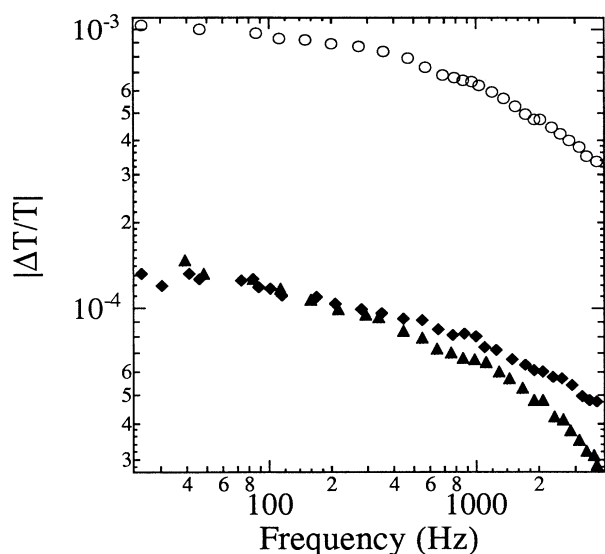

FIG. 2. Absorption spectrum of the (MEH-PPV)/C$_{60}$ composite film.

FIG. 4. The dependence of the photoinduced absorption features of (MEH-PPV)/C_{60} displayed in Fig. 2 on the chopping frequency. The 1.4-eV feature is shown as circles, the 1.15-eV feature as triangles, and the 2.2-eV peak as diamonds.

the MEH-PPV cation (polaron) and the lower g-value line to C_{60}^- anion. The assignment of the lower g-value line to C_{60}^- is unambiguous, for this g value was measured earlier for C_{60}^-; C_{60}^- is the only organic species with $g < 2$;[17] the higher g value is typical of conjugated polymers. The LESR signal vanishes above 200 K; this rules out permanent photochemical changes as the origin of the ESR signal and demonstrates the reversibility of the photoinduced electron transfer.

The temperature dependence of the LESR signal intensity, displayed in Fig. 8, shows an Arrhenius behavior with activation energy of $\Delta E \approx 15$ meV. This result suggests a phonon-assisted back-relaxation mechanism of the photoinduced charge separated state.
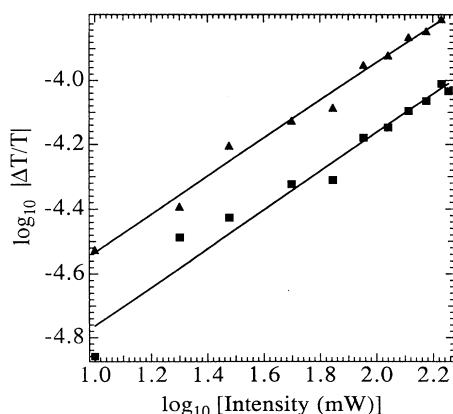

FIG. 5. The dependence of the photoinduced absorption features displayed in Fig. 2 on the pump intensity. The 1.4-eV band is shown as triangles and the 2.2-eV band as squares.
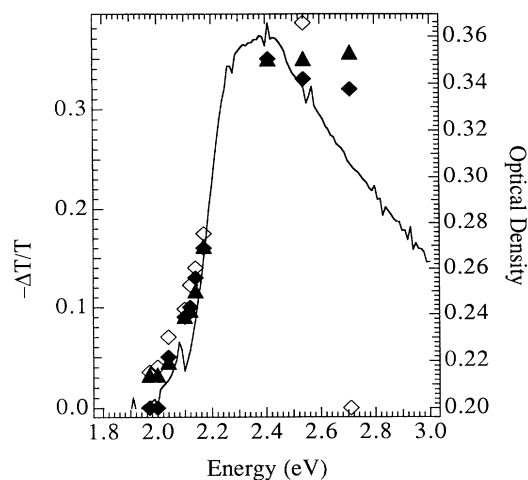

FIG. 6. The excitation profile (left axis) of the PIA peak at 1.33 eV (solid triangles), PIA edge at 1.15 eV (solid diamonds), and PIA plateau at 1.8 eV (open diamonds) as a function of the photon energy of the laser pump, compared with the MEH-PPV absorption spectrum (right axis).

B. PHDK/C_{60} composites

A soluble diketone derivative of poly(1,6 heptadiene), PHDK, which is a conjugated polymer with degenerate ground state, was investigated in near-steady-state PIA experiments. The absorption spectrum of the PHDK/C_{60} composite is shown in Fig. 9. In the mixed PHDK/C_{60} spectrum, the 2.3-eV peak from the PHDK and the 3.7-eV peak from the C_{60} are both clearly seen.

As demonstrated in Fig. 10, the photoinduced absorption spectrum of PHDK showed no significant change upon mixing with C_{60}. The PHDK exhibits a low-energy PIA band around 0.9 eV and a second band at 1.55 eV.
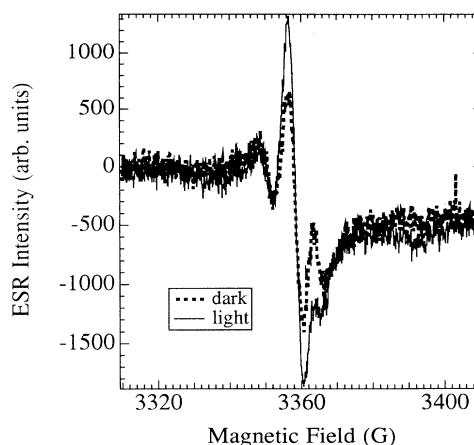

FIG. 7. LESR spectra of (MEH-PPV)/C_{60} composite upon successive illumination with 2.41-eV argon-ion laser with 150 mW. The dark ESR signal is drawn as a dashed line and the LESR signal as a solid line.
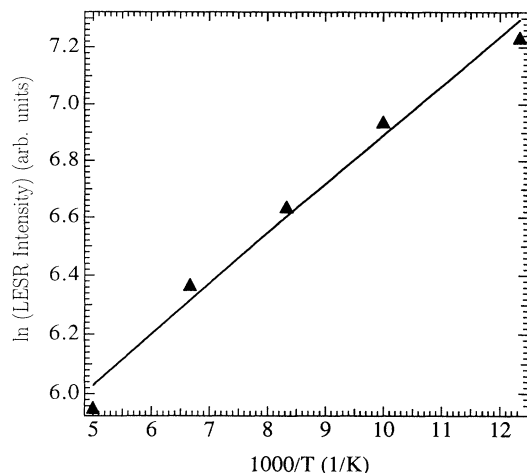
FIG. 8. Temperature dependence of the LESR signal in (MEH-PPV)/C_{60} composites.

After mixing PHDK with C_{60}, the PIA spectrum is essentially identical to that of the pure polymer. This may arise for either of the following two reasons.

(i) Photoinduced electron transfer does occur, but rapid back-transfer takes place ($\ll$ microseconds) so that the near-steady-state PIA spectrum cannot detect the charge separated state.

(ii) The photoinduced charge transfer does not occur due to faster competing processes.

There is no detectable luminescence from PHDK so we cannot use luminescence quenching to check for charge transfer. Thus, as anticipated for a degenerate ground-state system, the radiative recombination channel is not competitive with the nonradiative channel associated with structural relaxation into solitons, i.e., the Su-Schrieffer-Heeger mechanism.
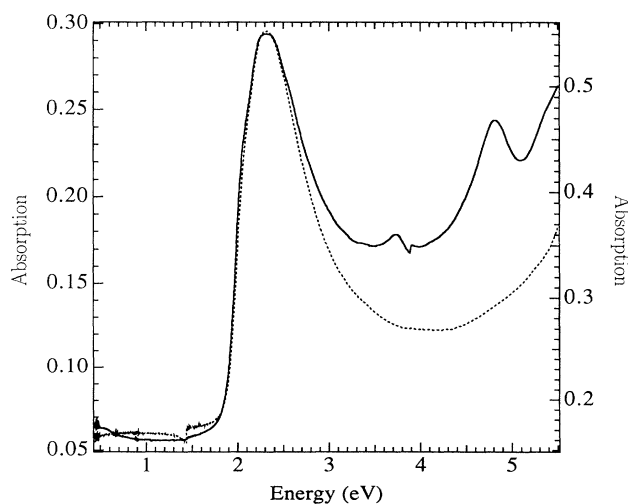

FIG. 9. Absorption spectra of soluble PHDK derivative (dashed line) and mixed with C_{60} (solid line).
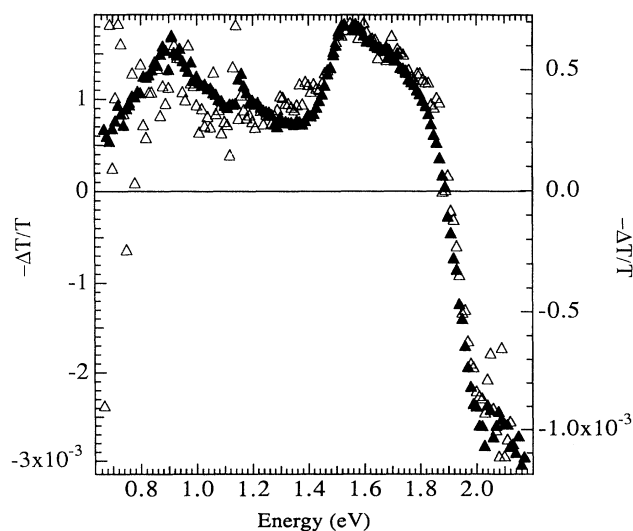

FIG. 10. Photoinduced absorption spectra of PHDK alone (open triangles, left-hand axis) and mixed with C_{60} (solid triangles, right-hand axis) obtained by illumination with 2.41-eV argon-ion laser with 50 mW.

Since the estimated photoinduced electron-transfer time in the (MEH-PPV)/C_{60} composites ($\leq 10^{-12}$ s) (Ref. 1) is longer than that required for soliton formation in degenerate ground-state polymers ($\leq 10^{-13}$ s),[6] photoexcitations will relax into soliton-antisoliton pairs on the donor polymer before electron transfer can occur. The lower energy of the soliton-antisoliton pair (relative to the initial photoexcited electron-hole pair) and the energy barrier to break the soliton-antisoliton pair into a pair of polarons prevents charge transfer. Thus, we conclude that the absence of any signature of photoinduced charge transfer in PHDK/C_{60} composites is due to (ii) above; charge transfer does not occur because the stabilized charged solitons form more rapidly.

These experimental results clarify an important criterion for the design of donor-acceptor couple suitable for electron transfer and long-lived charge separation. As in the case of conjugated polymers with degenerate ground state, the excited-state dynamics of the donor unit can quench the electron transfer.

C. P3OT/C_{60} composites

Figure 11 shows the absorption spectrum of a P3OT/C_{60} composite compared to that of P3OT alone. Upon adding the C_{60} to P3OT, a change in the P3OT absorption spectrum is observed; the π-π^* absorption of P3OT is considerably broader with a tail extending into the gap. This observation is in accordance with earlier reports indicating significant mixing of the P3OT and C_{60} ground-state electronic wave functions.[13] Morita, Zakhidov, and Yoshino[13] proposed a weak ground-state doping mechanism upon adding C_{60} to P3OT. This, however, would imply the presence of a C_{60} anion spin signal in the ground state of the P3OT/C_{60} composite. As shown below, the C_{60} anion signal appears only in light-induced
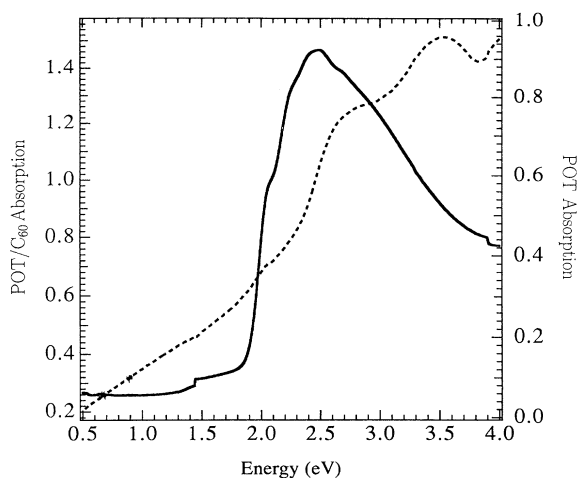
FIG. 11. Absorption spectra of P3OT alone (solid line) and mixed with C_{60} (dashed line).
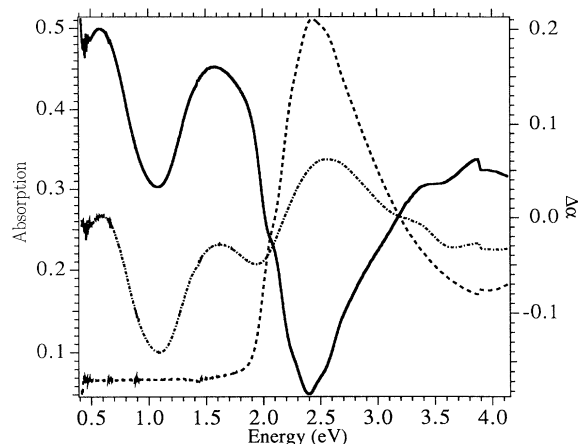
FIG. 12. Absorption spectra of P3OT (dashed line) and P3OT doped with $FeCl_3$ (dot-dashed line). The difference spectrum is shown on the right-hand axis as a solid line.

ESR, ruling out doping-induced charge transfer in the ground state. The spectral changes in the P3OT/C_{60} composite in Fig. 11 originate from partial charge transfer in the ground state, from $DA \rightarrow D^{\delta+} - A^{\delta-}$ (D for donor and A for acceptor). The specific evidence indicating the formation of a charge-transfer complex rather than a fully charge separated $D^+ - A^-$ pair is the absence of a spin signal from the A^- anion. The strong quenching effect on the luminescence reported by Morita, Zakhidov, and Yoshino[13] is consistent with photoinduced electron transfer.

To identify the spectral features associated with charged excitations in P3OT, we performed optical absorption measurements on P3OT which was chemically oxidized by $FeCl_3$. Upon oxidatively doping the P3OT with $FeCl_3$, charge transfer occurs with the formation of polarons; the $FeCl_3$ dopes the polymer by accepting an electron from the polymer to produce the $(FeCl_4)^-$ anion and the polaron cation P^+. Pairs of polarons subsequently combine to form lower-energy bipolarons (B^{2+})

$$P^+ + P^+ \rightarrow B^{2+} ,$$
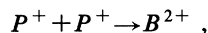
as indicated by the two bipolaron subgap absorption bands shown in Fig. 12. This signature indicates the complete charge transfer of electrons from the ground state of the polymer of the $FeCl_3$ acceptors. The spectrum of P3OT doped with $FeCl_3$ is similar to that previously reported for doped P3OT by Kim *et al.*[18]

Figure 13 shows the photoinduced absorption spectra of P3OT alone and in composite with C_{60}. The PIA spectrum of P3OT with a sharp PIA band at 1.05 eV and a broad PIA band centered at 1.25 eV is considerably different from the PIA spectrum reported earlier.[18] The 1.05-eV band has a different relaxation mechanism than the other bands as shown in Fig. 14. The chopping frequency dependence of the 1.05-eV band has been fitted to a monomolecular decay mechanism given by

$$dn/dt = -n/\tau + G ,$$

where G is the pumping term given by $G_0(1 + \cos\omega t)$, and τ is the lifetime of the excitation. Solving for the component of $n(\omega)$ in phase with the pumping term gives

$$n(\omega) = n_0\tau/(1 + \omega^2\tau^2) .$$

The lifetime derived from the best fit to this equation is $\tau \approx 175$ μs. This specific evidence of monomolecular decay behavior is indicative of an excitation with a well-defined lifetime in contrast to the power-law dependence of $n(\omega)$ typically found for trapped charged excitations.[19] Because of this monomolecular decay and the long lifetime, we assign this 1.05-eV peak to a triplet excitation. We attribute the difference in the photoexcitation spectrum of our P3OT compared to that previously reported
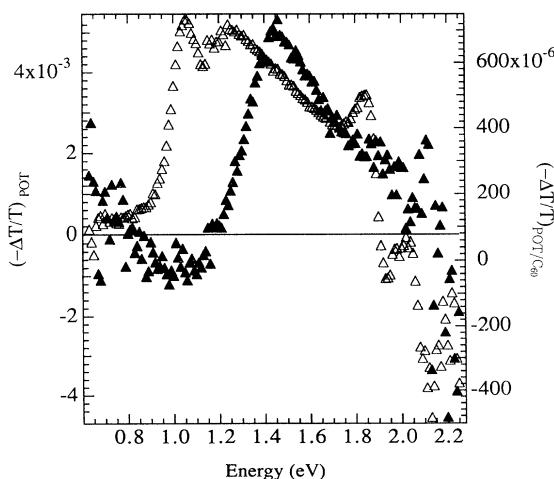
FIG. 13. Photoinduced absorption spectra of P3OT (open triangles) and the P3OT/C_{60} composite (solid triangles) at 80 K obtained by pumping with argon-ion laser at 2.41 eV with 50 mW.
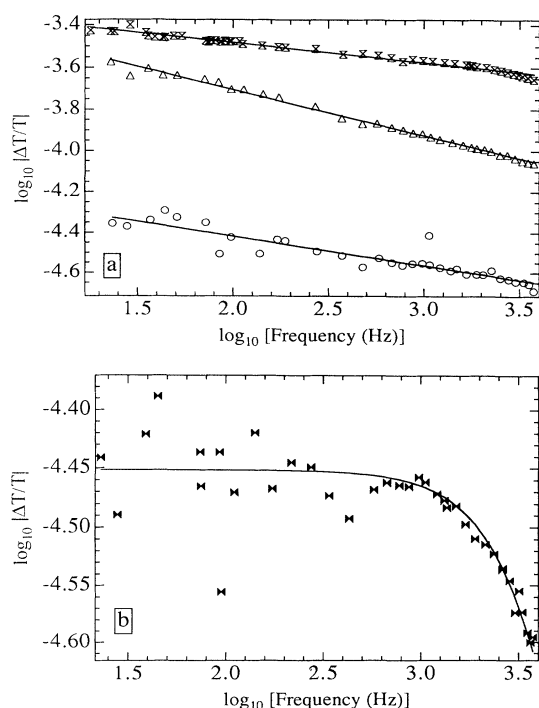
FIG. 14. The dependence of the photoinduced absorption features of P3OT displayed in Fig. 13 on the chopping frequency. (a) The 1.25-eV feature is shown by the double triangles and the solid line fit is a power law with power 0.09. The 1.85-eV feature is shown by triangles and fit to power law 0.22, and the 2.15-eV feature is shown by circles and fit to power 0.14. (b) The frequency dependence of the 1.1-eV feature with best-fit monomolecular decay shown as solid line.

to the lower defect level and possibly increased order in our carefully purified and fractionated material. A similar shift in PIA states from trapped charged excitations to metastable triplet excitons has been observed in MEH-PPV on going from a disordered film to an oriented blend and in PPV by using an improved synthesis technique.[19,20]

Figures 14 and 15 demonstrate that the other PIA bands follow more closely a power-law dependence on chopping frequency with $\Delta T/T$ increasing as ω decreases, even at the lowest chopping frequencies. The dependence of the PIA features on pump intensity has also been investigated; all show a power-law dependence on pump intensity with exponents between 0.6 and 0.8.

Upon adding C_{60} and P3OT, there are significant changes in the photoinduced absorption; see Fig. 13. In the composite, only one PIA is observed, centered at 1.45 eV, along with an onset of photoinduced infrared absorption at low energies. This is to be compared with the peaks at 1.05 and 1.25 eV in P3OT alone. The PIA spectrum of the P3OT/C_{60} is similar to that which was observed previously for trapped charged excitations on P3OT,[18] as well as to the absorption spectrum of the FeCl$_3$-doped P3OT shown in Fig. 12. This similarity supports the identification of the PIA features in the
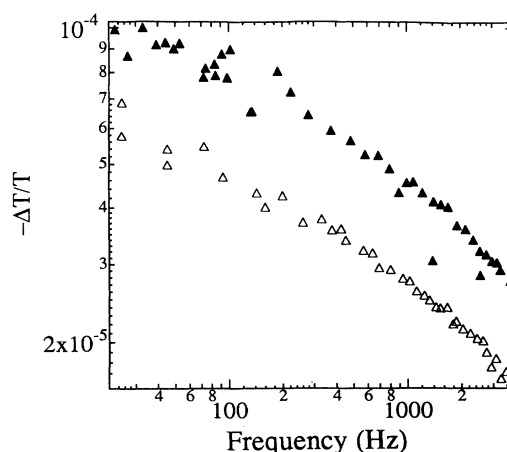

FIG. 15. The dependence of the photoinduced absorption features of P3OT/C_{60} displayed in Fig. 13 on the chopping frequency. The solid and open triangles show the 1.5-eV PIA and the 2.2-eV photoinduced bleaching magnitude, respectively.

P3OT/C_{60} composite as arising from a charged excitation. The *photoinduced* charge transfer observed in the presence of C_{60} is complete charge transfer from the excited state of the polymer to the C_{60} acceptor resulting in the formation of both P3OT$^+$ and C_{60}^-. An explicit absorption band of C_{60}^- could not be identified in P3OT/C_{60} composite. To clarify whether this band is superimposed on the polaron band of P3OT around 1.45 eV, spin-dependent PIA experiments are underway. As shown below, the LESR provides the evidence that C_{60}^- is formed upon photoexcitation.

The light-induced ESR spectrum of the P3OT/C_{60} composite is shown in Fig. 16. Complete charge transfer and charge separation from P3OT onto C_{60} requires the observation of two distinctly different spins; the polaron on the conducting polymer backbone and the C_{60} anion.
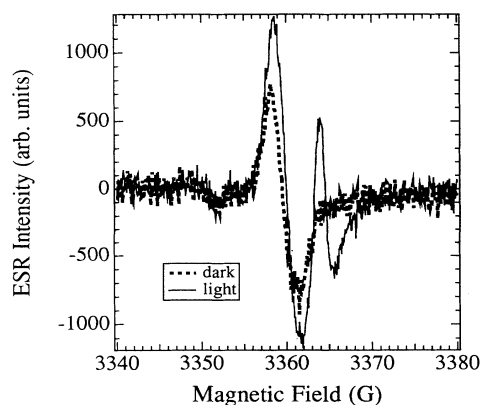

FIG. 16. LESR spectra of P3OT/C_{60} composite upon successive illumination with 2.41-eV argon-ion laser with 100 mW. The dark ESR signal is drawn as a dashed line and the LESR signal as a solid line.

In complete analogy to the (MEH-PPV)/C_{60} case, there are two spins observed upon illumination as demonstrated in Fig. 16. The $g \approx 2.00$ spin with $\Delta H_{FWHM} \approx 4$ G is assigned to the P3OT polaron (donor cation), and the $g \approx 1.9938$ spin with $\Delta H_{FWHM} \approx 3.7$ G is assigned to the C_{60}^{-} anion. The accumulation effect of the charge-separated state upon successive illumination cycles is not observable in P3OT/C_{60} composites in contrast to (MEH-PPV)/C_{60}, implying a shorter lifetime for the charge separated configuration. This indicates a more efficient back-relaxation mechanism of the charge separated state in the P3OT/C_{60} composites.

D. Time scales

By observing which processes are quenched by photoinduced charge transfer and which occur more rapidly than the photoinduced charge transfer, we can estimate the time scale of the photochemical reaction. From the luminescence quenching observed in (MEH-PPV)/C_{60} mixtures, we determine that the charge-transfer rate is larger than 10^{12} s^{-1}.[1] The observation that the charge transfer is preempted by the faster relaxation of the photoexcited states to the soliton states deep in the gap of the degenerate ground-state PHDK puts an upper limit on the charge-transfer rate of 10^{13} s^{-1}.[6] The absence of the triplet photoinduced absorption band in the P3OT/C_{60} mixture implies that the charge-transfer reaction occurs more rapidly than the intersystem crossing to the triplet state. This intersystem crossing rate is determined to be about 10^{12} s^{-1} in MEH-PPV.[21] Thus, the quenching of the triplet photoinduced absorption in the P3OT/C_{60} mixture is consistent with our estimated charge-transfer rate.

IV. CONCLUSION

We have generalized the study of the photoinduced electron-transfer process from a semiconducting polymer (as donor) to C_{60} (as acceptor) to several different semiconducting polymers. There is evidence for interaction of the ground-state wave functions of the polymer and C_{60} only in the case of P3OT. However, ESR studies do not show C_{60}^{-} spins in the ground state, implying that there is only a donor-acceptor complex formed; i.e., C_{60} does not dope P3OT. Evidence for photoinduced charge transfer is obtained from the PIA spectra and from LESR data. Upon photoexcitation, electron transfer occurs from both P3OT and MEH-PPV to C_{60}, but not from PHDK to C_{60}. The difference between these materials is that both P3OT and MEH-PPV have nondegenerate ground states, whereas PHDK has a degenerate ground state. Thus, in PHDK, photoinduced electron transfer is "short-circuited" by a faster competitive process, the formation of soliton-antisoliton pairs deep in the energy gap. In the nondegenerate ground-state polymers, the excitations do not relax as deeply into the gap as for degenerate materials; the singlet excitation energies for MEH-PPV and P3OT are observed to be just below the gap as evidenced by their luminescence spectra. The charge-transfer rate is faster than the luminescence decay rates and thus quenches the emission. From these observations, we are able to estimate the rate of the charge-transfer reaction to be between 10^{12} and 10^{13} s^{-1}.

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