Direct observation of charge-transfer dynamics in a conjugated conducting polymer poly(3-octylthiophene)-fullerene composite by time-resolved infrared spectroscopy

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Transient infrared-active vibrational (IRAV) modes observed in the π-conjugated conducting polymers upon photoexcitation are usually used to characterize the dynamics of the photoinduced charge separation and recombination processes. In this paper, the dynamic behavior of photogenerated charge carrier in the poly(3-octylthiophene) (P3OT) conducting polymer doped with fullerene (C_{60}) has been studied by using step-scan time-resolved Fourier-transform infrared spectroscopy at room temperature in the $2500-900$-cm^{-1} ($0.31-0.11$-eV) frequency region. Upon photoexcitation with a 10-ns laser pulses, it is observed that IRAV modes appear in the similar vibrational frequency regions for pure P3OT and C_{60}-doped P3OT; however, the observed IRAV modes is enhanced by 800% in intensity in the presence of small amount of C_{60} (e.g., 10%). Our results also show that the charge separation occurs instantaneously within the laser pulse width (10 ns), whereas the charge recombination processes occur in the microseconds to a few milliseconds time domain. In addition, the observed enhancement in the IRAV modes upon C_{60} doping indicates an enhanced photogeneration efficiency of the charge separation.

INTRODUCTION

Conducting polymers possess the known advantages of synthetic polymers, such as the processability from solution or the melt, flexibility, low density, and versatility for chemical modifications. Many applications have been proposed and studied for conjugated polymers,[1,2] such as field-effect transistors,[3,4] light-emitting diodes,[5] nonlinear optical and photovoltaic devices.[6,7] Molecular order and alignment have an important impact on the properties of conjugated polymers. A highly oriented fibrillar polyacetylene shows a conductivity comparable to copper (up to 10^5 S/cm),[8] and when aligned, the polymer in the light-emitting diodes emits highly polarized light.

In conducting polymers, the quasi-one-dimensional electronic structure is strongly coupled to the chemical (geometrical) structure.[9] As a result, the charged excitations (polarons and bipolarons) are self-localized around local structural distortions with electronic states within the energy gap due to the electron-phonon coupling.[10,11] The conduction in conducting polymers is hopping of electrons between these charged carriers, which involves mainly the conduction between chains (interchain conducting), and also the conduction along conjugated polymer chains (intrachain conducting).

Electronic absorption and vibrational spectroscopy of conjugated conducting polymers have been analyzed experimentally and theoretically.[9] These charged excitations can be studied spectroscopically by direct optical pumping above the energy gap with an intense light source.[11,12] In order to probe the photogeneration of charge carriers in conducting polymer, photoinduced absorption measurements in the visible and near-infrared region are generally used.[13] However, difficulties due to band overlap usually occur.[14] On the other hand, due to polymer structural distortion as a result of cre-

ation of those excitations mentioned above, the symmetrical (Raman-active) vibrational modes in the midinfrared region become infrared-active modes, so-called IRAV modes. Therefore, the charge separation and recombination dynamics in the conducting polymer upon photoexcitation can be monitored by following the temporal behavior of the IRAV absorption. There are several studies on the photoinduced IRAV modes in conducting polymers, most of which are carried out by using low-temperature Fourier-transform infrared (FTIR) difference spectroscopy.[9,10,15–18] As a result, no dynamics on the charge separation and recombination has been reported until recently. Using picosecond time-resolved ir measurement, single-wavelength probing of the photoinduced IRAV modes on conjugated-polymer–fullerene blends has been reported.[14] The results show the presence of photoinduced charge transfer in these mixtures, with the charge recombination occurring on multiple time scales spanning several orders of magnitude. However, real-time measurement of the IRAV modes in a broad spectral range has not yet been reported.

In this paper, the photoinduced IRAV modes in poly (3-octylthiophene) (P3OT) conducting polymer have been investigated in the spectral region of $2500-900$ cm^{-1}, by using the nanosecond step-scan time-resolved FTIR spectroscopy, which has the ability to probe the whole midinfrared region simultaneously. The effect of the presence of an electron acceptor, such as C_{60}, on the charge separation and charge recombination processes has also been studied.

EXPERIMENT

Sample

Regiorandom poly(3-octylthiophene) was synthesized according to a modified method,[19] with a mean molecular weight of $M_{av} \sim 80$ kDa.[20] Fullerene (C_{60}) was purchased

from Alfa Aesar (Ward Hill, MA) and used without further purification. After mixing P3OT and C_{60} in toluene at a weight ratio of 10% C_{60}, P3OT-C_{60} composite films were prepared on CaF_2 windows, by evaporating the solvent to give appropriate optical densities at $\lambda_{max} \sim 450-500$ nm in the visible absorption spectra and $\lambda_{max} \sim 1450$ cm^{-1} in the infrared absorption spectra for polymer.

Time-resolved FTIR spectroscopy

As described previously,[21] transient FTIR measurements were carried out on the Nicolet Magna-IR 860 step-scan FTIR spectrometer (Nicolet Instrument Corp, Madison, WI). Briefly, a 50-MHz mercury-cadmium-telluride (MCT) detector (Kolmar Technologies Inc., Conyers, GA) with a linear infrared light-intensity response was used with appropriate ac- and dc-coupled preamplifiers. The overall time resolution of the system is ~80–90 ns. Data were taken with temporal resolutions of 50 ns, 100 ns, and 10 μs, at a spectral resolution of 8 cm^{-1}. The spectral region covers 3000–900 cm^{-1} (0.36–0.11 eV), by use of the combination of a MCT detector that has a low-frequency cutoff at 600 cm^{-1}, CaF_2 windows that have a low-frequency cutoff at ~900 cm^{-1}, and a germanium-based ir band-pass filter that has a high-frequency cutoff at 3200 cm^{-1}. The study was carried out in the time domain of 20 ns to 10 ms. Data are presented in the spectral region of 2500–900 cm^{-1} (0.31–0.11 eV), as shown below. Transient signals were co-added 5–6 times to improve the signal to noise ratio. The nanosecond neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (Quantum-Ray DCR-3, Mountain View, CA) provides an output at 532 nm as its second-harmonic generation (SHG) with a laser energy of 3 mJ/pulse at a repetition rate of about 3 Hz and was externally triggered by the Nicolet Omnic data acquisition system. Steady-state FTIR spectra were also taken by using the Nicolet FTIR spectrometer. All the measurements were carried out at room temperature.

RESULTS AND DISCUSSIONS

Figure 1 shows the steady-state visible and infrared absorption spectra for P3OT, C_{60}, and their composite with 10% C_{60}. Comparing with those in toluene [Fig. 1(a), inset], inhomogeneous spectral broadening and a slight blueshift in the absorption maximum are observed in the visible region when samples are in the form of film [Fig. 1(a)]. This actually has made it possible to efficiently photoexite the system with laser at 532 nm that has been used in our experiment. The addition of C_{60} is found to change steady-state infrared spectra of P3OT in the frequency region of 1750–650 cm^{-1} as shown in Fig. 1(b). It should be mentioned that in Fig. 1, the absorption spectra of films have been normalized, such as the absorption band intensity of the P3OT-C_{60}(10%) sample has been multiplied by 1.5 times. This factor has to be used when we calculate the enhancement of the observed transient IRAV upon adding C_{60}.

The use of step-scan time-resolved FTIR allows us to monitor the transient IRAV modes in the mid-infrared as a function time. Figure 2 show the time-resolved IRAV absorp-
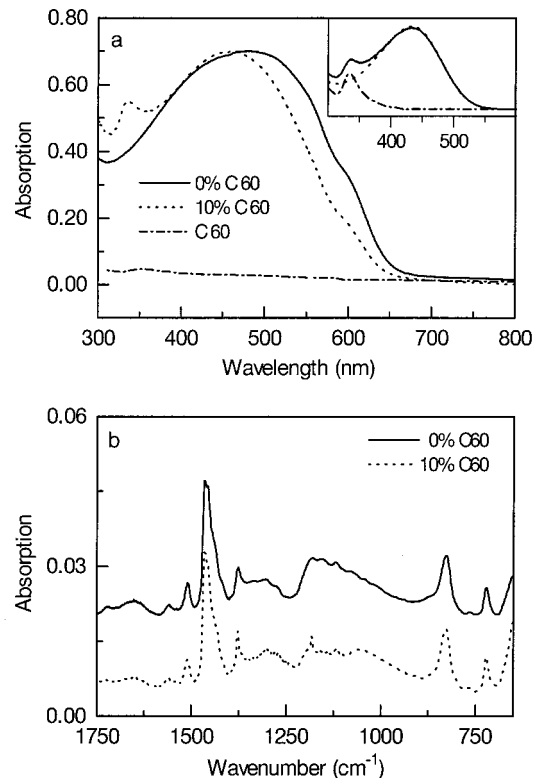

FIG. 1. Steady-state absorption spectra for P3OT, C_{60}, and their composite: (a) Visible absorption spectra of P3OT-C_{60} (solid line), with 10% of C_{60} added. P3OT (dotted line) and C_{60} (broken line) on a CaF_2 window, in the 300–800-nm region. The insert shows the corresponding spectra of each in toluene. (b) Infrared spectra of P3OT-C_{60} (solid line) and P3OT only (dotted line) in the frequency range of 1750–650 cm^{-1}. In both the visible and infrared spectra, the absorption intensity of P3OT-C_{60} film has been enlarged (1.5 times) for spectral normalization.

tion spectra for P3OT-C_{60}(10%) composite on CaF_2 window in the frequency range of 2500–900 cm^{-1} (0.31–0.11 eV). The spectra are collected at various delay times after laser excitation as indicated. Our collection spans the time domain of photogeneration and the decay processes of the IRAV absorption bands observed for this polymer. Four localized IRAV absorption bands at 1440 cm^{-1} (a broad band with a shoulder at 1380 cm^{-1}), 1200 cm^{-1}, 1090 cm^{-1}, and 1010 cm^{-1} are observed. These can be assigned to uniform translational motion of charged excitation along the polymer chain (polaron or T modes).[14,22] The ring-bending (R) modes[10] due to the weak coupling of charge distortion on the thiophene ring are not observed in our measurements because they are normally below 900 cm^{-1} (i.e., below the cutoff of the CaF_2 windows used).

Figure 3 shows time-resolved IRAV absorption spectra for P3OT only on a CaF_2 window in the frequency range of 2500–900 cm^{-1} at various delay times. The observed IRAV absorption band feature is essentially identical to that shown in Fig. 2, except that the band intensity of those T modes in the P3OT-C_{60} composite is much higher than that of those in pure P3OT film. The enhancement of the observed transient IRAV modes can be estimated by using the broad band at
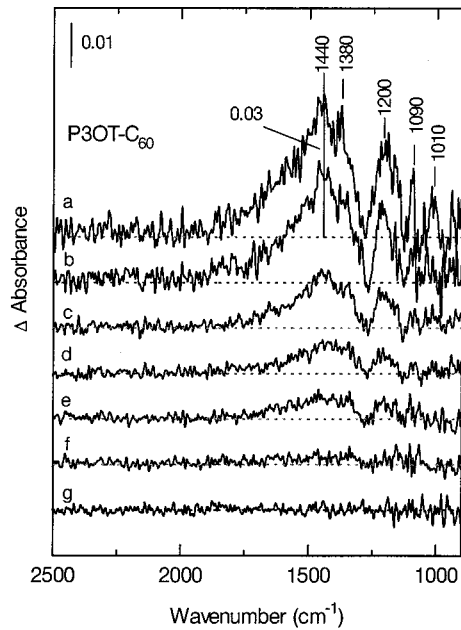
FIG. 2. Room-temperature time-resolved IRAV absorption spectra for P3OT-C_{60}(10%) composite on a CaF_2 window in the frequency range of 2500–900 cm^{-1} at various delay times after laser excitation at 532 nm, as indicated: (a) 450 ns, (b) 1.5 μs; (c) 6 μs; (d) 37 μs; (e) 160 μs; (f) 600 μs; (g) 2.5 ms. This covers the time domain of photogeneration of the charge separation and recombination processes of polymer.
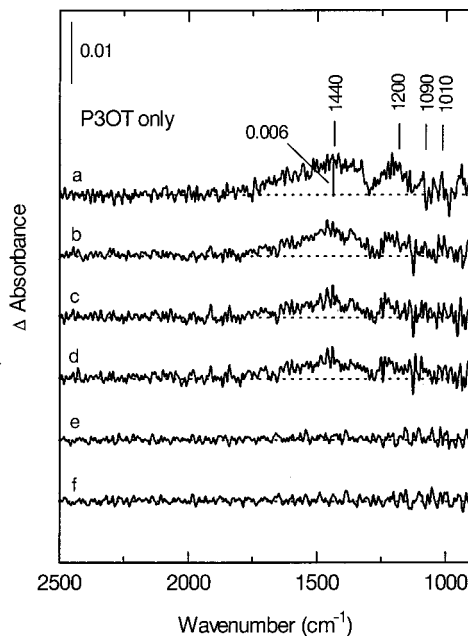

FIG. 3. Room-temperature time-resolved IRAV absorption spectra for P3OT only on the CaF_2 window in the frequency range of 2500–900 cm^{-1} at various delay times after laser excitation at 532 nm, as indicated: (a) 1.5 μs; (b) 8 μs; (c) 30 μs; (d) 45 μs; (e) 75 μs; (f) 800 μs. This covers the time domain of photogeneration of the charge separation and recombination processes of polymer.
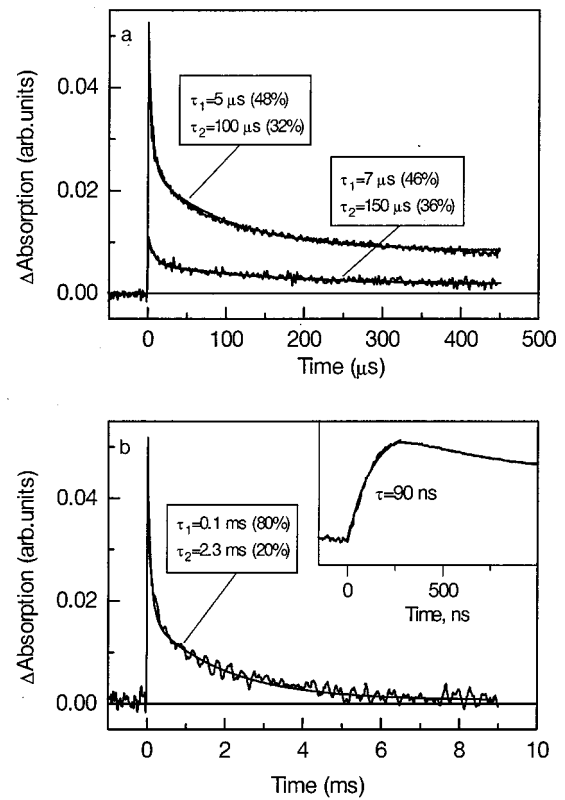

FIG. 4. The temporal behavior of the averaged IRAV modes in the time regime of microseconds to milliseconds. (a) The change of the integrated absorption band intensity in the 2000–1000-cm^{-1} region for P3OT-C_{60}(10%) composite (upper curve) and P3OT-only (lower curve), in the time regime of 0–450 μs (b). The change of the integrated absorption band intensity in the 2000–1000-cm^{-1} region for P3OT-C_{60}(10%) composite in the time regime of 0–9 ms. The inset in (b) shows the rise phase (0–1 μs) of the IRAV mode. The fitted results are also shown to give at least biexponential relaxation processes (with lifetimes and amplitudes shown in each case), and a monoexponential rise phase.

1440 cm^{-1} as follows: In curve *a* of Fig. 2, $\Delta Abs_{1440\,cm^{-1}}$ ≈ 0.03. Since $\Delta Abs_{1440\,cm^{-1}} \approx 0.006$ in curve *a* of Fig. 3, the ratio of these two values gives an enhancement factor of approximately 5 times upon adding 10% C_{60}. Taking account of the optical density factor (~ 1.5) in the steady-state spectra (Fig. 1) as mentioned above, the overall enhancement of IRAV modes becomes 7–8. For the P3OT-C_{60} composite with a smaller amount of C_{60} (such as 2% or 5%), a slightly larger enhancement factor (~ 10–12) has been estimated.

The photoinduced or doping-induced infrared absorption bands can be explained by the amplitude mode theory[23,24] or the effective conjugation coordinate theory.[25] According to these theories, the normal vibrations that induce oscillations in bond alternation can be observed in the infrared spectra of photoexcited conducting polymers. The strong intensities of those observed IRAV modes are due to vibration-induced charge fluxes.[9] Doping P3OT (which is a strong electron donor[18]) with C_{60} molecules that have large electron affinity values, makes charge transfer energetically favorable. This

accounts for the observed enhancement of IRAV modes as a result of doping with C_{60} as shown in Fig. 2.

Figure 4 compares the temporal behavior of the integrated absorption band of the IRAV modes from 2000 to 1000 cm^{-1} for both the 10% doped and the undoped P3OT in the time regime of microseconds to milliseconds. The time dependence of the overall integrated signal is shown here with good signal-to-noise ratio. It is also found that each individual band in this frequency region shows a similar time dependence (data not shown). The fitted results in the time window of 450 μs show that the decay process of the IRAV mode has approximately three exponential components: two fast components having lifetimes of 5–7 μs ($\sim$40–50 % in amplitude) and of 100–150 μs ($\sim$30–35 % in amplitude) for both the doped and undoped P3OT [Fig. 4(a)], and a slow component of $\sim$2.3 ms ($\sim$20%) lifetime as seen in Fig. 4(b). This indicates that the complete decay of the observed IRAV mode occurs within a few milliseconds. It should be pointed out that since the charge recombination occurs on a time scale between few microseconds to a few milliseconds, the complex decay phase of the charge recombination processes can also be described by using power-law function, or a combination of exponential and power law functions, as has been used previously.[13,14]

The formation of the rapid charge separation for P3OT-C_{60}(10%) has also been monitored by following the transient IRAV absorption spectrum, as shown in the Fig. 4(b) insert. The fitted results give an apparent rise time of $\sim$90 ns, which is roughly the rise time of the measurement system used in our study.[21] This suggests that the formation of the charge separation may occur in less than 90 ns when using 10-ns pulsed laser excitation. An earlier study has shown that bound polarons are formed in the primary time regime of a few picoseconds using picosecond laser excitation for poly(p-phenylenevinylene).[26] It has also been reported that the photoinduced charge transfer from π-conjugated polymers to its dopant C_{60} occurs on the sub-picosecond time scale with high efficiency.[27,28] These, together with our results presented here, indicate that bound polarons are probably formed rapidly within the nanosecond laser pulse width or shortly after the excitation.

The microsecond and millisecond fast relaxation components ($\sim$80% in amplitude total) in Fig. 4 can be assigned to the geminate charge recombination process, in which the bound polaron recombines rapidly, as also pointed out previously.[14,26] The slow components essentially reflect the dynamics of the long-lived charge species. It is generally believed that upon photoexcitation, a geminate charge pair is produced along the conjugated polymer chains (and also between polymer and C_{60}), which recombines rapidly and gives rise to fast decay components in the charge recombination process. Some of the photogenerated geminate charge pairs may be further separated,[10] due to the presence of the photoinduced forward charge transfer between P3OT and C_{60} (forming P3OT$^+$ and C_{60}^-), and/or due to the electron hopping to neighboring species (P3OT or C_{60}). This gives rise to the observed slow charge recombination processes. In addition, these charge recombination processes are mainly diffusion controlled, i.e., they may follow complex kinetics, which can be described by using power-law functions,[13,14] or multiple exponential functions,[29] which is consistent with our data shown in Fig. 4.

Using time-resolved FTIR spectroscopy, our data reveal that the charge separation process occurs in less than a hundred nanoseconds, and the charge recombination processes are in the time domain of microsecond to milliseconds. This observation is in agreement with a previous study[14] that showed that about 80% of the fast charge separation has recombined within tens of nanoseconds following a picosecond pulsed-laser excitation in the case of poly(3-hexylthiophene)-C_{60} system. The significance of the current study is that, since the energy conversion of a bulk heterojunction photovoltaic device critically depends on the efficiency of charge carrier collection, higher charge carrier mobilities and longer lifetime of charge separation would certainly be useful in achieving a metastable charge-separated state for fabrication of photovoltaic devices.

In summary, by using step-scan time-resolved FTIR spectroscopy, nanosecond to microsecond transient IRAV absorption spectra have been obtained at room temperature. The enhancement of IRAV band intensity has been observed by adding a few percent of the electron acceptor C_{60}, indicating an enhancement of the photoinduced charge separation. This makes P3OT-C_{60} composite a relatively good candidate for use in photovoltaic devices. Our study shows that time-resolved FTIR spectroscopy is very useful in studying the dynamics of charge separation and recombination processes in conjugated conducting polymers.

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