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Picosecond photoinduced absorption and polarization memory in polythiophene derivatives

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Although the fast dynamics of photoexcitations has been thoroughly explored in the conjugated polymer *trans*-polyacetylene, the experimental picture is much less complete for polymers in which the ground state is nondegenerate. We report time-resolved photoinduced-absorption data from films of one family of such polymers: the soluble polythiophene derivatives, poly(3-hexylthiophene-2,5-yl) and poly(3-octylthiophene-2,5-yl). Fast ($<10^{-12}$ s) bleaching of the interband transition is observed at 2.06 eV, accompanied by photoinduced absorption in the band gap at 1.17 eV. The results indicate a shift of a fraction of the oscillator strength, consistent with rapid structural relaxation to form polarons with associated band-gap states. By varying the polarization of the optical probe relative to that of the pump, photoinduced dichroism is observed. The magnitude of the initial dichroism implies that in spin-cast films the polymers are (locally) chain extended and chain aligned. The time decay of the polarization memory is consistent with rapid trapping of the initially mobile charged excitations.

I. INTRODUCTION

Picosecond photoinduced absorption (time-resolved excitation spectroscopy) measurements have played a central role in the study of the dynamics of the formation of nonlinear excitations (solitons and polarons) in semiconducting polymers.[1] Following the initial theoretical results of Su and Schrieffer,[2] photoinduced bleaching of the interband (π-π^*) transition was observed in *trans*-polyacetylene and demonstrated to occur on the predicted time scale ($\sim 10^{-13}$ s).[3-5] The associated shift of oscillator strength into the infrared due to the formation of the gap state was subsequently observed with picosecond resolution.[6] Thus, in *trans*-$(CH)_x$, a conjugated polymer with a twofold-degenerate ground state, a reasonably complete experimental picture of the dynamics of soliton-pair formation is available.

A bonus of these studies was the discovery of photoinduced dichroism and polarization memory.[5] Pump-probe measurements were carried out on nonoriented films of *trans*-$(CH)_x$ with the polarization of the probe beam parallel to and perpendicular to that of the pump beam. The observation of photoinduced dichroism[5] indicated significant chain extension and chain alignment in the macroscopically random material, consistent with the relatively high degree of crystallinity of *trans*-$(CH)_x$.[7] The time decay of the polarization memory provided information on the spatial diffusion of the photoexcitations: decay of the induced dichroism can only occur when a typical self-localized photoexcitation has diffused over distances such that the local chain axis is randomly oriented with respect to the orientation where the excitation originated.[5]

Although the fast dynamics of *trans*-polyacetylene have been thoroughly documented, experimental studies of the dynamics of nonlinear excitations in polymers in which the ground state is nondegenerate have only just begun. In extending these studies to such nondegenerate systems, it is of interest to explore whether the subpicosecond shift of oscillator strength is a general feature of conjugated polymers. In this paper we address this question through experimental studies of the soluble polythiophene derivatives: poly(3-hexylthiophene-2,5-yl) (P3HT) and poly(3-octylthiophene-2,5-yl) (P3OT). We find subpicosecond bleaching of the interband π-π^* transition at 2.06 eV, similar to that observed in polythiophene.[8] Accompanying this bleaching, we observe fast photoinduced absorption at 1.17 eV, indicating that rapid formation of gap states also occurs in these nondegenerate ground-state polymers.

The observation of photoinduced dichroism suggests that, as in polyacetylene, significant chain alignment exists on a microscopic scale. The decay of the dichroism is consistent with the trapping of the photoexcitations within a few hundred picoseconds; this picture is supported by the decay of the photoconductivity under similar conditions. The larger signal, lower dichroism, and faster decay in the interband bleaching, compared with the subgap photoinduced absorption, indicates that the bleaching is dominated by processes other than the direct shift of oscillator strength into the gap (e.g., the formation of neutral bipolaron excitons as a result of the confinement force which results from the nondegenerate ground state). The two materials show very similar photoinduced behavior: the most significant difference is that the subgap dichroism is much longer lived in the P3OT films.

II. EXPERIMENTAL METHODS

The polyalkylthiophenes were prepared using the $FeCl_3$ oxidative coupling synthesis[9] and subsequently purified;[10] details of the synthesis and purification have been reported elsewhere.[11] The films of P3HT and P3OT used in the transient photoinduced absorption measurements were prepared by spin casting from solution (3% by weight in trichlorobenzene). By this means one may control the film thickness and obtain films which are uniform over several square centimeters; films for these experiments were about 3000 Å thick (as determined by a Sloan Dektak surface contact measurement).

The time-resolved photoinduced absorption measurements were carried out in the standard pump-and-probe configuration. The excitation source for the degenerate experiment (pump and probe at the same photon energy, 2.06 eV) was a synchronously pumped, cavity-dumped dye laser (rhodamine-6G), pumped by the frequency-doubled output of a pulse-compressed neodymium-doped yttrium-aluminum-garnet (Nd-YAG) laser. This produced pulses at a repetition rate of 0.8 MHz with an autocorrelation full width at half maximum (FWHM) of ≈1 ps. For the nondegenerate experiments, the probe beam of infrared light at 1.17 eV (1.06 μm) was split off from the pulse-compressed output of the YAG laser, yielding pulses with an 82-MHz repetition rate, and an autocorrelation FWHM of ≈8 ps; the dye laser (with an 82-MHz repetition rate) was the pump source.

The pump beam was mechanically chopped at 3 kHz, and the modulated absorption detected with a lock-in amplifier. The measurements were carried out at room temperature, with the polymer films in vacuum ($<10^{-4}$ Torr). Care was taken to ensure that the spatial overlap of the pump-and-probe pulses did not change as the delay between the pump-and-probe pulses was varied.

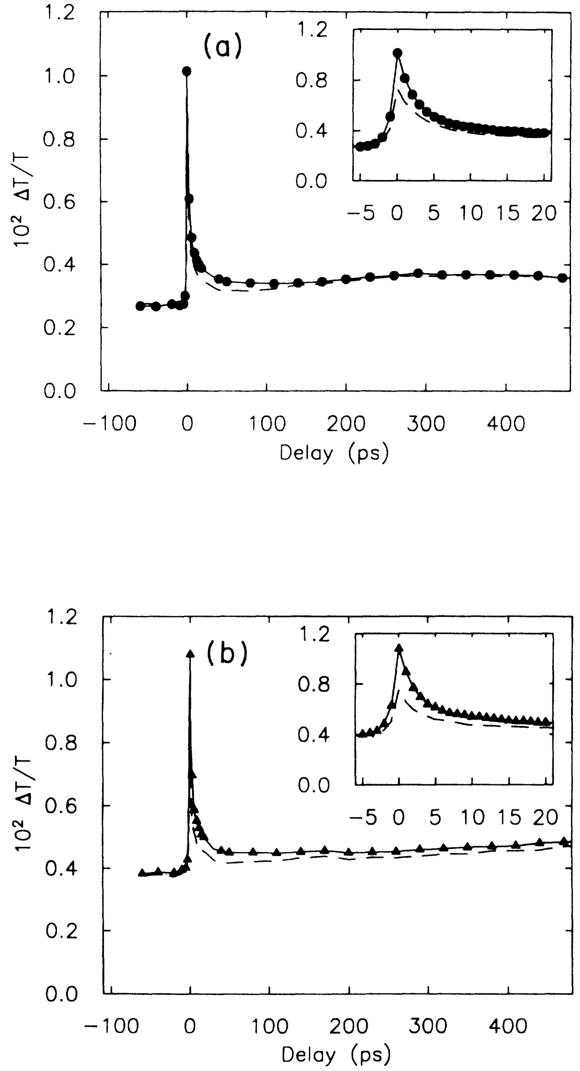

FIG. 1. Photoinduced bleaching at 2.06 eV due to pumping at 2.06 eV, for (a) P3HT and (b) P3OT. The top curve in each (solid circles and triangles) is the response with the pump-and-probe beams polarized parallel to each other; the dashed curves are for pump-and-probe beams at right angles. The insets show the short-time decay on an expanded scale.

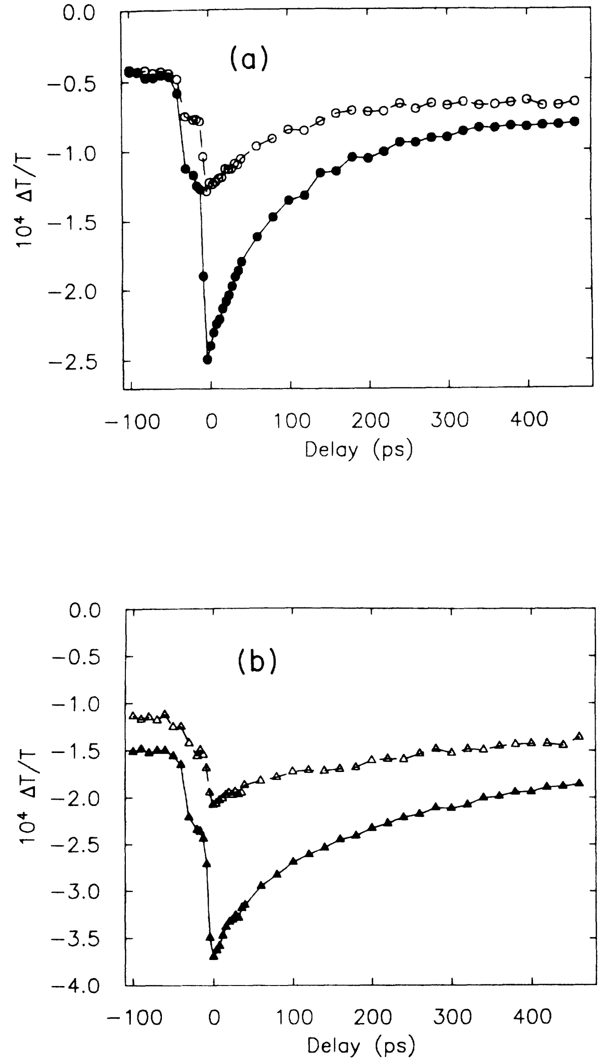

FIG. 2. Photoinduced absorption at 1.17 eV due to pumping at 2.06 eV, for (a) P3HT and (b) P3OT. The solid circles and triangles are for parallel pump-and-probe polarizations; the open circles and triangles are for perpendicular pump-and-probe polarizations.

III. RESULTS

In Fig. 1 we plot the time dependence of the photoinduced bleaching of the π-π^* interband transition (pump and probe both at 2.06 eV) for probe-delay times out to 450 ps. The insets of Fig. 1 show the short-time decay on an expanded scale. The rise time of the bleaching is resolution limited by the pulse width, less than one picosecond. The subsequent decay exhibits two components: a fast component, which decays in ~ 5 ps (see inset), and a longer-lived tail. This is similar to the photoinduced bleaching seen in polythiophene.[8] The magnitude of the peak bleaching in P3HT [Fig. 1(a)] is slightly smaller than that in P3OT [Fig. 1(b)]; the decay times and general appearance of the decay curves for the two materials are similar.

Figure 2 shows the photoinduced absorption at 1.17 eV, following pumping into the π-π^* interband transition at 2.06 eV. Again, the rise time is resolution limited by the probe pulse width, less than 8 ps. The wings evident at a delay of -25 ps arise from side lobes on the compressed infrared probe; the wings are also present in the autocorrelation trace. The decay, however, is qualitatively different from that in Fig. 1. The fast decay seen clearly in Fig. 1 is absent in Fig. 2; only a slower decay (≈ 250 ps) can be seen, with the induced absorption falling to a longer-lived tail. Again, the magnitude of the peak signal in P3HT [Fig. 2(a)] is slightly larger than that in P3OT [Fig. 2(b)], and the shapes of the decay curves for the two materials are similar. However, for both P3HT and P3OT, the peak photoinduced absorption at 1.17 eV (Fig. 2) is only about 5% of that of the peak photoinduced bleaching at 2.06 eV (Fig. 1).

A qualitative difference is also evident in the photoinduced dichroism for the different probe energies (Figs. 3 and 4). Whereas the dichroism induced at 2.06 eV is essentially gone by 150 ps (Fig. 4), the dichroism at 1.17 eV is long lived (Fig. 3); in P3OT, considerable dichroism is evident when the infrared probe pulse arrives before the pump pulse, i.e., 12 ns after the previous pump pulse.

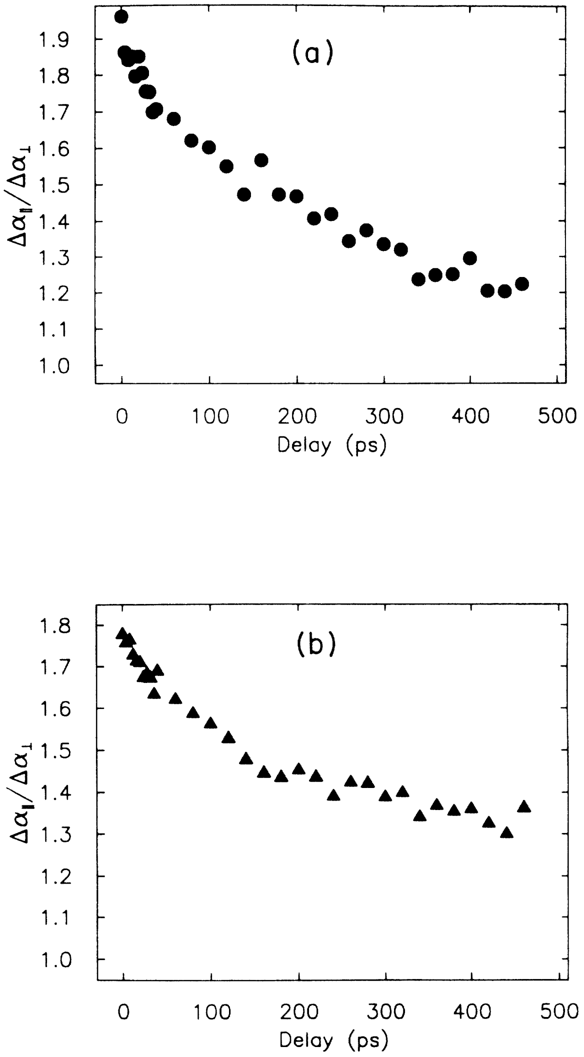

FIG. 3. Photoinduced dichroism at 1.17 eV (ratio of parallel and perpendicular curves in Fig 2) for (a) P3HT and (b) P3OT.

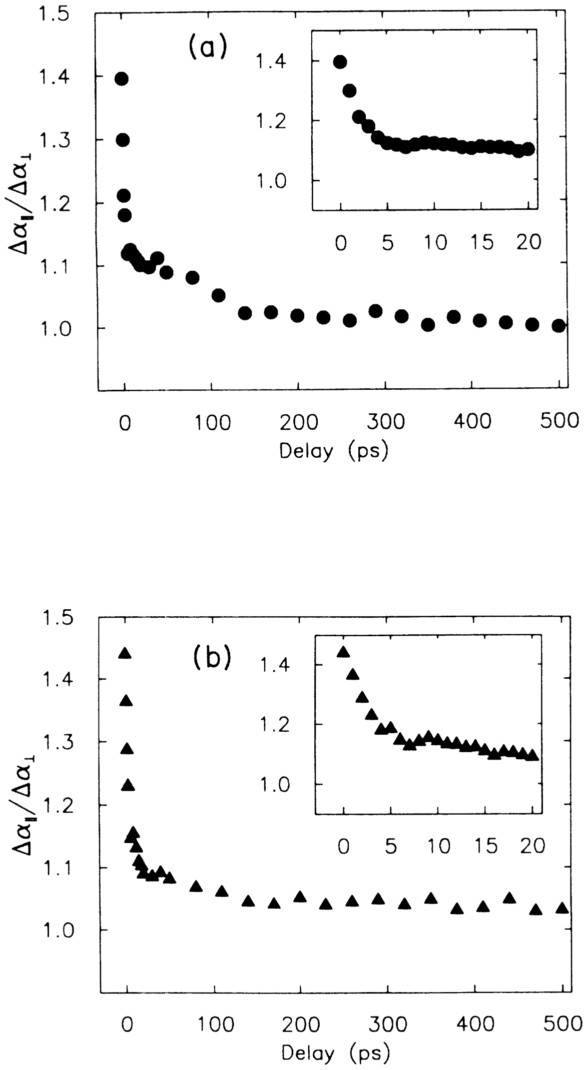

FIG. 4. Photoinduced dichroism at 2.06 eV (ratio of parallel and perpendicular curves in Fig. 1) for (a) P3HT and (b) P3OT.

IV. DISCUSSION

A quantitative comparison of the bleaching signal observed when the pump and probe are degenerate with the absorption signal when the pump and probe are nondegenerate must consider the different processes which contribute at each energy, following direct photogeneration of electron-hole pairs. If the electron and hole are generated on a single chain, then they will likely recombine quickly, because of their confinement by the lattice energy of the nondegenerate ground state,[1] and their attraction resulting from the (screened) Coulomb interaction. The radiative decay of this neutral "bipolaron exciton" in polythiophene has been monitored through the photoluminescence;[12] the measured luminescence lifetime (<10 ps) is far shorter than the natural radiative lifetime because of the dominance of the nonradiative pathway.[13,14]

Alternatively, free polarons (positive and negative) may be formed, either on the same chain, or separated onto neighboring chains. Light polarized parallel to the chains will form positive and negative polarons on the same chain; light polarized perpendicular to the chains will form positive and negative polarons separated onto neighboring chains.[14] In either case, the formation of polarons is expected to result in a shift of oscillator strength from the π-π^* transition to the localized gap states, and to an increase in the photoconductivity. Although the branching ratio for the formation of free polarons (relative to the neutral bipolaron exciton) on a single chain is not known, fast-transient-photoconductivity measurements on P3HT indicate that the single-chain free-pair-creation probability is greater than the probability of creating a pair separated onto neighboring chains.[15]

The photoinduced bleaching of the interband transition (Fig. 1) shows contributions indicative of these different processes. The fast component is consistent with a loss of oscillator strength to the neutral bipolaron exciton, decaying rapidly via a combination of radiative and nonradiative recombination. This channel apparently dominates the photoinduced bleaching, for only a small fraction ($\sim 5\%$) of the bleaching signal is observed as photoinduced absorption at 1.17 eV. However, a quantitative determination of the fraction of the oscillator strength which shifts into the gap-state transitions cannot be made without a more complete measurement of the photoinduced absorption spectrum in the picosecond regime.

The long-time bleaching response at 2.06 eV shows a minimum at $\cong 50$ ps, and a long-lived, nearly constant tail. The minimum is more pronounced when the probe beam is polarized perpendicular to the pump [dashed lines in Figs. 1(a) and 1(b)]. A similar dip has been observed in 1000-Å films of polythiophene, followed by a pronounced oscillation; this oscillation was interpreted as the result of a thermal strain wave.[8] In our measurements, however, no oscillation can be clearly resolved. The effects of such a thermally induced strain wave, if present in these measurements, would likely be damped out in our much thicker films. Since the nearly constant tail in the photoinduced bleaching is isotropic (the dichroism has fallen to nearly unity) and since it does not correlate with the decay of the 1.17-eV signal, we conclude that it is dominated by (possibly nonuniform) heating. The bleaching evident at negative time delays probably results from in-phase heating due to the chopped pump beam. This signal is decreased, but not eliminated, by reducing the cavity-dumper repetition rate.

The photoinduced absorption at 1.17 eV, by contrast, displays only a slower decay. In both P3HT and P3OT, the initial decay at 1.17 eV is exponential. In P3HT [Fig. 2(a)] the time constant of the initial decay is 150 ps; in P3OT [Fig. 2(b)] the time constant is 270 ps. Subsequent to about 60 ps in both materials, a clear crossover occurs from an exponential to a power-law decay, $t^{-\alpha}$. The exponent (α) of the power law is $\alpha \approx 0.37$ in P3HT and $\alpha \approx 0.22$ in P3OT. This crossover is consistent with an initial recombination of the excitations, limited after 60 ps by strong trapping. The decay of the transient photoconductivity in P3HT shows a similar response;[15] the photoconductivity initially decays in about 75 ps, followed by a power-law decay, providing evidence that the charged photoexcitations which contribute to the photoconductivity are the same species which cause the subgap photoinduced absorption.

We conclude that subsequent to photoexcitation, gap states form, with a shift of oscillator strength from the π-π^* interband transition to transitions involving the self-localized gap states. Although these purely electronic absorption measurements do not give direct information on the lattice relaxation, the shift in oscillator strength and the implied formation of states in the gap are consistent with self-localization as a result of structural relaxation to form polarons.[1] Steady-state photoinduced absorption measurements in P3HT show a broad feature peaking at ≈ 1.3 eV, which was identified with bipolarons.[16] However, the absorption signature of polarons should exhibit a peak at about the same energy; the 1.17-eV probe lies on the low-energy shoulder of this feature.

The photoinduced dichroism provides additional information on the dynamics of photogenerated excitations. For a sample with macroscopically random chain orientation (such as a spin-cast film), the observation of dichroism indicates local chain extension and alignment.[5] Light polarized parallel to the chains creates electron-hole pairs primarily on the same chain; light polarized perpendicular to the chains creates pairs primarily on different chains.[14] The dichroism, $\delta\alpha_\parallel/\delta\alpha_\perp$, defined as the ratio of the photoinduced signal for the pump-and-probe beams polarized parallel to each other to that with the polarizations at right angles, may be written[17]

$$\frac{\delta\alpha_\parallel}{\delta\alpha_\perp}=\frac{3(f_e+f_{p_\parallel})\alpha_\parallel+f_{p_\perp}\alpha_\perp}{(f_e+f_{p_\parallel})\alpha_\parallel+3f_{p_\perp}\alpha_\perp}\ . \tag{1}$$

In this equation, the subscripts e, $p_\parallel$, and $p_\perp$ refer to the neutral bipolaron exciton, intrachain polarons, and interchain polarons, respectively; f_i is defined by $f_i \equiv \eta_i \Delta\alpha_i$, where η_i is the quantum efficiency for generating excitations of type i, and $\Delta\alpha_i(\omega)$ is the change in absorption due to the existence of each excitation. $\alpha_\parallel$ and $\alpha_\perp$ are the absorption coefficients parallel to and perpendicular to the chains, respectively. If electron-hole pairs are excited only on single chains, then $\delta\alpha_{\parallel}/\delta\alpha_{\perp}$ initially should be 3; for increasing contributions due to excitations on different chains, this ratio decreases toward the isotropic value, $\delta\alpha_{\parallel}/\delta\alpha_{\perp}=1$. This equation does not include contributions from microscopically amorphous regions; in these regions a short-lived dichroism should be expected, rapidly disappearing as the excitations diffuse over the atomic-scale distances needed to destroy polarization memory on the randomly coiled chains. The fact that at the shortest times discernable with our resolution $\delta\alpha_{\parallel}/\delta\alpha_{\perp}<2$ is consistent with a significant fraction of the thin film samples being amorphous.[17,18]

Since the dichroism can decay only when the photoexcitations have diffused over distances such that the local chain axis is randomly oriented relative to where the excitations oriented, the decay of the polarization memory provides indirect information about the excitation mobility. The dichroism induced at 1.17 eV in P3HT [Fig. 3(a)] decays slowly, from 1.95 initially to 1.3 at 300 ps. Again, the decay shows a transition to a power-law decay after about 100 ps (exponent of 0.2). The dichroism in P3OT [Fig. 3(b)] decays more slowly, from 1.8 initially to 1.4 at 200 ps; again, a power-law decay is seen after about 100 ps (exponent of 0.1). For longer times, the dichroism changes very little, exhibiting a value of about 1.3 at 12 ns. This provides evidence that the self-localized photoexcitations diffuse slowly via multiple trapping and release after approximately the first 100 ps. This picture is strengthened by comparison with the photoconductivity data on P3HT taken under similar conditions: the photoconductivity falls more rapidly than the photoinduced absorption,[15] indicating that the carriers become essentially immobile well before they recombine.

The difference between the dichroism decay for the induced bleaching at 2.06 eV and that for the induced absorption at 1.17 eV again points to the different processes which contribute at each energy. In the bleaching of both materials [Figs. 4(a) and 4(b)] the dichroism decays rapidly ($\cong 5$ ps) from an initial value of about 1.4 to about 1.1, followed by a much slower decay to the isotropic value of 1.0. The rapid decay of the dichroism occurs on the same time scale as the decay of the bleaching in Fig. 1. This provides additional evidence that the fast decay is due to the contribution of the neutral bipolaron exciton: it is only formed subsequent to pair creation on *single* chains [see Eq. (1)], and hence shows a strong dichroism which decays with the decay of the excitation. Finally, as noted earlier, the absence of significant dichroism at long times in Fig. 4 (compared with Fig. 3) shows that the long-lived tail in the bleaching is primarily due to an isotropic effect such as the shift of the interband transition as a result of rapid heating of the sample by the pump beam.[19]

The principal difference between the photoinduced changes in absorption in the two materials is that the subgap photoinduced absorption, as well as the induced dichroism, decays more slowly in our P3OT films than in the P3HT films. This is reasonable in that the chains are slightly more separated in P3OT. However, other differences such as molecular weight and different preparation environment (relative number of defects) may contribute to these differences as well.

Photoinduced anisotropy in P3HT has also been demonstrated for macroscopically isotropic films in fast-transient-photoconductivity measurements. As with the photoinduced dichroism, the anisotropy in the transient photocurrent is determined by the relative sizes of the products, $\alpha_{\parallel}\eta_{p_{\parallel}}$ and $\alpha_{\perp}\eta_{p_{\perp}}$ [as in Eq. (1)].[15] Since the transient-photoconductivity data imply that $\alpha_{\parallel}\eta_{p_{\parallel}}>\alpha_{\perp}\eta_{p_{\perp}}$, we conclude that subsequent to the absorption of a photon in an intrachain ($\parallel$) process there is a significant branching ratio for the generation of free polarons, and that this branching ratio is sufficiently large to favor intrachain rather than interchain photogeneration of polarons (i.e., $\alpha_{\parallel}\eta_{p_{\parallel}}>\alpha_{\perp}\eta_{p_{\perp}}$). This is the case even though intrachain-generated polarons have higher energy than the confined neutral bipolaron exciton [at least within the Su-Schrieffer-Heeger (SSH) model].[1] Although the dynamics of the photogeneration process take place with the system far from equilibrium, the photogenerated excitations cool on a subpicosecond time scale, and a quasiequilibrium is established. In this regime, the intrachain branching ratio for polaron production may result from the increased entropy of polarons over bipolarons at low excitation densities.[20]

V. CONCLUSIONS

A principal conclusion of the experimental results is that there is rapid trapping of the photoinduced carriers. This is implied by the long-lived polarization memory (in photoinduced absorption) and by the clear evidence that the carriers become immobile well before they recombine. That the charged carriers seen in transient photoconductivity are the same species as those which cause the subgap photoinduced absorption reported here is reasonable based on the comparison of the decays in the two experiments: the decay of the photoinduced absorption shows a crossover from an exponential to a power-law decay on the same time scale that the photoconductivity dies away. Based on the excitation spectroscopy of the trapped species in the millisecond time scale (and longer), we infer that the long-lived trapped species are primarily bipolarons, whereas polarons are the dominant species in the picosecond regime. The time scale for conversion of like-charged polaron pairs into long-lived bipolarons is not presently known.

Subpicosecond bleaching of the interband π-π^* transition at 2.06 eV has been observed for P3HT and P3OT, similar to that reported for polythiophene. Accompanying this bleaching, we observe fast photoinduced absorption at 1.17 eV, indicating that rapid formation of gap states occurs in these nondegenerate ground-state polymers, consistent with the Su-Schrieffer mechanism. The size of the peak bleaching response (at 2.06 eV) is 20 times greater than the peak induced absorption (1.17 eV); this, together with the qualitative differences in the decay curves at the two energies; imply that only a fraction of the photoinduced bleaching results from a shift of oscillator strength to the self-localized gap states. It is impossible to deduce what this fraction is without a more complete frequency spectrum of the photoinduced changes.

We therefore emphasize that photoinduced bleaching is, by itself, not sufficient to establish the general validity of the mechanism. One must also demonstrate the shift of oscillator strength into the gap-state transition(s), as in *trans*-$(\mathrm{CH})_x$ and as implied for the P3AT's by the observation of photoinduced absorption at 1.17 eV following resonant photoexcitation. Based on these data, we conclude that the Su-Schrieffer mechanism provides a reasonable description of the final-state relaxation following photoexcitation in poly(3-hexylthiophene-2,5-yl) and poly(3-octylthiophene-2,5-yl).

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