Subpicosecond photoinduced electron transfer from conjugated polymers to functionalized fullerenes

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We report time-resolved excited state absorption measurements which demonstrate subpicosecond photoinduced electron transfer using soluble derivatives of poly(*p*-phenylene vinylene) as donors blended with a functionalized fullerene (methanofullerene) as acceptor. The subpicosecond photoinduced absorption spectra of the polymer/methanofullerene blends show that electron transfer from the donor to the acceptor occurs within a picosecond of photoexcitation of the conjugated polymer. Precise determination of the electron transfer dynamics was obtained by monitoring the dichroic ratio. The charge separated state is metastable and persists into the millisecond time domain, yielding an asymmetry of 10 orders of magnitude between the forward and reverse electron transfer times. The increased miscibility of the functionalized methanofullerene with the conjugated polymer is important for preparation of films with sufficiently high acceptor concentrations for practical devices based on photoinduced charge separation. [S0021-9606(96)51210-9]

I. INTRODUCTION

Recently, photoinduced electron transfer from conjugated polymers to C_{60} has been reported.[1] The forward electron transfer from the excited state of the conjugated polymer to the C_{60} occurs in the subpicosecond time domain.[2] Since the charge transfer is faster than any competing process by several orders of magnitude, the quantum efficiency for charge transfer and charge separation is nearly unity. The charge separated state is metastable, with the electron on the C_{60} and the positively charged hole remaining on the polymer chain. The photoinduced electron transfer improves the quantum efficiency for photogeneration of charge carriers; the photoconductivity increases over that of the polymer host. With addition of only 1% C_{60}, the peak transient photocurrent and the time constant for the decay of the photocurrent are enhanced by over an order of magnitude, resulting in several orders of magnitude increase of the steady state photoconductivity compared to the pristine polymer host.[3] The high quantum efficiency and metastability of the photoinduced charge separation have been utilized for the conversion of the photon energy into electricity in conjugated polymer/C_{60} photovoltaic cells.[4]

Because of the tendency for C_{60} to phase separate and crystallize, there is limited solubility of C_{60} in conjugated polymers. To achieve a high concentration of metastable excited states and efficient charge separation following photoexcitation, as required for applications, one needs to extend the solubility range. Furthermore, uniform, optical quality conjugated polymer/C_{60} thin films are required for optoelectronic device applications. To accomplish this, a series of soluble functionalized C_{60} derivatives has been synthesized.[5] The molecular structure of one of these, denoted as (6,6)PCBCa (phenyl-C_{61}-butyric acid cholesteryl ester; MW $=1164$) is shown in Fig. 1. With these soluble C_{60}-derivatives, one can make homogeneous, stable, optical quality films containing up to 1:1 mole fraction methanofullerenes in conjugated polymer matrices.

Since the functionalization of C_{60} via addition across a 6,6 ring junction reduces the number of π electrons in the molecule to 58 and causes a splitting of the LUMO energy levels, it is necessary to verify whether the photoinduced electron transfer from conjugated polymer to methanofullerene occurs on a time scale comparable to the subpicosecond electron transfer time found earlier in conjugated polymer/C_{60} blends. We report here the subpicosecond photoinduced absorption spectra of the polymer/methanofullerene blends which show that electron transfer from the donor to the acceptor occurs within a picosecond of photoexcitation of the conjugated polymer. Precise determination of the electron transfer dynamics was obtained by monitoring the dichroic ratio. The charge separated state is metastable and persists into the millisecond time domain, yielding an asymmetry of 10 orders of magnitude between the forward and reverse electron transfer time. The photophysical properties of conjugated polymer/methanofullerene composites are essentially identical to those of conjugated polymer/C_{60} composites. Because of the improved miscibility of the methanofullerenes in conjugated polymers, the functionalization of C_{60} provides a promising approach toward improvement of the optoelectronic performance of the devices made from these blends.

II. EXPERIMENT

The two conjugated polymers used in this study were poly [2-methoxy-5- (2′-ethyl-hexyloxy) *p*-phenylene vinylene)], (MEH-PPV) and poly[2,5-bis(cholestanoxy)1,4-phenylene vinylene] (BCHA-PPV). Both polymers were obtained from UNIAX Corporation and used as received. The

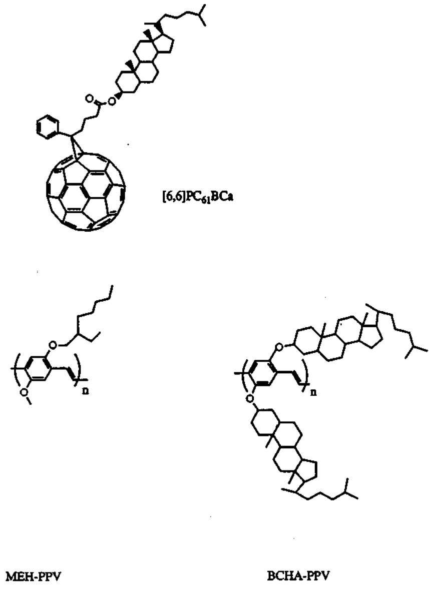

FIG. 1. Molecular structure for [6,6]PCBCa, MEH-PPV, and BCHA-PPV.

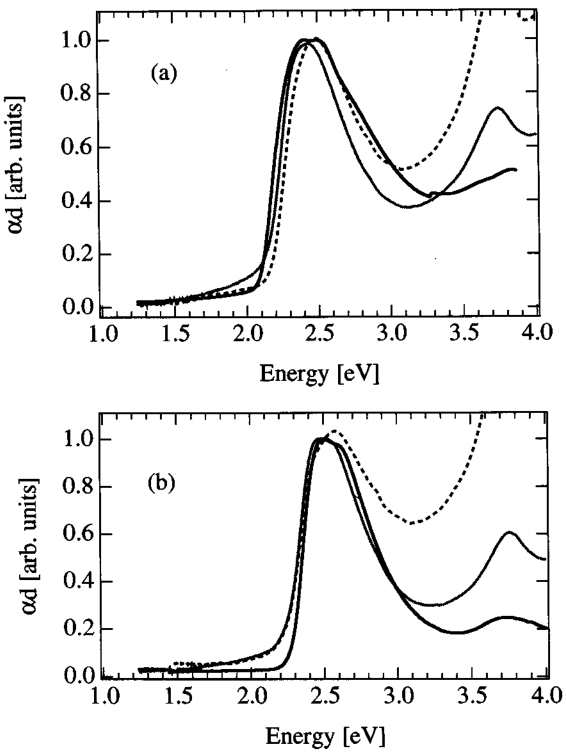

FIG. 2. Linear absorption spectra of MEH-PPV and MEH-PPV/[6,6]PCBCa blends (a) and of BCHA-PPV and BCHA-PPV/[6,6]PCBCa (b). The solid lines represent the pristine polymer, the dotted line represents the 2% blend of polymer and [6,6]PCBCa, and the dashed line represents the 50% blend.

synthesis and characterization of the methanofullerene 1-(3-cholestanoxycarbonyl)propyl-1-phenyl [6,6]C_{61}, henceforth denoted as [6,6]PCBCa, has been described elsewhere.[5] Figure 1 shows the molecular structure of these polymers and the structure of the methanofullerene. Samples were prepared by dissolving [6,6]PCBCa with one of the PPV derivatives in xylene at a desired mole fraction, and then casting films onto sapphire substrates. The samples were optically uniform and showed no signs of crystallinity when viewed between crossed polarizers under an optical microscope.

The pump-and-probe instrumentation for the time-resolved photoinduced absorption (PIA) measurements has been described in detail.[6] The sample was photoexcited with a 2.01 eV pump pulse (pulse width 100 fs) and was then probed after a given delay time using a broad band white-light continuum. For measurement of the dichroic ratio, a 40 meV slice of the continuum centered at 1.38 eV was used to probe the sample. A polarizer, which was rotated by a stepping motor, was placed in the probe beam prior to the sample to select parallel or perpendicular polarization. The pulse width of the probe pulse at the sample was measured to be 150 fs using two-photon absorption in ZnSe.[7] For all measurements except the dichroic ratio, the polarization of the probe was parallel to that of the pump. The experiments were carried out with the sample at 300 K in a dynamic vacuum of 10^{-5} Torr.

For the millisecond PIA experiments, the 514.5 mm line of an argon ion laser was used to photoexcite (pump) the sample; the change in absorption was detected by monitoring a white light probe beam using a single grating monochromator and phase sensitive detection. A more detailed description of this apparatus has been published.[8]

III. RESULTS AND DISCUSSION

A. Linear absorption and the absence of the ground state charge transfer

The linear absorption spectra of the pristine PPV's and of the blends of the PPV's with [6,6]PCBCa are shown in Fig. 2. The addition of up to 50% [6,6]PCBCa to the PPV's does not alter the π–π^* transition. The increase in absorption at 3.75 eV is associated with the dipole-allowed transitions of [6,6]PCBCa; the weak tail in the absorption extending into the gap results from the weak absorption of [6,6]PCBCa in this region. Thus, the spectrum is essentially a simple superposition of the absorption spectra of the constituents. We conclude that there is no significant charge transfer in the ground state. This conclusion is supported by the fact that no increase in the dark conductivity was observed in blends of MEH-PPV and C_{60}, as would be expected in the case of ground state doping. On the contrary, however, the photoconductivity increased by several orders of magnitude.[3]

B. Subpicosecond photoinduced absorption

The picosecond time regime PIA spectra for the two composites, each with 2% [6,6]PCBCa, are shown in Fig. 3 along with the millisecond time regime PIA spectra of the same samples. The small oscillations on the picosecond spectra are due to fluctuations in the intensity of the continuum, and should be considered as artifacts. At early times

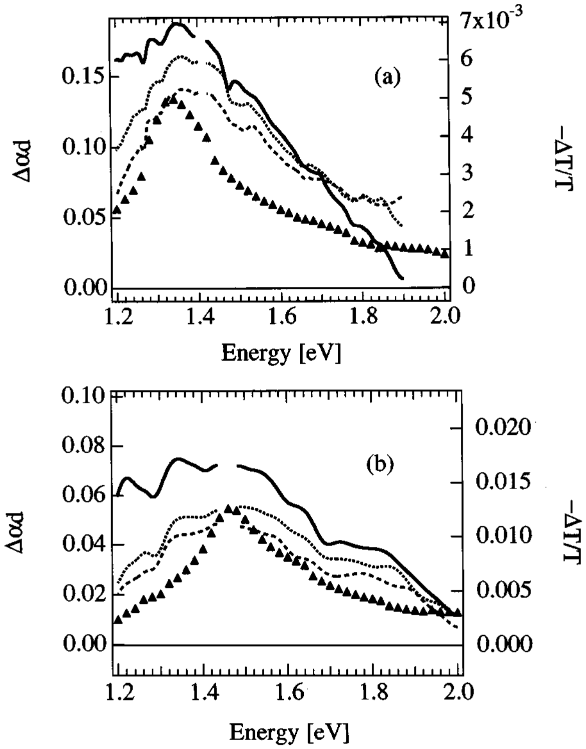

FIG. 3. The PIA spectra of a 2% mole fraction blend of MEH-PPV/[6,6]PCBCa (a) and of a 2% mole fraction blend of BCHA-PPV/[6,6]PCBCa (b). The solid line is the 1.2 ps spectra, the dotted line is the 10 ps spectra, and the dashed line is the 100 ps spectra. The solid triangles represent the millisecond PIA spectra.

(approximately 1 ps) after photoexcitation, the picosecond PIA spectra of both composites display a peak in the region near 1.4 eV (1.35 eV and 1.45 eV for MEH-PPV and BCHA-PPV composites, respectively) along with a shoulder extending to the low energy side. The latter is no longer apparent in the 10 ps spectra. The significance of this rapidly-decaying shoulder will be discussed in more detail below. The rapid formation of the PIA bands has been observed in blends of MEH-PPV and BCHA-PPV with C_{60} and is a distinct signature of the charge separated state.[1,2,8] Furthermore, the strong increase in the lifetime of these photoinduced bands enables the correlation of the millisecond PIA studies with the subpicosecond PIA response, as shown in Fig. 3. The curves in Fig. 3 with the solid triangles show the millisecond PIA spectra, which peak at 1.35 eV in MEH-PPV/[6,6]PCBCa and at 1.46 eV in BCHA-PPV/[6,6]PCBCa. The similarity between the picosecond PIA spectrum and the ms PIA spectrum implies that the photoexcitations observed in these two time regimes are the same.

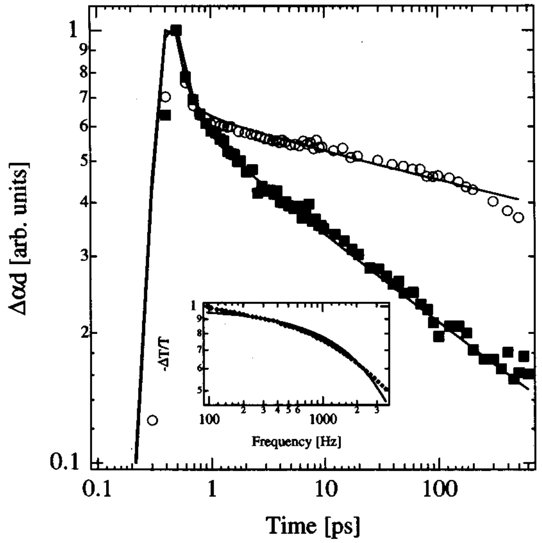

FIG. 4. The time dependence of the PIA at 1.45 eV of MEH-PPV (solid squares) and of MEH-PPV/[6,6]PCBCa (2%) (open circles). The fits are to power laws with exponents given in the text. The inset shows the frequency dependence of MEH-PPV/[6,6]PCBCa (2%) fitted to a bimolecular recombination equation with a bimolecular coefficient of 1.6 ms.

C. Decay of the subpicosecond photoinduced absorption

The enhanced lifetime of the charge separated state in both polymer/[6,6]PCBCa blends is also evident from the dynamics of the PIA at 1.45 eV in comparison to the dynamics of the PIA in pure polymer host at the same probe energy (see Figs. 4 and 5). The thin solid lines in Figs. 4 and 5 are fits using equation[11]

$$\Delta\alpha(\tau)\propto\int dtI_{\mathrm{pb}}(t-\tau)\int dt'\,\theta(t-t')I_{\mathrm{pp}}(t'). \tag{1}$$

In this expression t is the relative time delay between the pump and the probe pulses, I_{pp} represents the pump pulse intensity profile, and I_{pb} represents the probe pulse intensity profile. $q(t-t')$ is a step function, and $R(t-t')$ is the re-

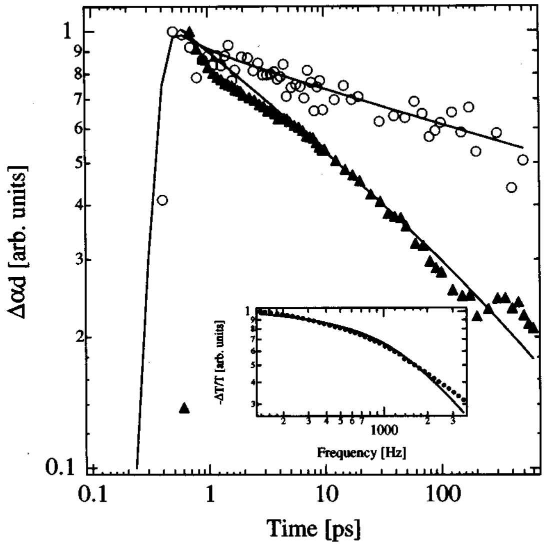

FIG. 5. The time dependence of the PIA at 1.45 eV of BCHA-PPV (solid triangles) and of BCHA-PPV/[6,6]PCBCa (2%) (open circles). The fits are to power laws with exponents given in the text. The inset shows the frequency dependence of BCHA-PPV/[6,6]PCBCa (2%) fitted to a bimolecular recombination equation with a bimolecular coefficient of 1 ms.

sponse function which describes the dynamics of the system with $R(t)=At^{-\alpha}$, where $\alpha=0.2$ for pure BCHA-PPV and $\alpha=0.08$ for BCHA-PPV/[6,6]PCBCa. The data clearly show the longer lifetime of the photoexcitations in the blend compared to the pristine polymer.

In the MEH-PPV case (Fig. 4), the relaxation is complex. In both pure MEH-PPV and MEH-PPV mixed with 2% M [6,6]PCBCa an initial sharp decrease of the photoinduced absorption is observed (at times less than 700 fs). At approximately 700 fs, however, a slower decay becomes dominant; this slower component is enhanced in the charge transfer blend compared to pristine polymer. The slow component can be well described with $R(t)=At^{-\alpha}$, where $\alpha=0.2$ for pure MEH-PPV and $\alpha=0.07$ for MEH-PPV/[6,6]PCBCa. We propose that the initial decay corresponds to the geminate recombination of the initial photoexcitations. For the 2% M blend, this initial decay is observed even in the presence of deep traps in form of [6,6]PCBCa. This implies that the initial photoexcitations have to migrate over significant distances on the polymer chains in order to encounter the [6,6]PCBCa molecules as acceptors.

For the 2 M% mixture, the average separation between [6,6]PCBCa molecules is approximately 50 monomer units. Thus, assuming the excitation is localized on one unit cell, the average distance the initial photoexcitation has to travel before encountering an acceptor is 100 Å. Using the relation $l\approx(Dt)^{1/2}$, where l is the diffusion length ($\approx$100 Å), D the diffusion constant and t the travel time ($\approx$700 fs), one estimates the diffusion constant to be on the order of $D\approx1$ cm^2/s. Using Einstein's relation for mobility (μ) in a nondegenerate electron gas, $\mu\approx eD/k_BT$, where k_B is the Boltzmann constant, T the temperature, and e the electron charge, one can estimate the mobility of the photoexcitations to be on the order of $\mu\approx10$ cm^2/V s, far too large for conjugated polymers. We conclude, therefore, that the spatial extent of the initial photoexcitations is much greater than the monomer repeat unit; the excited state wave function is delocalized over many repeat units.

Assuming that the electron is transferred immediately at the first encounter of a photoexcitation with an acceptor, increasing the acceptor concentration should eliminate the initial fast decay component of the PIA. The large concentration of acceptors within the sample would make migration effects which occur prior to encountering an acceptor unobservable.

To check this assumption, we plotted the relaxation decay of the blends with 2% and 50% [6,6]PCBCa concentration in Figs. 6 and 7. Concentrating first on MEH-PPV/[6,6]PCBCa, we find that the fast component evident in the decay of the PIA at 1.45 eV and 1.2 eV in the 2% blend is not apparent in the 50% blend; compare Fig. 6 open circles vs solid circles. This fast component has a 200 fs lifetime (single exponential approximation) in the 2% blend, and is attributed to the fraction of the photoexcitations which recombine geminately prior to encounter with a [6,6]PCBCa acceptor (as discussed above). The complete quenching of the fast component in the 50% blend results from the higher concentration of acceptors in this blend; all photoexcitations encounter an acceptor prior to geminate recombination. Thus the quantum efficiency for charge transfer is even greater in the 50% blend than in the 2% blend. Once charge transfer has occurred, the decay of the PIA follows decay dynamics which are similar to the decay in the 2% blend.

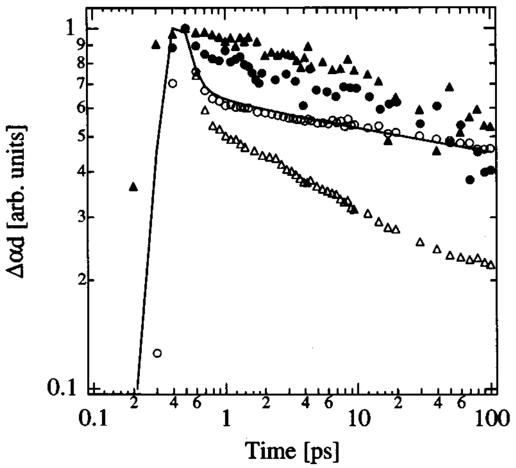

FIG. 6. The time dependence of the PIA of MEH-PPV/[6,6]PCBCa (2%) at 1.45 eV (open circles) and at 1.2 eV (open triangles), and of MEH-PPV/[6,6]PCBCa (50%) at 1.45 eV (closed circles) and at 1.2 eV (closed triangles).

In BCHA-PPV/[6,6]PCBCa, however, neither the rapidly decaying shoulder at 1.2 eV nor the slower peak at 1.45 eV are sensitive to higher concentrations of [6,6]PCBCa acceptors (Fig. 7). The origin of this insensitivity is not clear. One possibility is that there is a greater tendency for the [6,6]PCBCa acceptors to phase separate in BCHA-PPV so that higher concentrations do not lead to stronger D/A interaction. This would be surprising, however, for the molecular

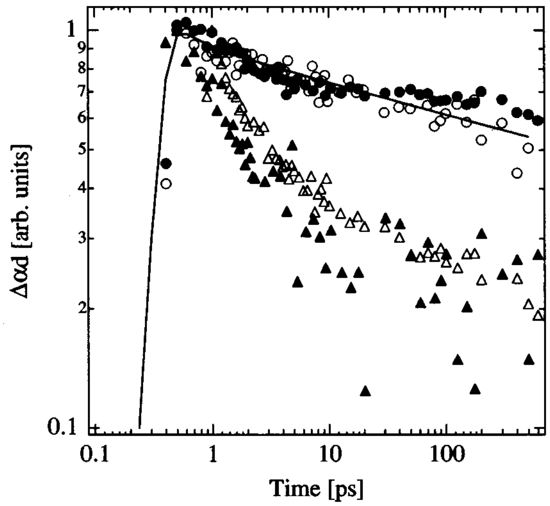

FIG. 7. The time dependence of the PIA of BCHA-PPV/[6,6]PCBCa (2%) at 1.45 eV (open circles) and at 1.2 eV (open triangles), and of BCHA-PPV/[6,6]PCBCa (50%) at 1.45 eV (closed circles) and at 1.2 eV (closed triangles).

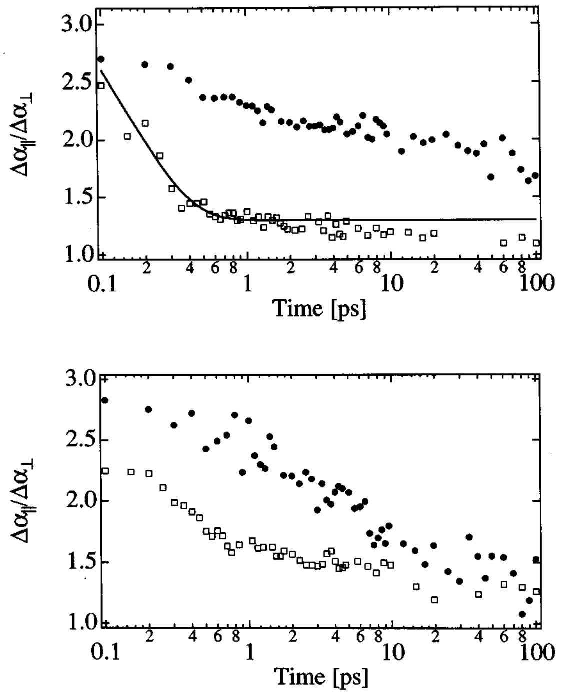

FIG. 8. (a) shows the dichroic ratio of MEH-PPV (solid circles) and of a 2% blend of MEH-PPV/[6,6]PCBCa (open squares). The solid line is a fit using a single exponential with a 200 fs time constant. (b) shows the dichroic ratio of BCHA-PPV (solid circles) and of a 2% blend of BCHA-PPV/[6,6]PCBCa (open squares). The decay time for BCHA-PPV/[6,6]PCBCa is approximately 1 ps. The probe energy is 1.38 eV for both (a) and (b).

structures of the side chains on BCHA-PPV and [6,6]PCBCa are similar.

D. Photoinduced dichroism

The decay time of the photoinduced dichroism shown in Fig. 8 sets an upper limit on the time scale of the forward electron transfer. The dichroic ratio is defined as the ratio of the photoinduced absorption with the pump and probe polarization vectors parallel, to that with the polarization vectors perpendicular[9]

$$\frac{\delta\alpha_{\parallel}}{\delta\alpha_{\perp}}=\frac{3(f_e+f_{p_\parallel})\alpha_\parallel+f_{p_\perp}\alpha_\perp}{(f_e+f_{p_\parallel})\alpha_\parallel+3f_{p_\perp}\alpha_\perp}. \tag{2}$$

In this expression the subscripts e, $p_\parallel$, and $p_\perp$ refer to neutral bipolaron excitons, intrachain and interchain polarons, respectively, and f_i is defined by $f_i \equiv \eta_i \Delta\alpha_i(\omega)$, where η is the quantum efficiency for generating excitations of type i, and $\Delta\alpha_i(\omega)$, is the change in absorption due to these excitations. Because of the delocalization of the $\pi-\pi^*$ electrons on an individual chain and the weak interchain coupling, the optical absorption matrix elements are strongest when the light is polarized along the chains. Highly oriented MEH-PPV, for example, shows $\alpha_\parallel/\alpha_\perp \approx 100$.[10] Thus, since the initially excited electron-hole pairs are created predominantly on individual chains, the dichroic ratio should be approximately 3 at the earliest times. In the pure material, the dichroic ratio will approach the isotropic value, $\Delta\alpha_\parallel/\Delta\alpha_\perp=1$, after sufficient time has elapsed for interchain transfer or diffusion of the photoexcitations over relatively long distances. If charge transfer from the polymer to [6,6]PCBCa is more rapid, and if the photoinduced absorption in the polymer/[6,6]PCBCa mixtures results from an intermolecular transition, the charge transfer process will quickly destroy any memory of the polarization of the original transition dipole. In this case, the dichroic ratio is expected to approach the isotropic value more rapidly than in the pristine polymer.

Consequently, measurements of the time decay of the dichroic ratio in MEH-PPV, BCHA-PPV, and their blends with [6,6]PCBCa provide insight into the dynamics of photoexcitations. As shown in Fig. 8, the initial value of the photoinduced dichroic ratio is close to 3 in both pristine polymers, confirming that intrachain excitations are photogenerated by the pump radiation. For the pure materials, the decay of the dichroism occurs over a relatively long time scale, with $\Delta\alpha_\parallel/\Delta\alpha_\perp$ dropping from 3 to 2 in approximately 10 ps. With the addition of 2% [6,6]PCBCa, the dichroic ratio in both the MEH-PPV/[6,6]PCBCa blend and the BCHA-PPV/[6,6]PCBCa blend decreases much more rapidly, implying that the polarization memory of the photoexcitations is being destroyed much faster in these composites. This rapid decay is interpreted as due to subpicosecond photoinduced electron transfer from the conjugated polymer to the [6,6]PCBCa acceptor, and is consistent with previous measurements made on blends of the same PPV derivatives and C_{60}.[2] We note that the decay of the dichroic ratio is left unchanged after increasing the concentration of [6,6]PCBCa from 2% to 50%.

To fit the decay of the dichroic ratio a single exponential was used to estimate a lifetime of 35 ps for pure MEH-PPV and 200 fs for MEH-PPV/[6,6]PCBCa [Fig. 8(a)]. Although a single exponential does not provide a precise description of the data, the decay time is approximately 1 ps for BCHA-PPV/[6,6]PCBCa [Fig. 8(b)]. The slower decay of the dichroic ratio in BCHA-PPV/[6,6]PCBCa compared to the decay in MEH-PPV/[6,6]PCBCa is similar to earlier results obtained from composites of the same polymers with C_{60}. We suggest that the slower decay results from the influence of the bulky, symmetric side groups in BCHA-PPV,[2] which reduce the overlap of the excited state wave functions. Thus, the forward electron transfer process occurs more rapidly in the MEH-PPV/[6,6]PCBCa blend than in the BCHA-PPV/[6,6]PCBCa blend. The bulky asymmetric side groups on BCHA-PPV prevent optimum overlap of the excited state wave function, thereby causing a bottleneck for the forward electron transfer. Nevertheless, the results indicate forward transfer in less than a picosecond.

E. Millisecond photoinduced absorption in MEH-PPV based composites

The millisecond PIA spectra of pure MEH-PPV, MEH-PPV/[6,6]PCBCa (2%) and (50%) are compared in Fig. 9. In the MEH-PPV/[6,6]PCBCa blends, the peak in the millisecond PIA spectrum is red-shifted by approximately 60 meV compared to the peak in the picosecond regime. In addition,

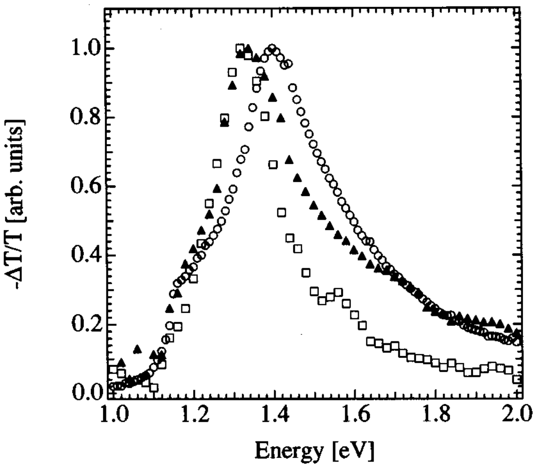

FIG. 9. The millisecond PIA spectra of MEH-PPV (open squares), MEH-PPV/[6,6]PCBCa (2%) (solid triangles), and of MEH-PPV/[6,6]PCBCa (50%) (open circles).

in the millisecond PIA spectrum, there is a significant asymmetry on the high energy side of the peak that extends beyond 2 eV and a small shoulder at 1.2 eV (see Fig. 9, solid triangles).

By measuring the dependence of the millisecond PIA on the chopping frequency, we were able to measure the lifetime of the charge separated state. The chopping frequency dependence (see insets to Figs. 4 and 5) of the charge separated state is best fit using a bimolecular recombination equation with a lifetime of 1.6 ms for the MEH-PPV composites compared to 1 ms for the BCHA-PPV mixtures. Thus, the asymmetry (ten orders of magnitude) in the forward and reverse electron transfer rates is remarkable, with the forward electron transfer occurring in the subpicosecond time scale and the reverse transfer occurring in the millisecond regime.

The PIA features for the pristine polymer films are dominated by the neutral triplet excitations in the millisecond time domain. [8,13,14] The small shoulder at 1.2 eV, and the large plateau extending beyond 2 eV in the MEH-PPV/[6,6]PCBCa spectra are similar to the spectral features of the MEH-PPV blends using pure C_{60},[1,8] their exact origin, however, is not known.

IV. CONCLUSIONS

We have demonstrated that subpicosecond photoinduced charge transfer occurs from both MEH-PPV and BCHA-PPV to a methanofullerene.

For MEH-PPV/[6,6]PCBCa blends, measurements of the decay of the dichroic ratio show that charge transfer occurs within 200 fs with a correspondingly high quantum efficiency for charge transfer. Increasing the concentration of [6,6]PCBCa from 2% mole fraction to 50% mole fraction results in a further increase in the quantum efficiency of charge transfer by eliminating photoexcitation decay during the initial diffusion of the photoexcitations prior to the electron transfer.

The dichroic ratio decay in blends of BCHA-PPV/[6,6]PCBCa shows a charge transfer time of order 1 ps. In this case, increasing the concentration of [6,6]PCBCa has no effect on the charge transfer time, as shown by the time dependence of the PIA. We attribute the slower charge transfer rate to the effect of the large symmetric side groups of BCHA-PPV which prevent optimum overlap of the excited state wave functions with a [6,6]PCBCa acceptor and act as an effective bottleneck for the electron transfer. However, the charge transfer is still more than two orders of magnitude faster than competing recombination processes, so that the quantum efficiency for charge transfer is very high in the BCHA-PPV/[6,6]PCBCa as well.

Finally, we compare the two systems studied here. The common features are the following:

(i) Similar linear spectra, i.e., no significant charge transfer in the ground state (see Fig. 2);
(ii) The addition of the methanofullerene has a similar effect on the time dependence of the PIA spectra when going from the pristine polymers to the blends (see Figs. 4 and 5);
(iii) Qualitatively similar dynamics and concentration dependences of the dichroic ratio (see Fig. 8).

The last two observations represent the signature of subpicosecond charge transfer in the blends.

Although direct evidence of ultrafast charge transfer is observed in both systems, the concentration dependence of the dynamics of the PIA spectra is different in the two systems (see Figs. 6 and 7). Qualitatively, we attribute these somewhat complex differences to the very different side groups on MEH-PPV and BCHA-PPV. The somewhat slower time scale for photoinduced electron transfer in BCHA-PPV blends is reasonable based on the more bulky BCHA side-groups; however, the insensitivity to concentration of [6,6]PCBCa in the BCHA-PPV blends is not understood. One possibility (as noted above) is that there is a greater tendency for the [6,6]PCBCa acceptors to phase separate in BCHA-PPV so that higher concentrations would not increase the D/A interaction.

These studies show that functionalization of C_{60} leads to enhanced solubility and processability and thereby provides a promising route to improving the efficiency of optoelectronic devices based on the photoinduced electron transfer from conjugated polymers onto buckminsterfullerene.[4] This is evident from the fact that high concentration blends of MEH-PPV (50%, see Fig. 6) show no initial decay of the photoinduced absorption; such early time decay of the excited state prior to charge transfer reduces the quantum efficiency of photoinduced charge separation. Thus, this study demonstrates that blends with high concentrations of acceptors and with high optical quality can be obtained by using functionalized derivatives of C_{60}. In this respect, however, the MEH-PPV blend appears to be superior to the BCHA-PPV blend. This tentative conclusion remains to be proven by tests currently underway using photonic devices based on these PPV-derivative/[6,6]PCBCa composites.

ACKNOWLEDGMENT

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[1] N. S. Sariciftci, L. Smilowitz, A. J. Heeger, and F. Wudl, Science **258**, 1474 (1992); see N. S. Sariciftci and A. J. Heeger (review), Int. J. Mod. Phys. B **8**, 237 (1994).

[2] B. Kraabel, D. McBranch, N. S. Sariciftci, D. Moses, and A. J. Heeger, Phys. Rev. B **50**, 18 543 (1994).

[3] C. H. Lee, G. Yu, D. Moses, K. Pakbaz, C. Zhang, N. S. Sariciftci, A. J. Heeger, and F. Wudl, Phys. Rev. B **48**, 15 425 (1993); K. Yoshino, X. H. Yin, S. Morita, T. Kawai, and A. A. Zakhidov, Solid State Commun. **85**, 85 (1993).

[4] N. S. Sariciftci, D. Braun, C. Zhang, V. Srdanov, A. J. Heeger, G. Stucky, and F. Wudl, Appl. Phys. Lett. **62**, 585 (1993); N. S. Sariciftci and A. J. Heeger, U.S. Patent 5 331 183, University of California, (1994); G. Yu, J. Gao, J. Hummelen, F. Wudl, and A. J. Heeger, Science **270**, 1789 (1995).

[5] J. C. Hummelen, B. W. Knight, F. LePeq, F. Wudl, J. Yao, and C. L. Williams, J. Org. Chem. **60**, 532 (1995).

[6] B. Kraabel, D. McBranch, N. S. Sariciftci, D. Moses, and A. J. Heeger, Mol. Cryst. Liquid Cryst. **256**, 733 (1994).

[7] T. F. Albrecht, K. Seibert, and H. Kurz, Opt. Commun. **84**, 223 (1991).

[8] L. Smilowitz, N. S. Sariciftci, R. Wu, C. Gettinger, A. J. Heeger, and F. Wudl, Phys. Rev. B **47**, 13 835 (1993).

[9] D. McBranch, A. Hays, M. Sinclair, D. Moses, and A. J. Heeger, Phys. Rev. B **42**, 3011 (1990).

[10] T. W. Hagler, K. Pakbaz, K. F. Voss, and A. J. Heeger, Phys. Rev. B **44**, 8652 (1991).

[11] Z. V. Vardeny and J. Tauc, *Picosecond Electronic Relaxations in Amorphous Semiconductors* (Academic, Orlando, 1984).

[12] W. P. Su and J. R. Schrieffer, Proc. Natl. Acad. Sci. USA **77**, 5626 (1980).

[13] L. Smilowitz and A. J. Heeger, Synth. Met. **48**, 193 (1992).

[14] Z. V. Vardeny and X. Wei, Mol. Cryst. Liquid Cryst. **256**, 465 (1995); J. Shinar, A. V. Smith, P. A. Lane, K. Yoshino, Y. W. Ding, and T. J. Barton, *ibid*. **256**, 685 (1995); X. Wei, Z. V. Vardeny, N. S. Sariciftci, and A. J. Heeger, Phys. Rev. B (in press).