Charge Separation and Recombination in a Photoconducting Polymer with Electron Donor−Acceptor Complexes

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The dynamics of electron−hole (e−h) pairs created by photoexcitation of charge-transfer (CT) states in films and solutions of oligomeric poly-*N*-epoxypropylcarbazole (PEPCz) doped with electron-accepting trinitrofluorenone were studied by investigating polarized transient absorption kinetics and spectra with picosecond and femtosecond time resolution. We observed very fast formation of the carbazolyl radical cation in PEPCz films, within the 100 fs excitation pulse. Transient anisotropy, which was calculated from polarized kinetics at the time delays of 100 fs and longer, is about 5 times lower in the films than in the solution of a monomeric analogue. This very fast loss of the excitation polarization memory in the films is attributed to hole transfer from the parent carbazolyl (Cz) moiety to the neighboring Czs. An asymptotic decay of the anisotropy is observed on the picosecond time scale, indicating that the fast charge separation is completed within a few picoseconds. The geminate recombination of e−h pairs in PEPCz films is nonexponential and extends into the nanosecond time domain. A dependence of the primary e−h separation efficiency on the excitation photon energy is concluded from recombination dynamics. After photoexcitation, limited hole transfer also occurs in PEPCz solution on the short oligomer chain, but recombination is much faster than in the films.

Introduction

Charge carrier photogeneration and transport in polymers with aromatic chromophores as side groups or with the chromophores dispersed in inert polymeric binders have been extensively studied during the last 2 decades. These processes are decisive for the photoconductive properties of polymeric matrixes and films. Carbazolyl (Cz) chromophores are among the most widely used moieties for charge photogeneration and transport in flexible electrophotographic layers, and poly-*N*-vinylcarbazole (PVK) has already been used for more than 30 years. PVK seems to be the most extensively investigated photoconducting polymer so far.[1] Recently, efficient photorefractive compositions based on PVK as a photoconducting matrix for electro-optical guest molecules or chemically modified polymers have also been developed.[2−4] The chemical structure effect on the photophysical processes can be understood by investigation of other Cz-containing polymers. For instance, it was discovered that polymers, which in contrast to PVK do not form excimer sites, possess higher photoconductivity.[5,6] Poly-*N*-epoxypropylcarbazole (PEPCz) is a good example of such a polymer.[7,8]

By now it is commonly accepted that charge carrier photogeneration in molecular solids with low dielectric constant ($\epsilon \approx 3-4$), such as PVK, PEPCz, and many molecular crystals, involves two main stages: formation of Coulombically bound geminate electron−hole (e−h) pairs and dissociation of these e−h pairs into free charge carriers.[9,10] Formation of the loosely bound e−h pair in molecular crystals of acenes, such as anthracene, tetracene and pentacene, has been attributed to

thermalization of hot e−h pairs,[10−12] created by autoionization of the excited neutral electronic state[10,11] or by direct photoexcitation of a charge-transfer (CT) state.[13] The photoconductivity of Cz-containing polymers is enhanced and extended into the visible part of the spectrum by adding electron acceptors, which form CT complexes with electron-donating Czs, and bound e−h pairs are created directly via photoexcitation of the CT state.[14] The dissociation of the thermalized e−h pairs has been described by means of the Onsager theory of geminate charge pair dissociation.[15] By application of this theory to the electric field dependence of the photogeneration efficiency, the initial separation distance r_0 of the thermalized e−h pairs in molecular crystals[10−12,16] and amorphous films[14,17,18] has been estimated. Assuming the δ-type initial distribution of the thermalized e−h pairs, the value $r_0 = 30 \pm 5$ Å was obtained for the PVK films doped with tetracyanobenzene (TCNB)[14] and trinitrofluorenone (TNF).[17] M. Yokoyama et al.[14] have studied the field-induced quenching of the CT luminescence and from the excitation wavelength dependence have suggested that the initial e−h separation occurs via the thermalization of the higher excited CT state. The main idea of such a charge-separation process from the nonrelaxed excited state is somewhat close to the ballistic charge pair thermalization model,[10−12] which implies that the charge pair separation is very fast in comparison to the migration of the thermalized charge. Monte Carlo simulations of the dissociation showed that energy disorder augments charge separation;[19] these calculations also indicated that the r_0 value is overestimated when the conventional Onsager theory is applied to disordered organic systems. This conclusion is also supported by the measured temperature dependence of the charge carrier yield,[20] which differs from Arrhenius dependence.

On the other hand, polarized transient absorption studies of PVK films[21] and solutions[22] doped with TCNB and TNF

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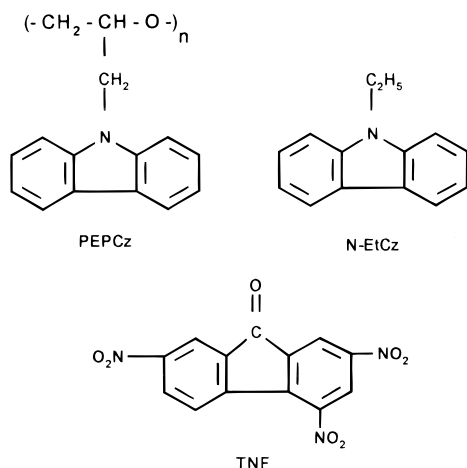† Institute of Physics.
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Figure 1. Chemical structures of the studied compounds.

revealed only rather slow 0.5−2 ns hole drift between carbazolyl moieties, implying a negligible impact of the excess thermalization energy on charge separation. However, comparison of Monte Carlo simulations of the three-dimensional hole migration with the hole scavenging dynamics in PVK films[23] suggested that the initial e−h separation r_0 is larger than the distance between electron donor and acceptor.

A mechanism of slow charge pair separation, following internal conversion and proceeding during the entire excited-state lifetime, was proposed by Noolandi and Hong.[24] It was supported by the wavelength dependence of the charge carrier yield observed in, for instance, some metal-free phthalocyanines.[25] Recent studies of charge photogeneration in the Y form of titanyl phthalocyanine demonstrate, however, that the charge-separation process is fast, occurring on a subpicosecond time scale.[26] Thus, a general mechanism of the charge photogeneration in organic photoconductors is not yet available, and the rate as well as molecular properties and physical conditions responsible for the efficiency of the process remains to be established.

In this contribution, the picosecond and femtosecond dynamics of the photogenerated ion pairs in poly-*N*-epoxypropylcarbazole (PEPCz) are examined by measuring polarized transient absorption spectra and kinetics in films and solutions of PEPCz and its monomeric analogue. From our results, it appears that charge separation after the excitation of the CT state occurs on the subpicosecond time scale via ultrafast hole transfer. Processes observed in PEPCz can be generalized, and the main conclusions drawn in this work should, therefore, be applicable to other amorphous organic photoconductors as well.

Experimental Section

Oligomeric PEPCz was synthesized by ionic polymerization of *N*-epoxypropylcarbazole. The number-averaged molecular mass as determined by gel-permeation chromatography was M_n = 1120, and the weight-averaged molecular mass was M_w = 1200. PEPCz was developed in Lithuania and used in organic electrophotography.[6−8] We studied PEPCz films and solutions doped with a typical electron-accepting substance, 2,4,7-trinitro-9-fluorenone (TNF). *N*-Ethylcarbazole (EtCz) was used as a PEPCz monomeric analogue. The chemical structures of these compounds are shown in Figure 1. PEPCz was reprecipitated 3 times from a benzene-methanol solution, and EtCz and TNF were recrystallized from benzene. When preparing samples, PEPCz or EtCz was first dissolved in 1,2-dichloroethane; then the acceptor was added into the solution. Polymer films were

prepared by casting the solution onto glass substrates, and the solvent was evaporated by drying for 5−6 h at a temperature of 60−65 °C. The film thickness measured with a Linnik microinterferometer was in the range 5−6 μm. The solvent 1,2-dichloroethane was stored over phosphorus pentoxide and distilled immediately prior to use.

Transient absorption spectra and most of the kinetics presented in this paper were measured with 3 ps time resolution using a conventional pump−probe spectrometer based on a passively mode-locked, feedback-controlled, and regeneratively amplified Nd[3+]:glass laser with a 1 Hz pulse repetition rate. Frequency-doubled and Raman-shifted pulses were used for excitation, and a white-light continuum generated in water was used for probing at variable delays. Signal and reference probe beams were spectrally filtered by a monochromator placed after the sample. No excitation intensity dependence of kinetics and spectra was observed over the 1−100 mJ/cm^{2} intensity range. Polarized transient absorption kinetics in PEPCz films were also measured with approximately 150 fs time resolution using a similar detection scheme as that for the picosecond measurements. In these experiments, samples were excited using 100 fs light pulses at a 5 kHz repetition rate from an optical parametric generator/amplifier pumped by an amplified Ti: sapphire laser system. A white-light continuum probe was generated by focusing part of the amplified Ti:sapphire pulses into a sapphire plate. Ground-state absorption spectra were recorded with a Jasco V-530 spectrophotometer. All measurements were carried out at room temperature.

Results

The absorption spectra of EtCz and PEPCz oligomer complexes with TNF in 1,2-dichloroethane are shown on a logarithmic scale in Figure 2a. The solutions have strong absorption bands at approximately 4.8, 4.2, and 3.6 eV due to the absorption of the carbazolyl (Cz) group and a more than 10 times weaker absorption band at 3.2 eV of TNF molecules. Additional, much weaker absorption appears in the visible spectral region due to the formation of $Cz^{\delta+}-TNF^{\delta-}$ CT complexes.[27] This absorption is shown more clearly in Figure 2b for the PEPCz film doped with 0.5 mol % of TNF. The red wing of the absorption spectrum of the doped film contains at least two bands, which can be approximated by two Gaussian functions. The deconvolution parameters of the absorption spectra of film and solutions are presented in Table 1. The differences between the parameters of the various samples are on the order of the experimental and fitting uncertainty, indicating that the formation of the $Cz^{\delta+}-TNF^{\delta-}$ complex does not depend significantly on whether the Cz group resides in the oligomer or is a monomeric analogue.

It is well-known that Cz-containing compounds doped with electron-accepting materials exhibit at least two CT bands.[27] The lowest energy CT band reflects the electron transition from the first HOMO of Cz to the LUMO of an electron-accepting molecule, whereas the higher energy CT band reflects the transition from the second HOMO of the Cz. The energy difference between the first and second HOMO orbitals in the Cz chromophore is about 0.5 eV.

Figure 3 shows the transient absorption spectra of the EtCz and PEPCz solutions with 5 mol % of TNF as well as that of a PEPCz film containing 2 mol % of TNF. The spectra were obtained for zero time delay between excitation and probe pulses. The transient absorption band with a maximum at approximately 800 nm is ascribed to the carbazolyl cation radical (Cz^+) and the transient absorption at $\lambda \leq 650$ nm to the TNF

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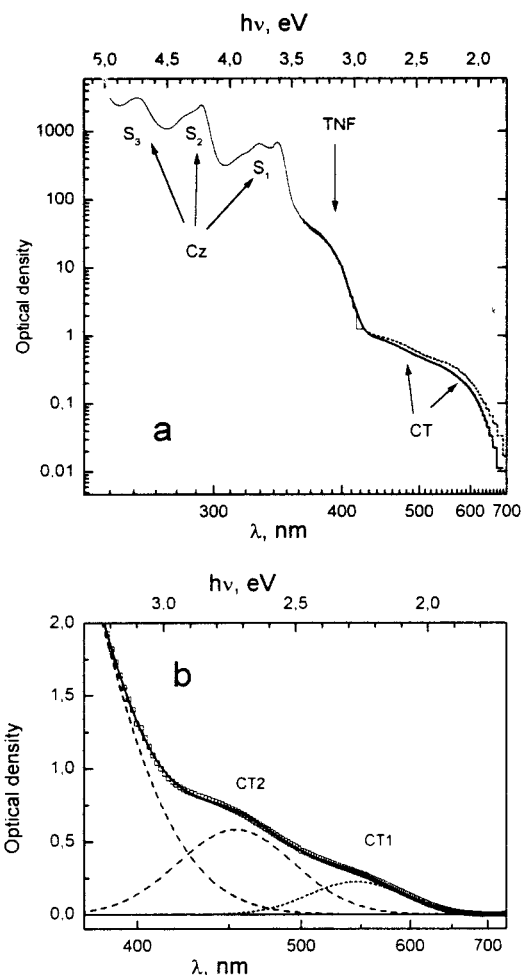*J. Phys. Chem. B, Vol. 102, No. 38, 1998* **7367**

Figure 2. (a) Absorption spectra of EtCz (dashed line) and PEPCz (solid line) solutions with 5 mol % of TNF molecules in 1,2-dichloroethane. The arrows indicate the positions of carbazolyl, TNF, and intermolecular charge transfer (CT) bands. (b) Absorption spectrum of a PEPCz film doped with 0.5 mol % TNF. The CT absorption region with deconvolution of the spectrum by Gaussian bands is shown.

TABLE 1: Fit Parameters for Deconvolution of the Absorption Spectrum of Cz−TNF Complexes into Two Gaussian Bands

	EtCz solution with 5 mol % TNF	PEPCz solution with 5 mol % TNF	PEPCz film with 0.5 mol % TNF
central energy 1, eV	2.28	2.3	2.27
width 1, eV	0.44	0.4	0.35
amplitude 1, AU	0.189	0.145	0.1
central energy 2, eV	2.77	2.81	2.72
width 2, eV	0.42	0.44	0.44
amplitude 2, AU	0.45	0.46	0.32

anion radical.[28] No temporal evolution of ΔA spectrum was observed within experimental accuracy in the experiments with 3 ps resolution.

Figure 4a shows the transient absorption kinetics at 800 nm in EtCz−TNF solution. The upper trace corresponds to perpendicular polarization of the excitation and probe light, while the lower trace is for parallel polarization. The transient absorption decay is monoexponential with a time constant of 45 ps. Figure 4b shows the time evolution of the transient absorption anisotropy calculated from the traces at parallel ($\Delta A_{\parallel}$) and perpendicular ($\Delta A_{\perp}$) excitation and probe polarization as

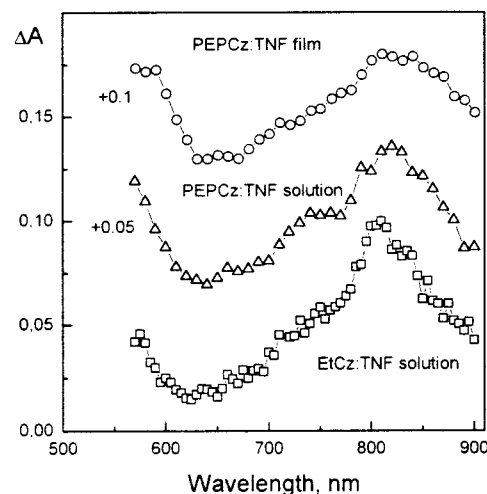$$r = (\Delta A_{\parallel} - \Delta A_{\perp})/(\Delta A_{\parallel} + 2\Delta A_{\perp}) \qquad (1)$$

Figure 3. Zero delay time differential absorption spectra of PEPCz film doped with 2 mol % TNF (circles) and PEPCz (triangles) as well as EtCz (squares) solution in 1,2-dichloroethane with 5 mol % TNF. Light pulses at 527 nm and 3 ps duration were used for excitation.
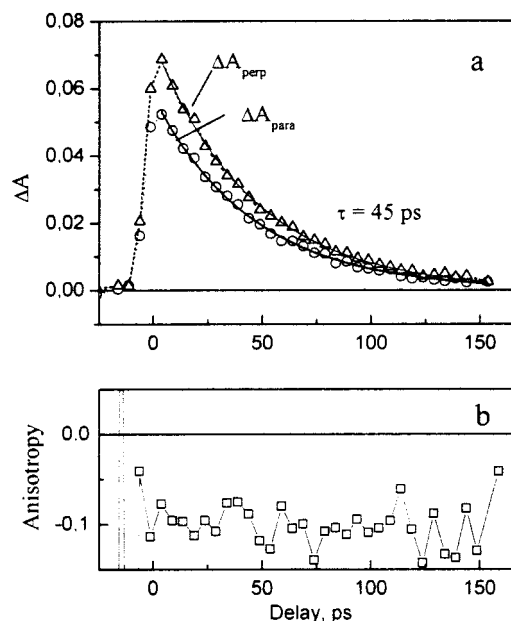

Figure 4. (a) Transient absorption kinetics of an EtCz−TNF solution excited at 527 nm and probed at 800 nm for parallel (circles) and perpendicular (triangles) polarizations of the probe light. Solid lines are monoexponential fits with a time constant of 45 ps. (b) Time dependence of the transient anisotropy calculated from the polarized kinetics.

Within experimental accuracy the anisotropy $r = -0.1$ is constant during the entire excited-state lifetime. According to the Perrin equation

$$r = \frac{1}{5}(3\cos^2\varphi - 1) \qquad (2)$$

this anisotropy value corresponds to an angle of $\varphi \approx 66°$ between the transition dipole moments from the ground state to the CT state and that of the absorption of the Cz$^+$. This angle should be considered only as very approximate, since other factors such as electronic−vibrational coupling or solvation effects usually also reduce the transient anisotropy. An angle close to 90° is expected, since it is known that the Cz$^+$ absorption dipole moment is in the plane of a Cz moiety, while the CT transition dipole moment is along the direction between
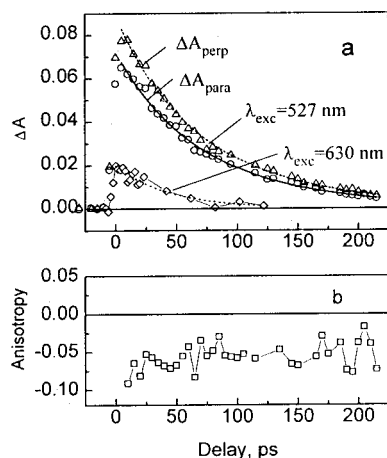
Figure 5. (a) Transient absorption kinetics at $\lambda_{pr} = 800$ nm of a PEPCz-TNF solution excited at 527 nm for parallel (circles) and perpendicular (triangles) relative polarizations of the excitation and probe light. Solid lines are biexponential fits with time constants of 45 and 95 ps and relative amplitudes of 40% and 60%, respectively. (b) Time dependence of the transient anisotropy calculated from the polarized kinetics.
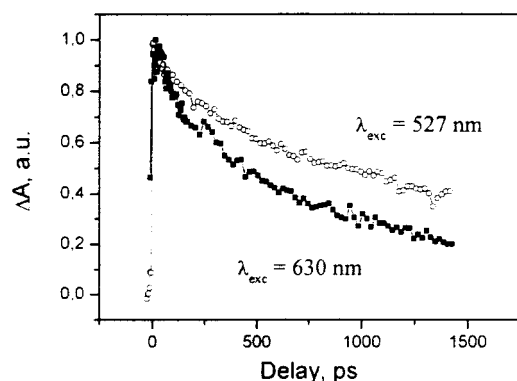

Figure 6. Transient absorption kinetics at $\lambda_{pr} = 760$ nm of PEPCz film doped with 0.5 mol % TNF excited by 3 ps pulses at 527 nm (upper trace) and at 630 nm (lower trace).

the Cz and TNF molecules. Rotational diffusion of the entire $Cz^+ - TNF^-$ complex is much too slow to affect the anisotropy relaxation on this time scale. This is also directly evident from the constant nondecaying anisotropy over 150 ps in Figure 4b.

The transient absorption kinetics of a PEPCz−TNF solution at different excitation wavelengths are presented in Figure 5a. A monoexponential decay with a time constant of 45 ps is observed when exciting at 630 nm, very similar to the recombination kinetics observed for the monomer solution. The relaxation after excitation at 527 nm is slower, and biexponential fitting in this case gives a short decay component of 45 ps, which is equal to that of the $EtCz^+ - TNF^-$ complex, while the long time component is ∼95 ps. The initial transient anisotropy is about −0.07 (Figure 5b) and decays to −0.05 during the first 50 ps.

Figure 6 shows the transient absorption kinetics at 800 nm in PEPCz films with 0.5 mol % TNF excited at 527 and 630 nm. At the shorter wavelength, the higher and the lower CT states are excited with approximately equal probability (Figure 2), while excitation at the long wavelength is into the lowest CT state. Both decays are nonexponential and much slower than the corresponding decays for solutions. The computer fitting of the kinetics by a biexponential function gives decay times for both excitation wavelengths of 180 ± 20 and 2000 ± 200 ps, while relative amplitudes of the fast decay component differ slightly: 19 ± 2% for 527 nm excitation and 30 ± 3%
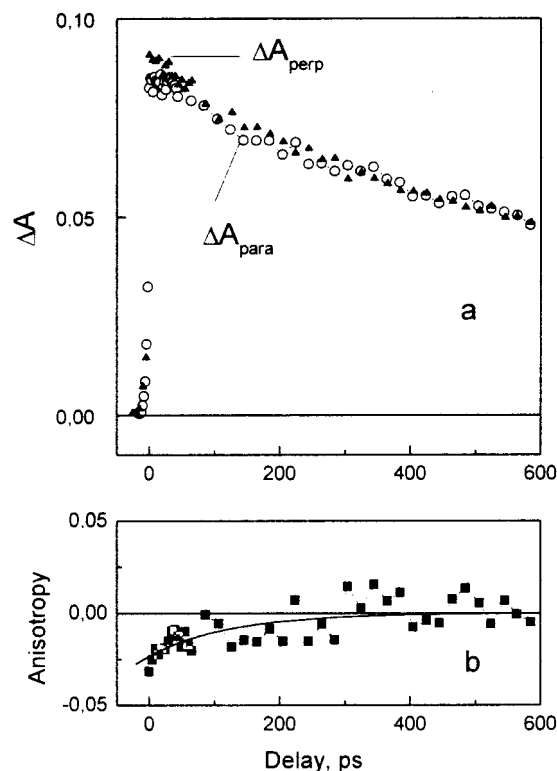

Figure 7. (a) Transient absorption kinetics at $\lambda_{pr} = 760$ nm of PEPCz film doped with 2 mol % TNF excited at 527 nm for parallel (circles) and perpendicular (triangles) polarizations of the excitation and probe light. (b) Time dependence of the transient anisotropy calculated from the polarized kinetics; solid line shows approximation by the exponential decay with a 120 ps time constant.

for 630 nm. The relaxation dynamics are not sensitive to the excitation intensity, indicating that the interaction between nongeminate e−h pairs is absent even at the highest excitation intensities and only geminate e−h recombination occurs.

Kinetics for parallel and perpendicular excitation and probe polarizations measured with the picosecond time resolution under 527 nm excitation are presented in Figure 7. The transient anisotropy calculated from the polarized kinetics is very low, only about −0.02, and decays within a few hundred picoseconds. A monoexponential fitting gives an ∼120 ps depolarization time, which due to the low experimental accuracy should be considered only as approximate. For some other films, the initial anisotropy was even lower. Polarized transient absorption was also measured using a femtosecond pump−probe technique (Figure 8). Kinetics exhibit a very fast formation of the Cz^+ absorption, and no significant dynamics of the transient absorption signal are observed on the subpicosecond time scale. Only a small depolarization from an initial anisotropy of −0.02 to a value of −0.01 with the ∼2 ps time constant is observed. The response function of the experimental setup did not allow resolution of the anisotropy decay at delay times shorter than 100 fs.

Discussion

We will first discuss the origin of the CT states and charge recombination in solution. The absorption spectra of the CT transitions are very similar in PEPCz and EtCz solutions, suggesting that the geometry of Cz−TNF complexes is similar for both cases. Similar transient absorption anisotropy is, therefore, expected for both cases. The lower anisotropy obtained in the PEPCz solution with 3 ps time resolution may
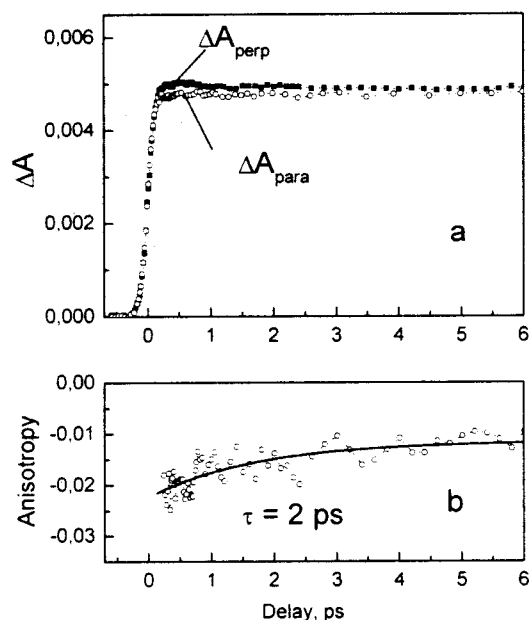
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Figure 8. (a) Transient absorption kinetics at λ_{pr} = 800 nm of PEPCz film doped with 10 mol % TNF excited at 527 nm measured with a femtosecond time resolution for parallel (circles) and perpendicular (squares) polarizations of the excitation and probe light. (b) Time dependence of the transient anisotropy calculated from the polarized kinetics; solid line shows approximation of the initial anisotropy dynamics by the exponential decay with a 2 ps time constant.

be due to nonresolved hole transfer from the parent Cz to neighboring Czs on the same oligomer chain. Assuming that these geometries are identical and that any correlation between the orientations of transition dipoles of the CT absorption and the Cz^+ absorption are lost when the hole is transferred from the parent Cz, the relative number of e−h pairs separated by some distance in PEPCz solution can be estimated to be about 30%. The fast and the slow Cz^+ decay components can be attributed to the nonseparated and separated charge pairs, respectively, suggesting a charge separation efficiency of 60% from the ratio of their amplitudes. This discrepancy of a factor of 2, from the value obtained from the anisotropy measurements, is too large to be explained as being solely due to experimental uncertainty. However, the hole transfer between the neighboring Cz moieties might not lead to complete depolarization of the Cz^+ absorption, since the directions of their transition dipole moment might be correlated. In that case, the anisotropy underestimates the charge separation efficiency.

The recombination of the separated charge pairs occurs in two steps, that is, hole transfer back to the parent Cz moiety and ensuing recombination. The lifetimes of 95 and 45 ps attributed to separated and nonseparated charge pairs, respectively, suggest a ∼50 ps hole back-transfer time. The approximately equal times for hole back-transfer and recombination determine the relative number of nonseparated charge pairs and hence the anisotropy value at long delay times. The observation of approximately 50% of the initial anisotropy observed at 100−200 ps delay times for the PEPCz solution as compared to the monomeric analogue solution suggests that half of the generated e−h pairs were separated by longer distances. The decay of anisotropy within the first tens of picoseconds (Figure 5b) can be ascribed to the recombination of the nonseparated e−h pairs.

The very fast formation of the Cz^+ absorption signal with a low anisotropy and fast partial depolarization within a few picoseconds observed in films imply that significant charge

separation occurs even within the 100 fs excitation pulse and is completed during several picoseconds. The fast decay component in the Cz^+ absorption (∼180 ps) and the picosecond component of the anisotropy decay (∼120 ps) may be assigned to recombination of the nonseparated e−h pairs. Some difference in the recombination rates of nonseparated e−h pairs in film and solution might be due to different dielectric permittivity, which also causes different solvation shells. The magnitude of the relative amplitude of the nanosecond component of charge recombination suggests a charge separation efficiency of 70−80% in PEPCz films with a low TNF concentration. Similar charge separation efficiency is obtained from anisotropy values.

Transient anisotropy has already been used to study charge separation in PVK,[21] but as the time resolution of the reported data was 30 ps, only a slow (∼2 ns) decay was observed. This was the main reason for suggesting that initially only nonseparated CT states are created and that slow charge separation prevails during the entire lifetime of the CT state. However, the anisotropy value was not determined. The low anisotropy value and its decay observed in the present experiments implies that charge separation (hole transfer away from the parent Cz moiety) occurs within a picosecond, probably driven by the excess energy of the excited CT state. Further dissociation of loosely bound e−h pairs into free charge carriers via thermally activated hole hopping is a rather slow process, which can be assisted by energetic disorder,[19] but the initial fast e−h separation is crucial for charge photogeneration.

The excitation wavelength dependence of the recombination dynamics (Figure 6) is another property of the system that is helpful for understanding the charge carrier photogeneration process. The excitation wavelength dependence of the CT luminescence quenching in tetracyanobenzene-doped PVK was examined,[14] and a decrease of the quenching efficiency was observed when the sample was excited at the long wavelength side of the CT absorption band. In agreement with this finding, it was concluded that charge carrier separation preferentially occurs when the higher CT state is excited. Our results show a dependence of the Cz^+ absorption decay kinetics on the excitation wavelength (Figure 6); the relative amplitude of the fast decay component increases with increasing excitation wavelength. However, this dependence is quite weak, and it almost vanishes for the films with the higher acceptor concentrations. The slow decay component, attributed to the recombination of separated charge pairs, remains even for excitation to the long-wavelength tail of the absorption band at 630 nm, when practically only the low-energy state is excited (see Figure 2). This is an indication that charge separation occurs at excitation to both the low- and high-energy excited states, but it seems that the efficiency of the initial e−h separation is larger for excitation into the higher state. A similar wavelength dependence of photoconductivity was observed in acene crystals[10−12,16] and explained within the framework of the ballistic thermalization theory. The excitation wavelength dependence of the Cz^+ transient absorption decay is an additional argument for a fast charge separation. The relaxation of higher excited electronic states in large organic molecules is very fast, usually proceeding on a femtosecond time scale. Polaron formation also occurs on the subpicosecond time scale. The initial charge separation must, therefore, be ultrafast, otherwise it could not compete with the electronic and vibrational relaxation of the higher excited CT state and no wavelength dependence of charge recombination kinetics would be observed.

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Fast charge pair separation is consistent with the ideas of Sebastian et al.,[13] who investigated the role of CT states in the photoconductivity of anthracene. They proposed that the energy of the surrounding polarization induced by a dipolar CT state can help the charge carrier overcome the Coulomb attraction force. The polarization of the nuclear system in molecular materials is a multistep process proceeding on the 10^{-14}–10^{-12} s time scale. During this time, the polarization energy may be transferred to the charge carrier, therefore propelling the separation of charges. At the same time, a polarization cloud is formed around the charge carrier, reducing its mobility and the probability of migration away from the site where it was created.

Conclusions

The main findings can be summarized as follows. (i) Photoexcitation of a weak electron donor–acceptor complex of the electron-donating carbazolyl group and an electron-accepting trinitrofluorenone (TNF) brings about the very fast formation of a carbazolyl cation radical and an electron acceptor anion, within the 100 fs excitation pulse, in poly-*N*-epoxy-propylcarbazole (PEPCz) films. (ii) Separation of generated electron–hole (e–h) pairs in PEPCz film occurs on the subpicosecond time scale via ultrafast hole transfer. Limited hole transfer after photoexitation is also concluded to occur for PEPCz solution, most likely only between neighboring carbazolyls on the short oligomer chain. The primary charge separation efficiency is about 70–80% in PEPCz film and about 30–60% in PEPCz solution. (iii) Recombination of e–h pairs in 1,2-dichloroethane solution of *N*-ethylcarbazole and TNF complexes obeys monoexponential kinetics with a time constant of 45 ps. PEPCz–TNF solution shows biexponential e–h recombination with 45 and 95 ps time constants, and both components have approximately equal amplitudes. The slower component is ascribed to recombination of separated e–h pairs, and it vanishes when the low-energy state is excited. In PEPCz films, the fast recombination component (about 180 ps) only has a minor contribution and the majority of e–h pairs recombine in a few nanoseconds. (iv) Charge separation efficiency in PEPCz films increases with increasing excitation photon energy, suggesting charge separation by hole transfer is faster than the thermalization of the excited CT state.

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