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Transient Photoconductivity of Acceptor-Substituted Poly(3-butylthiophene)

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Abstract: We have studied acceptor-substituted poly(3-butylthiophene) in an attempt to examine the role of acceptor molecules as intrinsic charge traps under light excitations by measuring the transient photoconductivity response following pulse excitation. The specially synthesized acceptor molecule is a chemically prepared high electron affinity (HEA) monomer, 1-(4-nitrophenyl)-2-(3-thienyl)ethene. In the copolymers prepared with this acceptor monomer we have observed simultaneous decrease of the sub-nanosecond photoconductivity and increase of the slow component ($t > 10$ ns) photoconductivity, with increasing HEA group concentration in the substituted poly-(butylthiophene)s. The slow component is attributed to a bimolecular recombination process.

1. Introduction

Photoconductivity (PC) in conjugated polymers has attracted considerable attention in recent years. The transient PC signal in conjugated polymers decays on a sub-nanosecond time scale due to radiative as well as nonradiative recombination processes of the charge carriers.[1,2] Modified matrices of conjugated polymers which contain charge traps in the excited state show quenching of the charge carriers recombination.[3] These modified matrices are of potential use in applications where longer lifetimes and higher yields are required.

New chemical and physical properties of conducting polymers were achieved by adding an appropriate functional group to the polymer chain.[4] In some previous works the functional group was placed as a pendant group apart from the conjugated backbone in order to maintain a high level of conductivity, so that spatial hindrance was minimized. Thiophene monomers, which are polymerized at the 2,5 positions, can be substituted at the 3,4 positions to produce a substituted conducting polymer. Consequently, these structures are good candidates for the purpose of modifying the electronic properties of the polymer. In some studies, this concept was implemented by adding high electron affinity (HEA) groups in order to change the energy gap between the HOMO and the LUMO bands.[5] More recently, such substituted conjugated polymers were used as electron collectors in a bilayer light emitting diode (LED) device with increased efficiency.[6] HEA groups, such as nitrobenzene, may be used as substitutes having strong excited state electron affinity in conjugated polymers, such as poly(3-alkylthiophene). In such systems, a dipole moment is induced by photoexcitation, leading
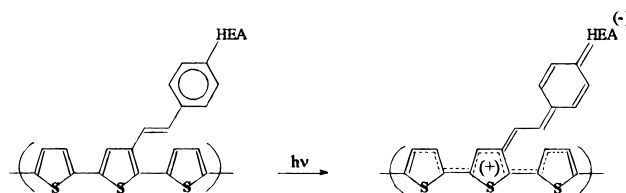

Figure 1. Photoactivation process of the bipolar state. The negative charge is trapped on the HEA group, while the positive charge is delocalized on the backbone.

to a bipolar excited state through a quasi-charge-transfer mechanism.[7] The amount of charge transfer is determined directly by the separation of the two polar sites. Hence, electrons will be, to some extent, localized in the vicinity of the acceptor group, inhibiting their recombination with the positive charge which is delocalized on the chain. As a result, a slow decay of the photoconductivity is to be expected. According to the multistate model[8] for strongly coupled ion pairs, there is an initial excited bipolar state in the acceptor-substituted polymer where the charges are not fully separated ("contact ion pair"). These bipolar pairs do not contribute to the initial photocurrent. The bipolar neutral state is relatively long lived and therefore allows the positive charge to hop to another site (or chain) in the polymer, leading to fully separated charge carriers ("solvation separated ion pair"). This process enhances the long lived charge concentration which contributes to the slow photoconductivity. The long lived charges recombine eventually via a bimolecular recombination process. Since the HEA group is attached to a π conjugation, perpendicular to the polythiophene backbone (on the β site of the thiophene ring), under illumination it is expected to behave as a trap ("acceptor") for electrons. The positive charges are expected to show chainlike behavior (positive polarons or bipolarons[9]), as demonstrated schematically in Figure 1.

Here we present a study of the dark conductivity and the transient photoconductivity in the homopolymer poly(3-butylth-

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(1) Moses, D.; Sinclair, M.; Heeger, A. J. *Phys. Rev. Lett.* **1987**, *58*, 2710.

(2) Bleier, H.; Donovan, K.; Friend, R. H.; Roth, S.; Rothberg, L.; Tubino, R.; Vardeny, Z. V.; Wilson, G. *Synth. Met.* **1989**, *28*, D189.

(3) Lee, C. H.; Yu, G.; Moses, D.; Pakbaz, K.; Zhang, C.; Sariciftci, N. S.; Heeger, A. J.; Wudl, F. *Phys. Rev. B* **1993**, *48*, 15425.

(4) Garnier, F. *Angew. Chem.* **1989**, *101*, 529.

(5) Otto, P.; Ladik, J. *Synth. Met.* **1990**, *36*, 327.

(6) Greenham, N. C.; Moratti, S. C.; Bradley, D. D. C.; Friend, R. H.; Holmes, A. B. *Nature* **1993**, *365*, 628.

(7) Creutz, C.; Chou, M. H. *Inorg. Chem.* **1985**, *89*, 1601.

(8) Mataga, N. In *Electron Transfer in Inorganic, Organic and Biological Systems*; Bolton, J. R., Mataga, N., McLendon, G., Eds.; Advances in Chemistry Series, Vol. 228; A.C.S.: Washington, DC, 1989; p 131.

(9) Heeger, A. J.; Kivelson, S.; Schrieffer, J. R.; Su, W. P. *Rev. Mod. Phys.* **1988**, *60*, 781.
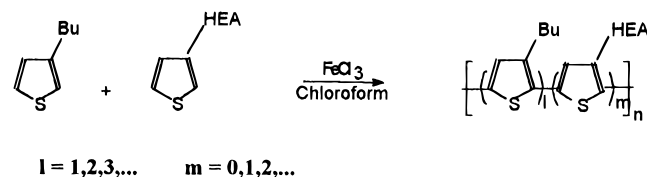
Figure 2. General polymerization of the copolymer 3-HEA-thiophene/3-butylthiophene. The 3-HEA-thiophene monomers are randomly distributed.
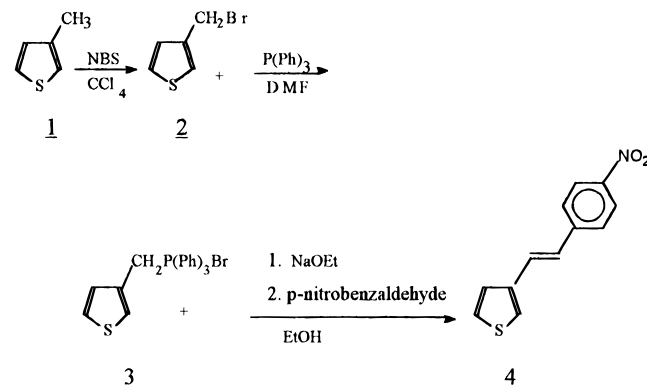

Figure 3. Synthesis of the active NBT monomer.

iophene) (PBT) and in acceptor-substituted PBT copolymers. The acceptor unit used here is the specially synthesized monomer 1-(4-nitrophenyl)-2-(3-thienyl)ethene (NBT). We find a considerable enhancement of the slow decay part of the transient photoconductivity upon acceptor substitution, which we attribute to charge trapping in the excited state.

2. Experimental Section

We have selected the conjugated polymer PBT because it is highly soluble and can be easily processed[10] and substituted with HEA ("acceptor") monomer groups.[11] The new copolymer systems contain a random distribution of the neutral monomer 3-butylthiophene and the active acceptor 3-HEA-thiophene. The synthesis of these copolymers was carried out by an oxidative coupling procedure[10,12] with the desired concentrations of the different monomers as shown schematically in Figure 2. The HEA group is attached to the third position of the thiophene ring in a general Wittig reaction[13,14] as shown in Figure 3. We chemically prepared the homopolymer PBT and the copolymers poly(NBT/BT) [P(NBT/BT)] with mixing ratios of 1:m (i.e., on the average 1/m of all 3-butylthiopene (BT) monomers are substituted by NBT).[11] (The synthesis of the BT monomer is described elsewhere.[15])

The synthesis of the functional monomer 3-HEA-thiophene is described here for the monomer 1-(4-nitrophenyl)-2-(3-thienyl)ethene (see **4**, Figure 3):

3-(Bromomethyl)thiophene (2): 3-Methylthiophene (**1**, Figure 3) (4 mL, 41.35 mmol) and NBS (7.36 g, 41.35 mmol) were dissolved in 100 mL CCl$_4$. The solution was refluxed under a high-intensity lamp for 2 h. The reaction mixture was cooled to ambient temperature and filtrated, and the solvent was evaporated. There was no further workup carried out. TLC showed the product **2** signature with traces of the starting material **1**.

The Phosphonium Salt of 2 (3): Triphenylphosphine (11.53 g, 44 mmol) and **2** (about 40 mmol) were dissolved in 48 mL of DMF, and the mixture was heated up. After 5 min, the product salt **3** started to precipitate. The mixture was then stirred for an additional 15 min,

cooled to ambient temperature, and filtrated, and the salt was washed with DMF, followed by ether to give 9.9 g of white powder.

1-(4-Nitrophenyl)-2-(3-thienyl)ethene (4): 4-Nitrobenzaldehyde (3.4 g, 22.5 mmol) and **3** (9.9 g, 22.5 mmol) were dissolved in 63 mL of absolute ethanol. A 208 mL solution of 0.4 M sodium ethoxide in ethanol was added, and the precipitation of a yellow product was seen immediately. The mixture was heated up in reflux for 2 h and then cooled to ambient temperature. One-third of the ethanol was evaporated, and water was inserted instead. The yellow product was filtrated. In order to obtain a pure product, it was separated off by a flash chromatography procedure (run by dichloromethane) yielding 3.015 g of yellow powder. The yield was 58%, mp 166 °C. ^{1}H-NMR (CDCl$_3$): $\delta = 6.5-6.9$ ppm (m, vinyl in a mixture of cis and trans, 2H), 7.1−7.4 ppm (m, thiophene, 3H), 7.6 ppm (d, $J = 9$ Hz, phenyl meta to nitro, 2H), 8.2 ppm (d, $J = 9$ Hz, phenyl ortho to nitro, 2H). IR (CHCl$_3$): 1640, 1110, 950, 870, 1520, 1350 cm^{-1}. MS: m/z 231, 184, 152, 141, 115, 45. High-resolution MS: m/z 231.0360 (calcd for C$_{12}$H$_9$NO$_2$S 231.0354). UV−vis (CH$_2$Cl$_2$): 352 nm.

Homo- and Copolymers: Polymerizations of the homopolymer and the copolymers were done on 1−4 mmol scale of the monomers dissolved in 0.1 M chloroform and 8 equiv of FeCl$_3$. Polymerization was carried out at 30 °C under nitrogen atmosphere until no HCl was detected (typically for 2−3 h). The black solid was washed by methanol until the methanol was colorless. The solid was then dissolved in CH$_2$Cl$_2$, and ammonia gas was bulbed through the solution for 30 min (in order to reduce back the polymer). The color changed from green solution (oxidized polymer) to orange (neutral polymer), and the solution was washed with water to remove the ammonium−iron complex salts. The solution was then washed again with 0.1 M ammonium hydroxide solution followed by brine and dried over magnesium sulphate. UV−vis showed no detected Fe^2/Fe^3. In order to remove the short oligomers, the polymer was precipitated from the CH$_2$Cl$_2$−methanol mixture.

In order to determine the ratio 1:m we used H-NMR measurements of the solutions in CDCl$_3$ on a Bruker-AC200 spectrometer. The ratio 1:m was obtained by taking the ratio of the integrated H-NMR signal of the benzillic 2H, which belongs to the butyl substitution (chemical shift $\delta = 2.7$ ppm), to that of the ortho 2H, which belongs to the nitrobenzene substitution ($\delta = 8.1$ ppm). The monomer and polymer structures were also confirmed by H-NMR measurements. The absorption spectra of the polymers solutions in dichloromethane were measured on an HP 8524A spectrophotometer. High-resolution mass spectra of the monomers were taken on a Finnigan MAT-711.

For the conductivity measurements,[16] thin films were mounted on alumina (or glass) substrates by spin coating, thus obtaining films of thickness of the order of 40−80 nm. The thickness of the films were measured using the α-step technique, and the comparative data were normalized to the film thickness. The dark conductivity and transient PC were measured by employing a microswitch transmission line configuration (Auston switch).[17] Microstripline gold electrodes (width of 0.6 mm on alumina) were deposited on the spin-coated polymer film, leaving a gap of 0.1 mm. The back side of the substrate was gold deposited, forming a transmission line with 50 Ω impedance with an expected frequency response over 10 GHz. The 50 Ω impedance matching was kept along the circuit using appropriate wiring and connectors. For the dark conductivity measurements, a Keithly 236 source measuring unit was used for taking the $I-V$ characteristics. An ohmic behavior was measured up to 100 V across the 0.1 mm gap (electric field bias of 10^4 V/cm). For the temperature dependence of the dark and photoexcited conductivity measurements, the samples were mounted onto a cold finger Air-Product LT-3-1100 cryostat in a vacuum better than 10^{-4} Torr. For the transient PC measurements, one of the electrodes was biased up to 100 V, while the other was connected to a Tektronix 2430 digital oscilloscope via CLC144 Comlinear DC−1.1 GHz band amplifier. Excitation pulses of width of 6−8 ns at 3.5 eV (355 nm) were obtained from the third harmonics of a Quanta-Ray DCR-10 Nd:YAG laser, operated at a repetition rate of 10 Hz, with an

(10) Kulszewicz-Bajer, I.; Pawlicka, A.; Plenkiewicz, J.; Pron, A.; Lefrant, S. *Synth. Met.* **1989**, *28*, 335.

(11) Greenwald, Y.; Poplawski, J.; Wei, X.; Ehrenfreund, E.; Speiser, S.; Vardeny, Z. V. *Mol. Cryst. Liq. Cryst.* **1994**, *242*, 145.

(12) Suginoto, R.; Takeda, S.; Yoshino, K. *Chem. Express* **1986**, *1*, 635.

(13) Campbell, R. W.; Hill, H. W., Jr. *J. Org. Chem.* **1973**, *38*, 1047.

(14) Hagen, S.; Roth, S.; Hanack, M. *Synth. Met.* **1991**, *41−43*, 1557.

(15) Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *38*, 3347.

(16) Moses, D. *Philos. Mag.* **1992**, *B66*, 1.

(17) Auston, D. H. In *Picoseconds Optoelectronics Devices*; Lee, C. H., Ed.; Academic Press: New York, 1988; Chapter 4.

(18) Greenwald, Y.; Wei, X.; Jeglinski, S.; Poplawski, J.; Ehrenfreund, E.; Speiser, S.; Vardeny, Z. V. *Synth. Met.* **1995**, *69*, 321.
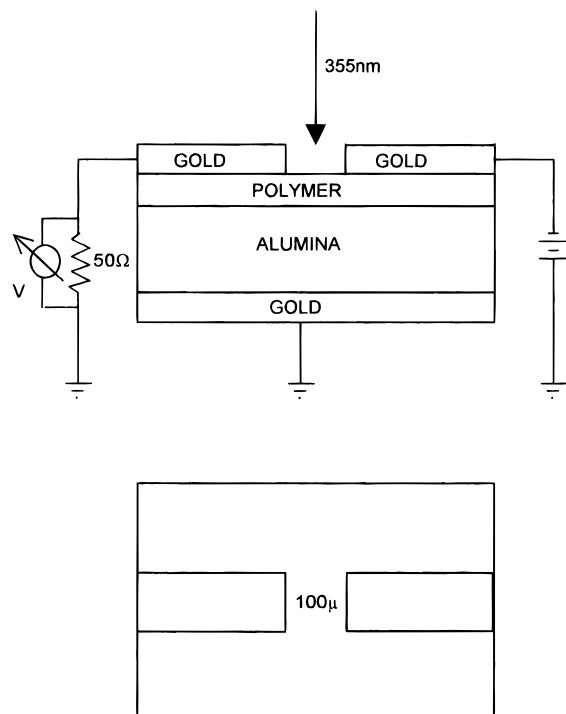
Figure 4. (top) Microswitch strip line (Auston Switch) configuration. (bottom) Top view of the microstripline gold electrodes spin coated on the polymer film. Thicknesses and sizes are given in the text.
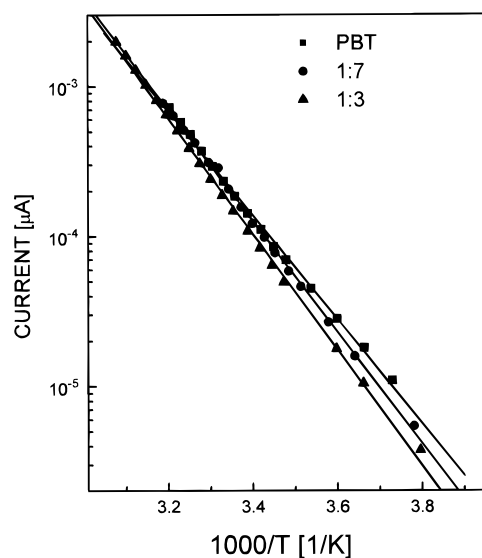

Figure 5. Arrhenius plot of the dark conductivity: current (log scale) *vs* inverse temperature.

average laser power in the range of 1−100 mW, giving light intensities of 0.1−10 mJ/(pulse cm²). The sample configuration and the circuit involved are shown in Figure 4.

3. Results

The samples' resistivities at room temperature were on the order of 10^8 Ω cm decreasing exponentially with increasing temperature. An Arrhenius plot of the dark current is shown in Figure 5 for PBT and two copolymers P(NBT/BT) 1:*m* with *m* = 7 and 3. The linear dependence reveals an activated mechanism for the dark current flow in the polymer. Comparison of the Arrhenius plots of the different samples PBT and P(NBT/BT) 1:*m* (*m* = 3, 5, and 7) shows an increase in the activation energy, E_a, with increasing acceptor concentration; the values of E_a are summarized in Table 1.
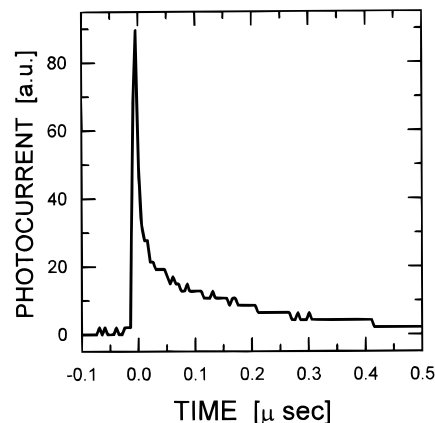

Figure 6. Time-resolved PC of the P(NBT/BT) 1:3 copolymer.
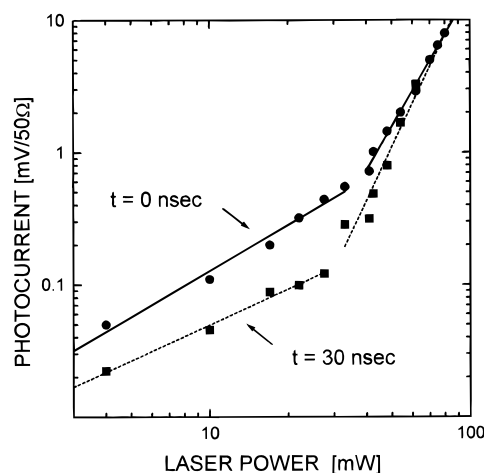

Figure 7. Log−log plot of the PC intensity dependence of the P(NBT/BT) 1:7 copolymer at the peak (≃0 ns) and at 30 ns (the slow decay component). The straight lines are fits to power law dependence $I_{PC} \propto I_L^\alpha$, with $\alpha \simeq 1$ for $I_L < 30$ mW and $\alpha = 3.4$ (peak) and 4 (30 ns delay) for $40 < I_L < 90$ mW.

Table 1. Activation Energy (E_a), Peak Photoconductivity, PC at 100 ns Delay, Fractional Charge for the Slow Decay ($t > 10$ *ns*) (Q_s) (see Eq 1), and Relative Bimolecular Rate Constants for the Homopolymer PBT and Two P(NBT/BT) 1:*m* (*m* = 3 and 7) Copolymers Studied in the Auston Switch Configuration

	E_a dark (eV)	peak PC (10^{-5} S/cm)	PC at 100 ns (10^{-5} S/cm)	Q_s (%)	k_{PBT}/k_{cop}
PBT	0.68	10	0.03	10	1
1:7	0.74	9	0.8	70	8
1:3	0.78	7	2	90	21

The time-resolved transient photocurrent decay spectrum of a P(NBT/BT) 1:3 copolymer film at room temperature is presented in Figure 6. A clear slow decay, which lasts up to few microseconds, was observed. This slow decay is a strong indication for charge trapping.

Figure 7 shows the dependence of the PC signal on the average laser power, in the range 1−100 mW. At low intensities, both the fast (measured at the peak at ≃0 delay) and slow (30 ns delay) decay PC components are linear with the intensity, I_L, whereas at high intensities, the dependence is superlinear, I_L^α, with $\alpha = 3.4$ and 4, respectively. The linear dependence at low intensities is typical for the usual single-photon process. The superlinear behavior at higher intensities is indicative of multiphoton processes, which might lead to photoionization. We stress here that all the experimental results shown here were reversible and were obtained repeatedly while varying the light intensity over the whole range.
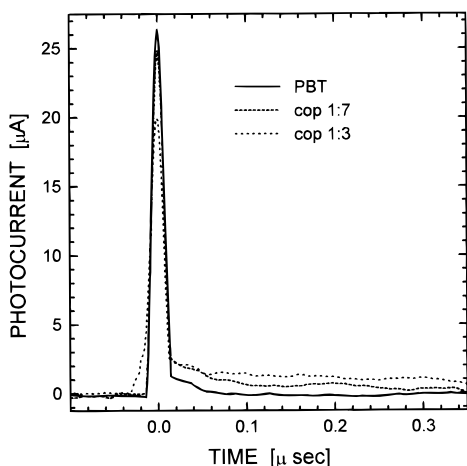
Figure 8. Linear plot of time-resolved PC for PBT and P(NBT/BT) 1:*m* copolymers with *m* = 3 and 7. The data plotted were taken at room temperature and with electric field of 10^4 V/cm. The light intensity is low ($\simeq 2$ mJ/cm^2 per pulse) and corresponds to the linear part of Figure 7.
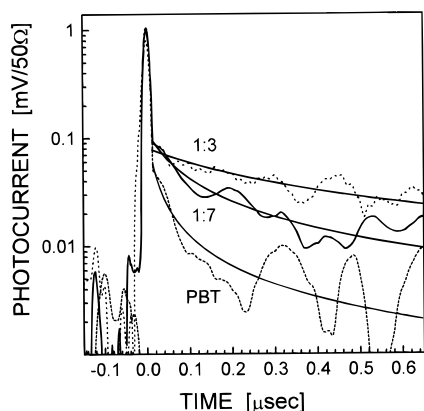

Figure 9. Semilog plot of the transient PC for PBT and P(NBT/BT) 1:*m* copolymers with *m* = 3 and 7. The solid lines are fits of the bimolecular decay (eq 2) to the data.

Comparative transient PC data of the homopolymer PBT and P(NBT/BT) 1:*m* (with *m* = 7 and 3) copolymers are presented on a linear plot in Figure 8. These results were obtained at low light intensities where the PC signal is linear with intensity. The PBT sample shows the highest photocurrent peak value, giving a photoconductivity of about 3×10^{-4} S/cm. It decreases by about 10% and 30% for *m* = 7 and 3, respectively. In Figure 9, we show the same data as a semilog plot in order to enhance the small signal at long delays. For the PBT sample, the slow component is very small and becomes nearly zero at about 100 ns (about 3 orders of magnitude smaller than the peak value). It increases considerably as the acceptor concentration increases. For P(NBT/BT) 1:3 copolymer, the PC current at 100 ns is smaller than the peak value by only a factor of $\simeq 10$ and it is in the range of 10^{-5} S/cm. This is a dramatic increase of the PC at 100 ns in the substituted PBT—up to 2 orders of magnitude over that of the homopolymer PBT on the same time scale. Another measure of the relative importance of the slow decay is the integrated fractional charge in the slow decay component, defined as

$$Q_s = \int_\tau^\infty I_{PC}\, \mathrm{d}t \Big/ \int_0^\infty I_{PC}\, \mathrm{d}t \tag{1}$$

where $\tau \simeq 12{-}14$ ns is the system recovery time following pulse excitation (see the abrupt change in slope from very fast response to very slow response in Figure 8) and I_{PC} is the

photocurrent. It was found that for the PBT sample Q_s is only 10%. Q_s increased up to 70% for the copolymer with the ratio of 1:7 of the acceptor monomer. In the copolymer with the ratio of 1:3, up to 90% of the charge is in the slow PC part. The measured PC signal in the P(NBT/BT) 1:3 copolymer lasts for few microseconds.

4. Discussion

The dark conductivity is limited by interchain charge transfer, which is an activated process. The activation energy E_a is inversely related to the conjugation length. Since the observed increase in E_a in our samples is correlated with the blue shift of the absorption peak,[18] we conclude that with increasing acceptor concentration the conjugation length decreases.

In order to account for the long time behavior of the photocurrent, we assume that, for $t > 10$ ns (the system recovery time following pulse excitation), the dominant charge recombination process is bimolecular. Thus, the long time behavior of the charge density, and of the PC current, is given by

$$n(t) = (n(0)^{-1} + kt)^{-1} \tag{2}$$

where $n(t)$ is the (negative or positive) charge carrier density at time t, $n(0) = n(t{=}0)$, and k is the apparent bimolecular rate constant. It is important to note that this mechanism ignores all the early processes like charge generation and monomolecular recombination which presumably end long before the slow PC is apparent. The bimolecular process is adequate only for those carriers that survive the monomolecular recombination. The solid curves in Figure 9 are the fits of the data to a bimolecular recombination process. The parameters obtained by fitting eq 2 to the data of Figure 9 are summarized in Table 1. It is apparent that k decreases with the acceptor concentration (Table 1). Relative to the homopolymer, it is reduced by factors of 8 and 21 for the 1:7 and 1:3 copolymers, respectively.

It is interesting to note that the bimolecular rate constants obtained by these fits and the activation energies E_a found from the dark conductivity measurements obey the following relation:

$$\ln(k_{cop}/k_{PBT}) \cong -\Delta E_a(cop)/k_B T \tag{3}$$

where k_{cop} and k_{PBT} are the rate constants for the copolymer and the homopolymer, respectively. ΔE_a is the difference in the respective activation energies; i.e. $\Delta E_a(cop) = E_a(cop) - E_a(PBT)$. This correlation, together with the temperature dependence of the slow part of the PC, indicates that the slow PC arises from an activated process. Moreover, we relate the slow component of the photocurrent decay and the dark conductivity with the same "bottleneck" which limits the charge transport at low charge density in the polymer. Both the dark conductivity and the recombination process are governed by the bimolecular or interchain charge transfer (hopping), which is an activated process.

5. Conclusions

By investigating the slow part of the PC decay, we have shown in this work that HEA groups, such as nitrobenzene, can serve as traps for electrons (acceptors) in the excited state and to delay the recombination of the photoinduced charge carriers. The slow decay of the sample shows a bimolecular recombination process. The unique correlation between the rate constant of the bimolecular recombination process and the activation energy found from the dark conductivity indicates that both the dark conductivity and the bimolecular recombination are dominated by the same bimolecular process: the interchain charge transfer (hopping), a temperature-activated process. The

decrease of the peak of the PC signal (at zero delay) in the HEA-substituted copolymers is possibly the result of the bipolar photoexcited state which lasts less than our time resolution (a few nanoseconds). This bipolar excited state is in effect a "trap" for the photoexcited electrons, inhibiting their recombination with the positive charge. Thus, relative to the homopolymer, there is a delayed charge separation in the copolymers, causing an initial drop in the PC (peak decreases) and enhanced slow component PC. Higher photoexcited charge concentration and related conductivity in the nanosecond time regime may be useful for new applications, such as electrooptic modulators, organic photodiodes, and in photorefractive devices.