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Long-lived photoexcited states in polydiacetylenes: The photoinduced-absorption spectra of PDA-4BCMU

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We report the results of steady-state photoinduced absorption experiments on PDA-4BCMU grown on silica substrate. We observe three photoinduced absorption bands at 0.82, 0.95, and 1.39 eV whose relaxation dynamics are identical for the two low-energy peaks but different for the 1.39-eV band. On the basis of the spectra, the pump intensity, modulation frequency, and signal phase dependences we conclude that the 0.82 and 0.95-eV absorption features are due to charged states while the 1.39-eV peak is originated by triplet excitons. The photogeneration of both charged and neutral states in PDA-4BCMU as previously observed in polycarbazolyldiacetylenes indicates that this is a general feature of polydiacetylenes. The relative weight of one excited species over the other one is influenced by the molecular and supramolecular organization of the polymer. [S0163-1829(98)02812-4]

I. INTRODUCTION

The nature of excitations in π-conjugated polymers has been extensively studied by the continuous wave photoinduced absorption (PA) technique. Among the conjugated systems, the polydiacetylenes (PDA's), $=\!\!(\mathrm{CR{-}C{\equiv}C{-}CR'}\!=\!\!)_n$, have attracted particular interest because they can be prepared in the form of macroscopic single crystals through solid-state topochemical polymerization of the corresponding monomers. In addition, the possibility of changing the substituents of the polymer backbone allows us to obtain a variety of materials with properly designed optical and electronic properties. For practical applications, PDA's grown on suitable substrates by the epitaxial technique or, when soluble, cast from solution are usually considered. Polymerization of diacetylenic crystals usually leads to polymers in the blue phase characterized by a well-defined singlet excitonic peak around 620 nm. Thermochromic[1] and solvatochromic[2] phase changes are, however, possible and in this condition a red form characterized by an absorption band around 540 nm is obtained. The study of the different forms of PDA's, due to their different conjugation length, provides additional information on the photophysics of these polymers. The PA spectra of this class of polymers so far reported by other authors usually deal with the blue form of PDA's. A strong PA peak around 1.4 eV has been observed for PDA-TS ($R{=}R{=}{-}\mathrm{CH_2SO_3C_6H_4CH_3}$) (Refs. 3 and 4) and attributed to neutral photoexcitations on the basis of the results of the study of its decay in the presence of an applied magnetic field.[5] For the same polymer no evidence of photoexcited charged states in the NIR region is reported. On the contrary, the presence of PA signals associated only with charged photoexcitations has been found in PDA-1OH ($R{=}{-}\mathrm{CH_3}$, $R{=}{-}\mathrm{CH_2OH}$) and PDA-9PA ($R{=}R'{=}{-}(\mathrm{CH_2})_9\mathrm{OCOCH_2C_6H_5}$).[4,6,7] In these cases the assignment has been substantiated by the presence in the low-frequency region of the PA spectrum of infrared activated vibrational (IRAV) modes, which are associated with charged states.[6,7] To make this picture more confused, IRAV modes are reported to be present also in PDA-TS and PDA-4BCMU ($R{=}R'{=}{-}(\mathrm{CH_2})_4\mathrm{OCONHCH_2COOC_4H_9}$).[6,7] In all these cases, no light-induced electron spin-resonance (LESR) signals were detected suggesting the photogeneration of doubly charged spinless bipolarons.[7] The presence of triplet excitons in the blue form of PDA-4BCMU (Ref. 8) and PDA-3BCMU ($R{=}R'{=}{-}(\mathrm{CH_2})_3\mathrm{OCONHCH_2COOC_4H_9}$) (Ref. 9) has been detected around 1.4 eV with picosecond PA spectra for *probe energies above 1.2 eV.*

For the red form of PDA's only a few experimental data are available for PDA-4BCMU (Refs. 8 and 10) and PDA-ClCin22 [poly(bis-*p*-chlorocinnamate, 10, 12-docosadiyn-1, 22-diol)].[10] The PA peak observed at 1.4–1.5 eV is attributed to neutral excitations (triplet excitons).

In the past few years we have been interested in studying a class of polydiacetylenes having the carbazolyl group attached directly[11–14] or indirectly,[14–20] through a $\mathrm{CH_2}$ spacer, to the main chain. Our interest in the polycarbazolyldiacetylenes (PCzDAs) is dictated by the particularly high value of the third-order polarizability[21,22] and enhanced photoconductive response[23] observed for polyDCHD ($R{=}R'{=}{-}\mathrm{CH_2NC_{12}H_8}$) as well as by the unusual excitation profile of the photocurrent in polyCPDO

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$(R=-\mathrm{NC}_{12}\mathrm{H}_8, R'=-\mathrm{CH}_2\mathrm{OH})$.[24] The large dipole moment and the photoconducting property of the carbazolyl ring seem to affect to some extent the properties of the polydiacetylene backbone.

The results of PA studies carried out on these polymers are the following ones. Only charged photoexcitations are detected for those PCzDAs having one carbazolyl substituent directly attached to the polymer backbone. On the other hand, neutral triplet excitons as well as charged photoexcitations have been observed for a series of blue PCzDAs symmetrically substituted with carbazolyl groups attached to the polymer backbone via one CH_2 spacer. By increasing the interbackbone distance in these polymers through the insertion of long aliphatic chains on the carbazolyl side group as in polyDCHD-S $[R=R'=-\mathrm{CH}_2$-(3,6-H_3C-$(\mathrm{CH}_2)_{11}\mathrm{NC}_{12}\mathrm{H}_8]$ neutral triplet excitons become the dominant photoexcitations while the charged species are strongly depressed.

The red forms of the PCzDAs reveal PA features at 1.5 eV (polyDCHD) (Ref. 16) and at 1.45 eV (polyDCHD-S) (Ref. 20) attributed to triplet excitons on the basis of their lifetimes and the lack of the IRAV modes.

We would like to stress here that unlike other conjugated polymers[25] the type and nature of photoexcited states in PCzDAs do not seem to be affected by the degree of order in the sample. Indeed similar PA spectra are obtained either in microcrystalline samples[14] or in epitaxially grown films.[18]

It is well known that both neutral and charged photoexcitations are important in different fields of application. The enhancement of the PA peak associated with neutral triplet excitons is promising for application of PDA's as nonlinear optical materials.[26] On the other hand the presence of charged states has been shown to favor the photoinduced electron transfer from conjugated polymers to other systems, like for instance C_{60}, with consequent ultrafast charge separation prior to recombination.[27] Hence a strong enhancement of the photocarriers efficiency occurs, which results in a significant increase of the photoconductivity of the conjugated polymer.[10,28] These effects have not been observed when the conjugated polymer is a red PDA-4BCMU.[10] No data are so far reported for the case of blue PDA's. On the other hand, for the red form of PDA's photoexcited charged states have not been observed.

The understanding of the mechanisms that favor the photogeneration of one of the excitations over the other could then greatly help in the design of the supramolecular architectures necessary to achieve a desired property. But, before reaching this goal it is necessary to establish whether the presence of both neutral and charged excitations is observed only for the polycarbazolyldiacetylenes like polyDCHD and its modified forms or it is a general feature of the PDA chain. For this reason we have carried out PA experiments on the blue form of a poly-4BCMU film on a silica substrate. The results of such a study will be here reported and discussed.

II. EXPERIMENT

Films of blue PDA-4BCMU were obtained as described in Ref. 29. A very thin film (about 300 Å) of monomer was first deposited under high vacuum on a well-cleaned silica substrate. The polymer chains obtained by UV irradiation were oriented by rubbing. On this surface, a thicker film (about 1500 Å) of 4BCMU monomer was deposited under high vacuum. The epitaxially grown monomeric film was again polymerized with UV light.

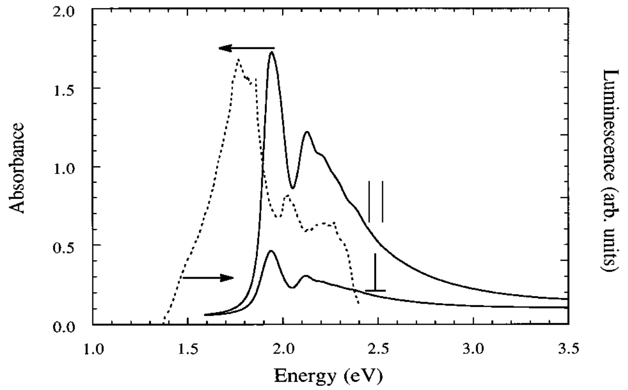

FIG. 1. Absorption spectrum of PDA-4BCMU for the electric field of the radiation parallel and perpendicular to the chain axis (full line). Luminescence spectrum (dashed line). $T=77$ K, $\lambda_{\mathrm{exc}}=488$ nm.

The electronic absorption spectra have been recorded using a Cary 5E spectrophotometer operating in the range 300–2200 nm equipped with a liquid nitrogen cryostat; the spectral resolution of all spectra was ~ 1 nm.

The PA spectra have been recorded using a homemade experimental setup. A continuous wave (CW) Ar^+ laser, mechanically chopped, has been used as pump and a tungsten-halogen lamp as probe. The excitation wavelength is the 488-nm lines of the laser. The differential changes of sample transmission (ΔT) due to pump excitation were dispersed by a Mc Pherson 218 monochromator and collected by a cooled PbS detector in the 0.6–1.4 eV range and with a photomultiplier tube in the 1.4–2.3 eV range. A Stanford SR850 DSP lock-in amplifier allowed a phase-sensitive detection. The PA spectra $(-\Delta T/T)$ have been obtained by normalizing ΔT to the transmission (T) of the sample. The photoluminescence spectra are recorded with the same experimental setup used for the PA experiments. All the low-temperature measurements have been performed with an hydrogen-helium expansion cryostat.

III. RESULTS AND DISCUSSION

Figure 1 shows the electronic absorption spectra of the film of oriented PDA-4BCMU at $T=77$ K in polarized light and its photoluminescence spectrum. The component of the absorption spectrum recorded with the electric field of the radiation parallel to the chain axis shows the excitonic absorption transition at 1.94 eV (638 nm) and its vibronic progression. The component of the absorption spectrum recorded with the electric field of the radiation perpendicular to the chain axis shows essentially the same features but with reduced intensity. The peak to peak anisotropy is about 4, indicating that a substantial degree of orientation is attainable with the growth technique. The intensity of the perpendicular absorption is due to three effects whose relative contribution can be evaluated in terms of chain misalignment, zigzag backbone structure, and electronic interchain cou-

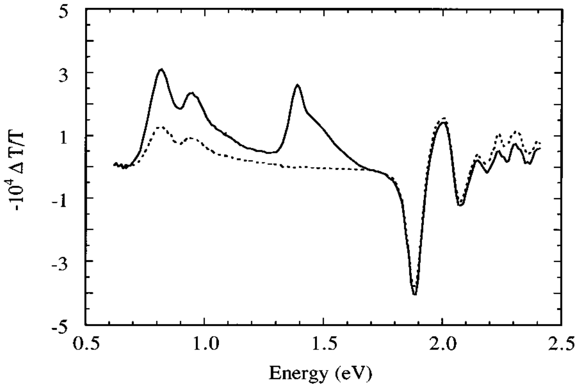

FIG. 2. Liquid-nitrogen photoinduced spectra of PDA-4BCMU for in-phase (full line) and out-of-phase (dashed line) detection ($T = 77$ K, $\lambda_{exc}=488$ nm, modulation frequency 20 Hz, pumping power 200 mW).

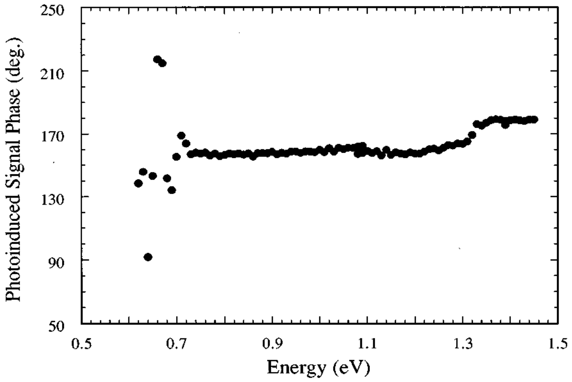

FIG. 3. Photoinduced signal phase of PDA-4BCMU ($T = 77$ K, $\lambda_{exc}=488$ nm, modulation frequency 20 Hz, pumping power 200 mW). Scattered points are due to noise.

pling. Chain misalignment has been shown to be the dominant contribution to the perpendicular absorption spectrum in polyacetylene[30] and polyDCHD.[18,31] It has also been shown that the effect of the interchain coupling, even though negligible in the absorption spectrum, plays an important role in the photophysics of the excited states.

The photoluminescence spectrum of PDA-4BCMU (Fig. 1) shows peaks at 1.77 and 1.86 eV and, in addition, a broad band above 2 eV with superimposed peaks at 2.01 and 2.22 eV resulting from the self-absorption of the polymer due to the overlap of the emission and of the absorption spectra in this region.

Figure 2 shows the photoinduced absorption spectra of PDA-4BCMU both with in-phase and out-of-phase detection. These spectra are recorded at $T = 77$ K with exciting wavelength 488 nm, modulation frequency 20 Hz, and 200 mW laser power. Unfortunately, the degree of orientation of the sample is not enough to allow a detailed study of the polarization properties of the PA spectra as previously performed for epitaxially highly oriented polyDCHD.[18] For this reason we have recorded only PA spectra with polarization of the exciting radiation parallel to the chain axis to maximize the signal. The probe light is unpolarized. The PA spectrum with in-phase detection shows three peaks at 0.82, 0.95, and 1.39 eV of comparable intensity. A prominent bleaching signal is observed at 1.89 eV followed, at higher energies, by marked oscillations. In the out-of-phase detected spectrum the peak at 1.39 eV is absent, while the lower-energy peaks are still present. This fact clearly shows that the lifetime of the photoexcitations associated with the 1.39-eV band is much smaller than that of the photoexcitations associated with the 0.82 and 0.95 eV peaks. The oscillating behavior observed for energies above the bleaching is indicative of electromodulation of the absorption due to the photoexcitation of charged states.[32–34] The different origin of the 0.82 and 0.95-eV peaks with respect to the 1.39-eV one is clearly shown in Fig. 3, where the spectrum of the photoinduced signal phase is reported. For the 0.82 and 0.95-eV bands a dephasing with respect to the laser phase of about 155° is observed. On the other hand, in correspondence to the 1.39-eV band a dephasing very close to 180° is detected.

The structure of these PA spectra is very similar to that previously reported for other blue PDA's like polyDCHD (Refs. 14,17,18) and polyDCHD-S.[19] In the former three photoinduced peaks with the same phase behavior here observed were detected at 0.82, 0.96, and 1.26 eV. The first two peaks were tentatively assigned to photoexcited doubly charged spinless bipolarons and the 1.26 peak to a triplet-to-triplet transition. In blue polyDCHD-S, the PA spectrum is dominated by a peak at 1.45 eV that was assigned to a triplet-to-triplet transition. In addition, small signals associated with charged states were detected in the spectral region 0.8–1 eV (Ref. 19). Moreover, strong oscillations in the bleaching region of the PA spectrum were detected also for the blue forms of both polyDCHD and polyDCHD-S. The comparative analysis among the PA spectra of blue PDA's suggests us to assign the PDA-4BCMU PA peaks at 0.82 and 0.95 eV to photoexcited charged states (polarons or bipolarons) and the 1.39-eV peak to a transition between photoexcited triplet excitonic states.

To substantiate this assignment, we performed a detailed analysis of the dependence of the PA spectra on the experimental parameters.

Figure 4 show the pump intensity dependence of the photoinduced signal peak and photoinduced signal phase for the 0.82 eV (a), 0.95 eV (b) (LE peaks), and 1.39 eV (c) (HE peak) bands. The bands at 0.82 and 0.95 eV show an $I^{0.3}$ dependence while the 1.39-eV band follows the $I^{0.5}$ law. All the signals show a dephasing of about 20°–30° in the range of the investigated intensities. The different intensity dependence of the LE peaks with respect to the HE one was observed also in the PA spectrum of polyDCHD,[14] further confirming our assignments of the 0.82 and 0.95 eV bands to charged states and of the 1.39-eV one to a triplet exciton. More puzzling is instead the strong intensity dependence of all the photoinduced signal phases. In a previous work on polyDCHD-S,[20] we showed that the photoinduced signal associated with the triplet-to-triplet transition does not show any dephasing in the same range of pumping intensity used in this work. Moreover, no variation of the lifetime of the photoexcited species with the pump intensity was observed. This fact was attributed to the monomolecular decay of the triplet exciton in the presence of trapping sites. According to these conclusions, we do not expect a contribution of the monomolecular kinetics to the decay of all the photoexcited species in PDA-4BCMU. It is possible that the decays are

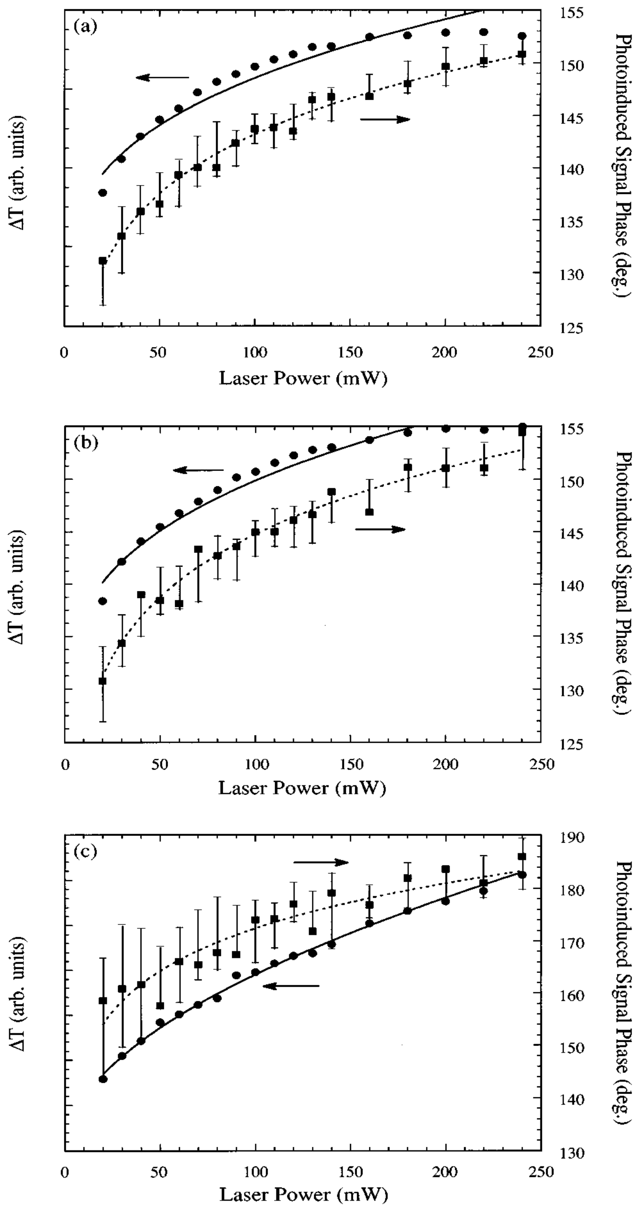

FIG. 4. Intensity dependence of the 0.82- (a), 0.95- (b), and 1.39-eV (c) photoinduced signals (full circles) and photoinduced signal phases (full squares) ($T = 77$ K, $\lambda_{\mathrm{exc}} = 488$ nm, modulation frequency 20 Hz). Lines are best fittings with power laws.

principally driven by the bimolecular kinetics. A bimolecular contribution to the decay kinetics of both charged states and triplets was previously reported for blue polyDCHD.[14,18]

In Fig. 5 we report the modulation frequency dependence of all the PA signals in the 5–3000 Hz range. For the LE peaks a power-law decay in agreement with previous observations[32,35–37] for charged carriers with a distribution of the lifetimes is observed. On the other hand, no dependence on the modulation frequency is detected for the HE band. These results are very similar to those previously reported for blue polyDCHD.[14,18] The presence of the bimolecular decay kinetics can be easily detected by the intensity dependence of the cutoff (knee) frequency in the modulation frequency dependence of the photoinduced signal.[14] We performed this kind of measurement but we did not detect any variation. However, this fact does not demonstrate that the

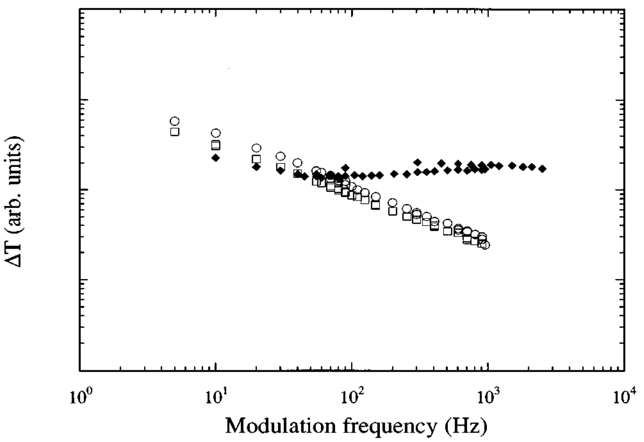

FIG. 5. Modulation frequency dependence of the 0.82- (open circles), 0.95- (open squares), and 1.39-eV (full diamonds) peaks ($T = 77$ K, $\lambda_{\mathrm{exc}} = 488$ nm).

bimolecular kinetics is negligible because in our spectra the cutoff frequency is not observed.

In order to account for the pump intensity and modulation frequency dependences of the photoinduced signal peaks we worked out a kinetic model for the density of the photoexcitations based on a monomolecular decay law, which includes the presence of traps to which the long-lived photogenerated states may be bound. As the pump intensity increases, the traps are filled and the efficiency to create long-living states that give rise to PA signals, is reduced. Such a process can be described by the following rate equation[38]

$$\frac{dn}{dt} = gI(t)\left(1 - \frac{n}{n_0}\right) - \frac{n}{\tau}. \tag{1}$$

Here n is the density of trapped photoexcitations; $I(t)$ is the pumping term with angular frequency ω, which we model as $I_0/2[1 + \sin(\omega t)]$, where I_0 is the density for unit time of the photogenerated electron-hole (e-h) pairs and g is a factor that accounts for the efficiency of the transformation of the e-h pairs into trapped photoexcitations (typically 10^{-3}–10^{-6});[30,39] n_0 is the density of traps and τ is the intrinsic lifetime of the photogenerated species. Equation (1) can be rewritten as

$$\frac{dn}{dt} = gI(t) - \left[\frac{1}{2\tau_I}(1 + \sin\omega t) + \frac{1}{\tau}\right]n, \tag{2}$$

where the parameter $\tau_I = (gI_0/n_0)^{-1}$ has the dimension of a lifetime. This kind of rate equation was proposed in the study of steady-state PA in oligothiophenes[38] and multiple quantum wells[40] to explain the observed steady-state saturation of the signal with increasing pump intensity. In the limit $n_0 \rightarrow \infty$, Eq. (1) becomes the kinetic law usually used for the description of the PA dynamics in conducting polymers.[11,14,32,36,37,41–45] An alternative explanation for the saturation of the picosecond excited state absorption was given in terms of phase-space filling by one[46] or two[47] dimensional excitons. We think that this mechanism, typical of fast process, cannot account for the long-living excited states here investigated.

The analytical solution of Eq. (2) is very difficult to obtain. However, as previously reported[14,44,48] for the monomolecular decay law, to get a solution we can approximate the modulation term as a square wave. After solving separately the two differential equations relative to the rise and the decay of the photoexcitation population density we impose the conditions of periodicity and continuity of $n(t)$. This method allows us to derive the modulus of the signal but not its phase. The steady-state density of trapped photoexcitations n_s in the case of the monomolecular decay described by Eq. (2) is then given by

$$n_s = gI\tau^* \frac{(1-e^{-(\pi/\omega\tau)})(1-e^{-(\pi/\omega\tau^*)})}{(1-e^{-\pi/\omega(1/\tau+1/\tau^*)})}, \tag{3}$$

where

$$\frac{1}{\tau^*} = \frac{gI}{n_0} + \frac{1}{\tau} = \frac{1}{\tau_I} + \frac{1}{\tau}. \tag{4}$$

τ^* is the total lifetime of the photoexcitation kinetics and it depends on the pump intensity.

In the limit $gI\tau/n_0 \ll 1$ $(\tau \ll \tau_I)$, $n_s = gI\tau \tanh(\pi/2\omega\tau)$ as in the classical monomolecular decay with square wave pump.[48] In the case $gI\tau/n_0 \gg 1$ $(\tau \gg \tau_I)$, i.e., total saturation of the signal, $n_s = n_0[1-\exp(-\pi/\omega\tau)]$ is independent on the pump intensity. Here for low chopper frequencies $(\omega\tau \ll 1)$, $n_s = n_0$, while for high frequencies $(\omega\tau \gg 1)$, $n_s = n_0\pi/\omega\tau$. Should the intensity dependence of the PA signal show both the limiting cases $[gI\tau/n_0 \ll 1$ $(\tau \ll \tau_I)$ and $gI\tau/n_0 \gg 1$ $(\tau \gg \tau_I)]$ in the investigated range of laser powers, the density of traps could be determined from the crossing point of the two extreme behaviors,

$$n_0 = \frac{gI\tau}{1+e^{-\pi/\omega\tau}}, \tag{5}$$

when the lifetime of the excitations is known (for instance from the modulation frequency dependence).

The analysis of Eq. (3) allows us to determine the behavior of the PA signals for the two limiting cases:

(i) $\omega\tau \ll 1$

$$n_s = gI\tau^* = \frac{gI}{g\dfrac{I}{n_0} + \dfrac{1}{\tau}} = \frac{n_0}{1+\dfrac{\tau_I}{\tau}} \tag{6}$$

for both $\omega\tau_I \ll 1$ and $\omega\tau_I \gg 1$. Notice that in Eq. (6) the intensity dependence of n_s can be roughly approximated by a power law.

(ii) $\omega\tau \gg 1$

$$n_s = \frac{n_0\pi}{\omega\tau\left(1+\dfrac{2\tau_I}{\tau}\right)} \quad \text{for} \quad \omega\tau_I \gg 1, \tag{7}$$

$$n_s = \frac{n_0\pi}{\omega\tau\left(1+\dfrac{\tau_I}{\tau}\right)} \quad \text{for} \quad \omega\tau_I \ll 1; \tag{8}$$

that is, in both cases the PA signal decays according to the ω^{-1} law. n_s of Eq. (7) can be again approximated by a power law while no intensity dependence appears in Eq. (8).

The PA signal $(-\Delta T/T)$ is directly proportional to the density (n_s) of the photoexcitations in the steady state. This relation allows us to fit the experimental data on the pump intensity dependence reported in Fig. 4 with Eq. 3. The pumping power (P) can be easily converted to density of absorbed photons per unit time I $(\mathrm{cm}^{-3}\,\mathrm{sec}^{-1})$ each one carrying an energy $hc/\lambda_{\mathrm{exc}}$ through

$$I = \frac{P\lambda_{\mathrm{exc}}}{hc}\frac{A}{V}, \tag{9}$$

where $A = 1\text{-}R\text{-}T$ (R is reflectivity, T is transmittance), and V is the film volume corresponding to the laser spot. For the sample under study the A/V ratio is approximately given by $10^5\ \mathrm{cm}^{-3}$. For $P = 1\ \mathrm{mW}$, we get $I = 2.45 \times 10^{20}\ \mathrm{cm}^{-3}\,\mathrm{sec}^{-1}$. The dimensionless term τ_I/τ entering these equations can be evaluated in terms of $(\tau_I/\tau)_{P=1}$, which refers to the pumping power of 1 mW,

$$\frac{\tau_I}{\tau} = \frac{n_0}{gI\tau} = \frac{n_0}{g2.45\times 10^{20}P\tau} = \left(\frac{\tau_I}{\tau}\right)_{P=1}\frac{1}{P}. \tag{10}$$

By using Eq. (3) to fit the P dependence of the PA signals for the LE and HE peaks one obtains the curves shown in Fig. 6. For the LE bands Eq. (3) allows us to obtain much better fittings than the power law [Figs. 6(a) and 6(b)]. Several pairs of the parameters τ and τ_I give very good fits provided that $\tau < 10^{-3}$ sec and $(\tau_I/\tau)_{P=1} = 31.17$ (0.82-eV peak), 32.26 (0.95-eV peak). The condition found for the lifetime is in agreement with our assignment of these peaks to trapped charged excitation. Moreover, the similarity of the $(\tau_I/\tau)_{P=1}$ ratios indicate that the two LE bands are strictly related, as previously found, also for polyDCHD. For the HE peak instead Eq. (3) gives a rough fit while the power law gives a result $(I^{0.51})$ compatible with a bimolecular kinetics. Here again the fitting procedure requires $\tau < 10^{-3}$ sec and $(\tau_I/\tau)_{P=1} = 108.57$. Notice that the decimal figures of $(\tau_I/\tau)_{P=1}$, though physically meaningless, are meaningful for the mathematical fittings as their values are critical for the minimization procedure.

The determination of the lifetime τ of the photoexcitations from the cutoff in the modulation frequency dependence of ΔT (Refs. 14,20,32) could allow the evaluation of n_0. Unfortunately this is not possible in our case because the modulation frequency dependence of the HE band does not show any cutoff, as one can see in Fig. 5. Moreover, the LE bands give power-law decays in contrast with the prevision of single decay channel kinetics. This fact suggests that a distribution of the lifetimes must be introduced to account for the experimental data. The lifetime distribution is easily understood as due to the different trap depths that may affect the lifetime of the trapped excitations. Detailed calculations of the cw kinetics of PA have not been so far reported. However, the description of a monomolecular decay in the absence of traps but with two different decay lifetimes was recently attempted.[49]

The traps density is related to the density of conjugation defects, i.e., chain twistings, chain ends, and oxidation sites.

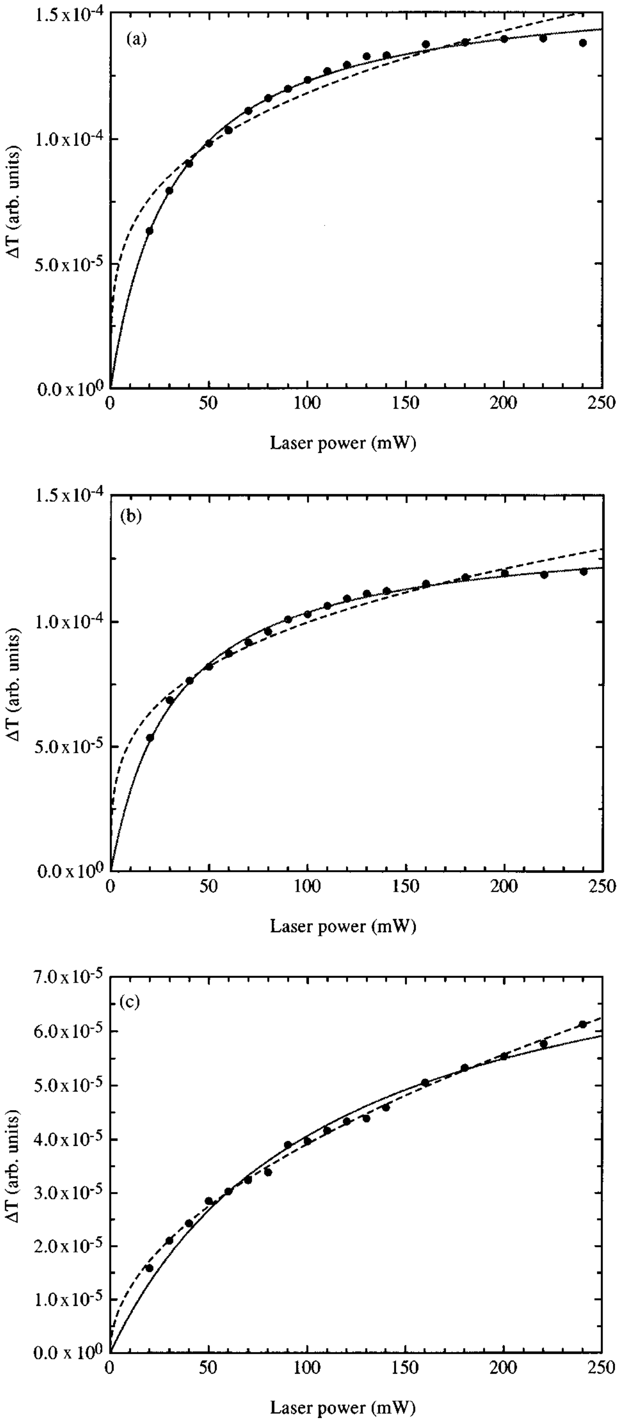

FIG. 6. Intensity dependence of the photoinduced signals at 0.82 (a), 0.95 (b), and 1.39 eV (c). Power-law fittings (dashed lines). Fittings with Eq. (3) of the text (full lines).

If the only defects present are the chain ends, the density of traps can be calculated from the volume ($V=5\times 10^{-6}$ cm^3), the density (1.6 g cm^{-3}) of the sample, and the polymerization index of PDA 4BCMU chains [$N=2400$ (Ref. 50)]. The result is a trap density around 10^{13} cm^{-3}. We can try to compare this value with that of n_0 from the fittings of the PA data. This would require an estimate of the lifetimes of the different defects. We will limit our considerations to the HE band due to the triplet excitons because the lifetime distribution of the photoexcitations responsible for the two LE bands prevents their use in the estimation of n_0. From the dependence of the HE band on the modulation frequency we infer that the lifetime τ is less then 10^{-3} sec. Then we get

$$n_0 = 2.45\times 10^{20} g\left(\frac{\tau_I}{\tau}\right)_{P=1}.$$

If we assume $g=10^{-6}$ we get $n_0=10^{13}$ for $\tau=10^{-3}$ sec and 10^{10} for $\tau=10^{-6}$ sec. This comparison, which seems to indicate the presence of defects essentially on chain ends, seems interesting. We are aware of all the approximations of the present calculations and believe that the formulation here developed can be used for the study of other systems in which all the parameters are known.[51]

The PA spectra here reported suggest to us another interesting observation. The HE band, due to a triplet-to-triplet exciton transition, in blue PDA-4BCMU is located at 1.39 eV, as previously observed by picosecond PA.[8,9] In red PDA-4BCMU this band is located at 1.5–1.6 eV (Refs. 8–10 and 50) and in the yellow form at 1.7–1.8 eV (Ref. 52). These energy shifts can be reasonably related to the different conjugation length in the different forms as observed in controlled length oligothiophenes.[43] However, more interesting is the comparison with other PDA's. In polyDCHD we detected a triplet exciton transition at 1.26 eV and in its soluble derivative (polyDCHD-S) at 1.45 eV for the blue form and at 1.4 eV for the red form thus showing that the conjugation length is not the only parameter affecting the transition energy. It is possible that the nature and depth of the traps affect this energy but we cannot exclude that the detailed characteristic of the excited states of these polymers can be dependent on the nature of the side groups and on the supramolecular ordering. Models for the electronic states concerning the conjugated skeleton alone cannot be adequate for the description of these materials.

The most interesting feature of the spectra here reported are the LE PA peaks. The comparison with the behavior of the PA spectra of other recently studied PDA's, unambiguously assigns these peaks to photoexcited charged states. This is an absolutely new feature for PDA-4BCMU. Even though this polymer was greatly studied in the past, and, in particular, with ultrafast spectroscopies,[8,10,52] which more directly probe the intrinsic photoexcited states, the PA spectrum of this polymer for probe energies *below 1.2 eV* was never reported. The experience gained in the study of polyCzDA's suggests that charged states for the blue form of these polymers appear in this spectral region. The fact that no photoinduced charge transfer to C_{60} was detected in PDA-4BCMU (Ref. 10) as instead found for other conjugated polymers could be due to the fact that the red form of the polymer was used. On one hand, the red forms of PDA's do not give rise to photoexcited charged states, as demonstrated by their PA spectra where only triplet excitons are detected. On the other, no theoretical evaluation of the excited electronic states for this form is available so that it is difficult to estimate if the transfer from red PDA's to C_{60} is favorable. We notice that, instead, in the blue forms of the same polymers also charged states (polarons or bipolarons) are observed. The fact that charged states are a quite general feature of blue PDA's opens new possibilities for molecular engineering. In fact, the electronic properties of blue PDA's can be modified to allow a charge transfer process with other systems. This fact could be of great importance for the realization of photovoltaic devices because (joined with the great order and consequent high mobility of the carriers in blue PDA's) an increase in the energy conversion of these devices could be obtained.

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