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Photoexcitations in polycarbazolyldiacetylenes

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We present the results of a photoinduced-absorption study carried out on an unsymmetrical polydiacetylene having a carbazolyl group directly bound to the acetylene moiety, i.e., poly-1(-N-carbazolyl)penta-1,3-diyn-5-acetoxy (polyCPDA). The absorption spectrum of microcrystalline samples in a KBr pellet shows a broad maximum at $\approx$ 2.2 eV. Photoexcitation of these samples at 2.54 eV gives rise to a luminescence emission from 1.4 to 2 eV with a maximum at $\approx$1.8 eV and two well-resolved photoinduced-absorption (PA) peaks at $\approx$0.45 and $\approx$1.1 eV. From the temperature, laser intensity, and chopper frequency dependence of the PA signals, we demonstrate that the dominant long-lived photocarriers are charged bipolarons formed by interchain charge separation. The lifetimes of the bipolarons in polyCPDA have been found of the order of seconds at 80 K. The intermolecular nature of the observed PA bands appears to be confirmed by the absence of any photoinduced signal in a solution of oligomers of the same polydiacetylene.

I. INTRODUCTION

In the class of conjugated polymers, polydiacetylenes (PDA's) have stimulated considerable interest due to their large cubic susceptibility $\chi^{(3)}(\omega)$ (Refs. 1- 5) and their electrical transport properties.[6] These polymers possess a conjugated backbone of double, single, and triple alternated bonds to which a variety of side groups can be attached. A great advantage of these conjugated polymers over the conventional materials with conjugated polyenic backbone is the possibility to form macroscopic single crystals through topochemical solid-state polymerization. Moreover, the electronic and mechanical properties of PDA can be tailored by a proper choice of the substituents. In particular the extent of the intermolecular interaction, which affects the one-dimensional properties of the conjugated polymers, can be greatly reduced by the insertion of bulky substituents.

The most widely studied PDA is the toluene sulphonate derivative PDA-TS as it forms large, highly perfect, single crystals. It is a semiconductor with an estimated band gap of 2.4 eV and a strong exciton absorption located around 2 eV.[7,8]

Simple tight-binding models for the evaluation of the nonlinear optical response function[9] indicate that $\chi^{(3)}(\omega) \propto (E_F/\ E_g)^6$ where E_F is the Fermi energy and E_g is the band gap. Since E_g is directly related to the extent of the electronic delocalization, in principle, a lowering of the energy gap in PDA can be achieved by attaching aromatic groups directly to the backbone. However it has been found that the polymerizability of monomers with two aromatic substituents is usually very low. For these reasons we have prepared and studied unsymmetrical PDA's with the carbazolyl group as one of the substituents (Fig. 1).

The optical properties and the photoconductive response of one of these polydiacetylenes, poly(CPDO), have been extensively studied and a sensible reduction of the band gap down to 1.6 eV has been proposed.[4,10] In this paper we report on the photoexcitation of poly(CPDA), carried out using the photoinduced absorp-

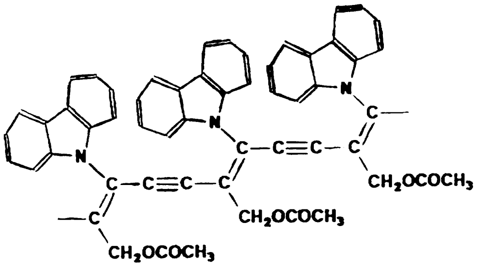

FIG. 1. Chemical structure of poly(CPDA).

tion technique.

In polydiacetylene, which possesses a nondegenerate ground state, the strong electron-phonon interaction leads to a self-trapping of the charges into a variety of nonlinear excitations such as shown in Fig. 2. While excitons and polarons can be formed by processes involving single-chain excitations, bipolarons are only formed by separation of the electron-hole pair onto different chains and subsequent fusion of two positive or negative polarons.

All these excitations are associated with electronic states in the gap, spectroscopically accessible (see Fig. 2). Even though, in principle, polarons and bipolarons exhibit a different number of photoinduced bands, it has been theoretically predicted that the intensity of one of the three polaronic bands might be low,[11] thus making it difficult to distinguish between different photoexcited species on this basis. More complete information on the nature of photoexcited states can be obtained by examining the photoinduced bands as a function of temperature, laser intensity, and chopper frequency.

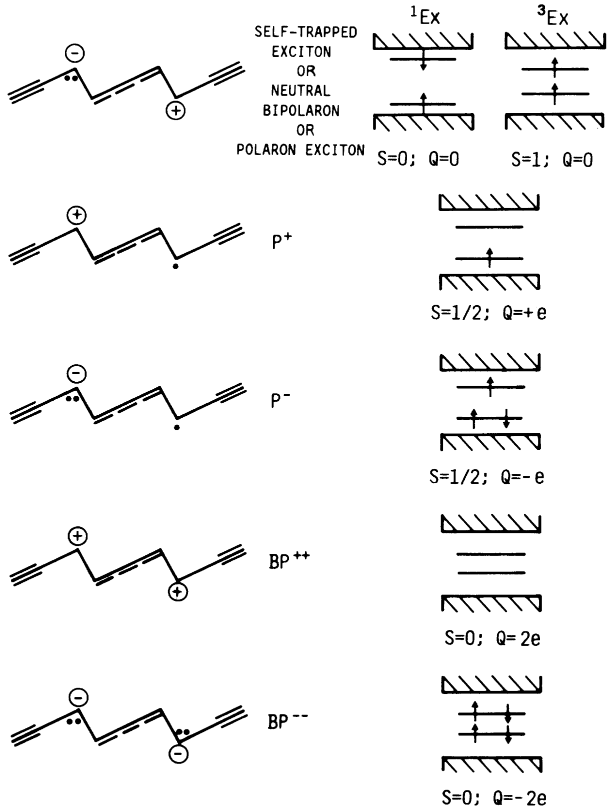

FIG. 2. Schematic diagram showing the possible nonlinear excitations in poly(CPDA) (left). Energy levels (right) for the neutral polaron exciton (shown in both its singlet and triplet states), positively charged polaron (P^+) and bipolaron (BP^{++}), negatively charged polaron (P^-) and bipolaron (BP^{--}).

II. EXPERIMENTAL

1(-N-carbazolyl)penta-1,3-diyn-5-acetoxy (CPDA) has been prepared according to the scheme described in Fig. 3. N-acetylcarbazole (1) was first prepared from carbazole by reaction with acetic anhydride under acid catalysis. Then conversion to N-α,β-chloroethinylcarbazole (2) was carried out by reflux in toluene for ≈30 h in the presence of PCl_5.

Successive reaction of this product with butyllithium in anydrous Et_2O, instead of sodium amide in liquid ammonia as reported in the literature,[12] gave N-ethynilcarbazole (3) in quantitative yield. Also in the final coupling stage between N-ethynilcarbazole and 3-Br-2-propyn-1-ol, the usual Chodkiewicz and Cadiot oxidative coupling[13] was substituted by a two-step procedure by preparing first the copper I salt of N-ethynilcarbazole (4) and then reacting it with 3-Br-2-propyn-1-ol in pyridine (40% yield). 1(-N-carbazolyl)penta-1,3-diyn-6-ol (CPDO) (5) with acetylchloride in dichloromethane and in the presence of pyridine gave CPDA.

After crystallization a product with melting point 84 °C was obtained (51% yield). The monomer was characterized by ir and ^{1}H NMR spectroscopies and by elemental analysis.

Thermal polymerization was carried out in microcrystalline samples dispersed in KBr pellet at 78 °C following the time evolution of the visible absorption spectrum. Oligomers soluble in dichloromethane were obtained by solvent extracting a microcrystalline sample bulk polymerized at the same temperature.

Electronic absorption spectra were recorded on a Perkin Elmer spectrophotometer model Lambda 9, equipped with the integrating sphere accessory or with the same apparatus used for photoinduced measurements. Photoinduced spectra were obtained on a homemade apparatus. Samples were mounted onto the cold finger of a cryotip Joule-Tomson cryostat (Air Products

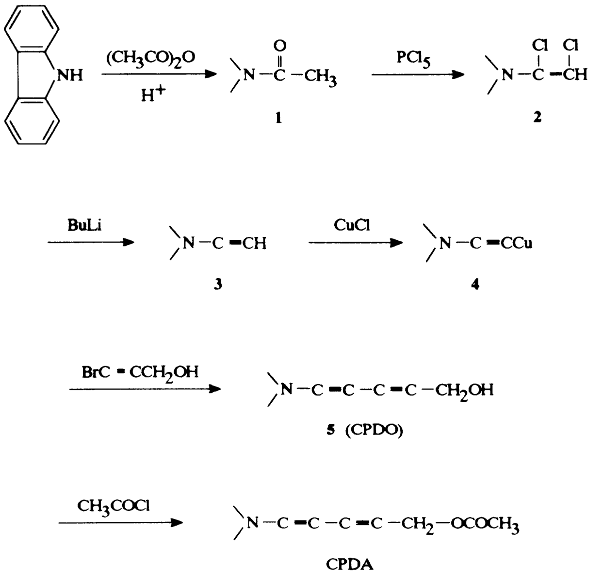

FIG. 3. Synthetic scheme of poly(CPDA).

and Chemicals). Sample temperature was monitored by a thermocouple placed on the cold finger.

Transmission (T) spectra were recorded in the range from 0.4 to 2.2 eV with an incident chopped light beam from an iodine-quartz lamp (probe). The transmitted light was dispersed with a McPherson 218 monochromator driven by stepping motor, and detected with a photomultiplier tube or a Peltier cooled PbS detector. The output of a EG&G 5205 lock-in amplifier was recorded by using as reference the frequency of the light chopper. Photoexcitation was provided by the 488- or 514-nm lines of a cw argon-ion laser (pump). The photoinduced variation in sample transmission (ΔT) was obtained by chopping the laser light between 0.7 and 600 Hz. ΔT, coming from the detector, was revealed by the lock-in amplifier using as reference the pump chopper frequency. The data, coming from the pump (ΔT) and probe (T), were stored and processed by on line IBM computer in order to obtain $-\Delta T/T$ spectra.

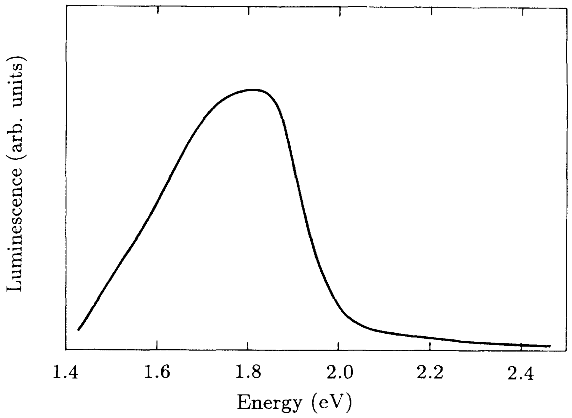

FIG. 5. Luminescence spectrum of poly(CPDA) at T = 80 K ($\lambda_{\rm exc}$=488 nm).

III. RESULTS

In Fig. 4 the electronic absorption spectrum of poly(CPDA) is shown at 80 and 300 K, indicating that no appreciable change in absorption occurs by lowering the temperature. Figure 5 shows the luminescence spectrum which peaks at ≈1.8 eV. The luminescence emission has been found to be proportional to the laser intensity as expected for a one-photon process. Bloor[14] demonstrated that in other polydiacetylenes the luminescence emission is associated with the presence of disorder as it is not observed in fully polymerized single crystals. Also, in our microcrystalline PDA, defects can act as traps for the exciton originated from the hot electron-hole pairs and become sites of radiative emission.

Figure 6 shows the photoinduced absorptions (PA) and bleaching at 77 K at two laser wavelengths normalized to the same number of absorbed photons. Two well-defined absorptions of comparable intensity are observed at 1.1 and 0.45 eV. The overall intensity of the PA spectrum decreases upon decreasing of the photon energy, similarly to what is already observed in polyacetylene upon excitation across the absorption band. Our data are, however, too poor to allow determining the origin of the photon energy dependence in poly(CPDA). What we want to stress here is that both peaks in Fig. 6 show the same behavior. Figure 7 shows the decrease of the intensity of the PA spectrum with increasing temperature. It is apparent that the two photoinduced bands exhibit similar temperature dependence at least up to 180 K. At room temperature the PA spectrum is still detectable and only one broad absorption roughly centered at ≈1 eV is observed.[15]

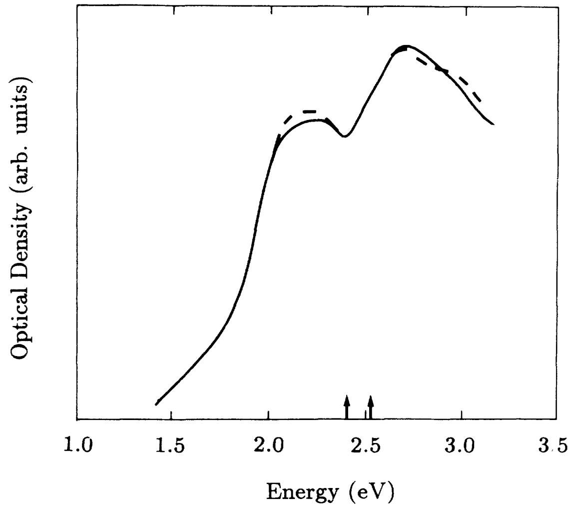

FIG. 4. Optical density spectra of poly(CPDA) in KBr pellet at T = 80 (full line) and 300 K (dashed line). Arrows show exciting laser lines.

To check the nature of the photoinduced bands (polarons, bipolarons, excitons, etc.) we have studied their dependence on the laser power and chopper frequency. Both bands exhibit the same square root dependence on the exciting intensity as illustrated in Fig. 8 and the same chopper frequency dependence in the high-frequency regime (Fig. 9), again this being indicative of

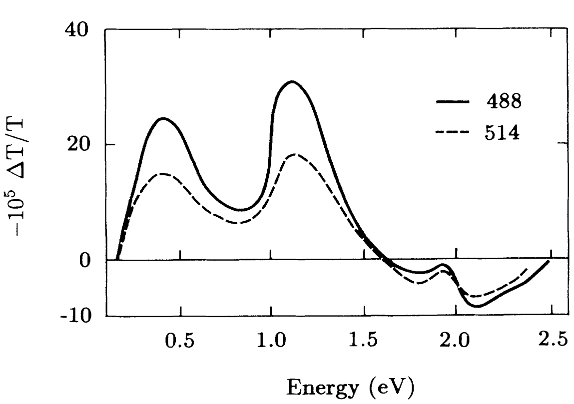

FIG. 6. Photoinduced spectra of poly(CPDA) using the 488- and 514-nm excitation wavelength, $f_{\rm chopper}$= 23 Hz, T = 80 K, laser power 50 mW (the spot light has 7 mm of diameter).

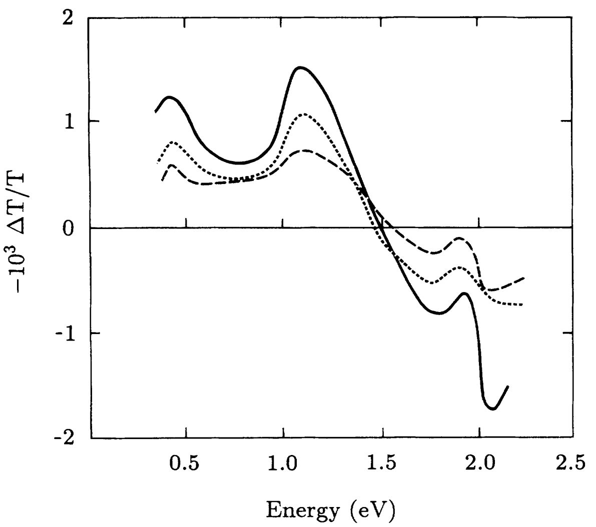

FIG. 7. Temperature dependence of the photoinduced spectrum of poly(CPDA). $T = 80$ (full line), 120 (dotted line), and 180 K (dashed line), $\lambda_{\text{exc}} = 488$ nm, laser power $= 200$ mW, $f_{\text{chopper}} = 13$ Hz.

a common origin.

These experimental data suggest that the two photoinduced peaks are associated with bipolaronic states. Indeed the sublinear dependence on the photon flux can be related to a bimolecular photogeneration mechanism in which two polarons (P), generated by interchain electron transfer, form a bipolaron (BP) and bipolarons decay by bimolecular mechanism. In fact the general rate equation for the BP is

$$\frac{dn_{\text{BP}}}{dt} = \beta_{\text{P}} n_{\text{P}}^2 - \beta_{\text{BP}} n_{\text{BP}}^{\alpha} \approx \left(G(t) - \frac{dn_{\text{P}}}{dt} \right) - \beta_{\text{BP}} n_{\text{BP}}^{\alpha} \tag{1}$$

with $\alpha=1$ or 2 depending on whether the recombination is monomolecular (trap mediated) or bimolecular (direct).

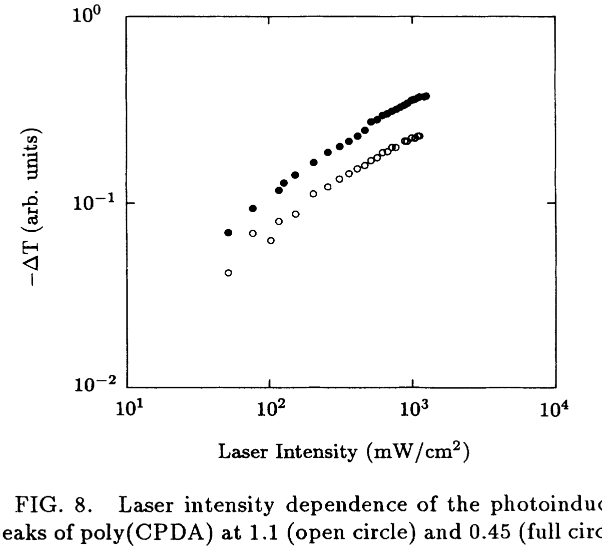

FIG. 8. Laser intensity dependence of the photoinduced peaks of poly(CPDA) at 1.1 (open circle) and 0.45 (full circle) eV. $\lambda_{\text{exc}} = 488$ nm, $f_{\text{chopper}} = 13$ Hz, $T = 80$ K.

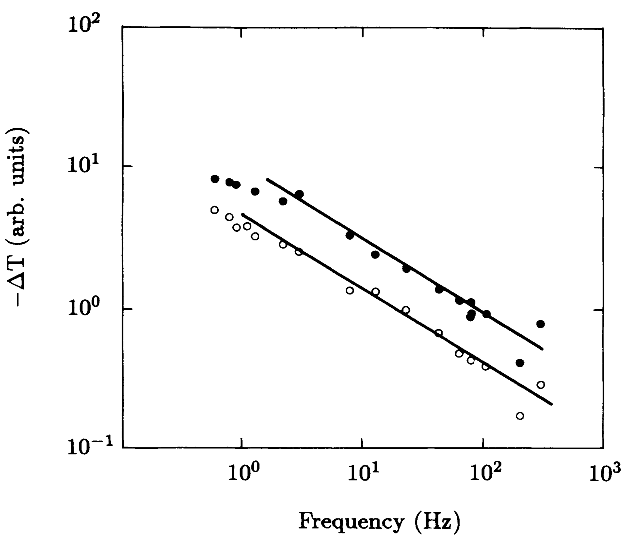

FIG. 9. Chopper frequency dependence in the high-frequency regime of the photoinduced peaks of poly(CPDA) at 1.1 (full circle) and 0.45 (open circle) eV; $\lambda_{\text{exc}} = 488$ nm, laser power 100 mW, $T = 80$ K.

Here β_{P} is the bimolecular recombination constant for polarons and β_{BP} is the rate constant for bipolarons decay. The pump rate is given by $G(t) = \sigma_{\text{P}} I(t)/\hbar\Omega$, where σ_{P} is the absorption cross section for polaron formation, Ω is the laser frequency, and $I(t)$ is the laser intensity. In photomodulation experiments, using lock-in detection, $I(t)$ has the form $I(t) = I_0 \exp(i\omega t)$, where $\omega = 2\pi f$, f being the chopper frequency (Hz). Under the steady-state conditions for the polarons kinetics Eq. (1) becomes

$$\frac{dn_{\text{BP}}}{dt} = \frac{\sigma_{\text{P}}}{\hbar\Omega} I(t) - \beta_{\text{BP}} n_{\text{BP}}^{\alpha} . \tag{2}$$

In the steady state, the carrier density would depend on I if the mechanism of decay is monomolecular ($\alpha=1$) but on $I^{1/2}$ when it is bimolecular ($\alpha=2$). In the case where a monomolecular decay time $\tau = 1/\beta_{\text{BP}}$ governs the relaxation of the photoexcited states, the chopper frequency dependence of the solution of Eq. (2) is given by

$$n_{\text{BP}}(t) \propto \frac{\tau}{\sqrt{1+\omega^2\tau^2}} e^{i(\omega t - \phi)} \tag{3}$$

with $\tan\phi = \omega\tau$, ϕ being the phase of the lock-in detection. Thus in the low-frequency limit ($\omega\tau \ll 1$) the PA signal, which is proportional to the amplitude of $n(t)$, would be roughly independent of frequency while in the high-frequency limit ($\omega\tau \gg 1$) it would decrease with increasing frequency as ω^{-1}.

In the case of the bimolecular decay [$\alpha=2$ in Eq. (2)] analytical solutions for the general case have not yet been reported, at least to our knowledge. However, some information on the time constant of this process can be derived by applying a photomodulation technique to analyze a transient decay ($G=0$) of bipolarons. This condition implies that the recombination time for bipolarons is very long compared to their formation time, in agreement with the usual assumption that bipolarons are metastable states.[7,16] In this case the density of excitations is

$$n_{\mathrm{BP}}(t) = \frac{n^0_{\mathrm{BP}}}{1+\beta_{\mathrm{BP}} n^0_{\mathrm{BP}} t} = \frac{n^0_{\mathrm{BP}}\tau}{t+\tau} , \qquad (4)$$

where n^0_{BP} is the concentration at $t = 0$ and the time constant $\tau = (\beta_{\mathrm{BP}} n^0_{\mathrm{BP}})^{-1}$ depends on the pump intensity. The change in transmittance ΔT is then given by

$$n^0_{\mathrm{BP}} - n_{\mathrm{BP}} = \frac{n^0_{\mathrm{BP}}}{1+\frac{\omega\tau}{\pi}} , \qquad (5)$$

where t is one-half of the modulation time of the PA measurements. Equation (5) predicts that in the low-frequency limit ($\omega\tau/\pi \ll 1$) the signal is roughly independent of chopper frequency, while in the high-frequency limit ($\omega\tau/\pi \gg 1$) it decreases as ω^{-1}. The region of crossover ($\omega\tau/\pi \approx 1$) provides the value of the time constant. Apparently these conclusions are the same as for the monomolecular process. However only for the bimolecular annihilation process does the crossover position depend on the pump intensity.

The experimental chopper frequency dependence in Fig. 10 is in agreement with the prediction of the bimolecular kinetics. Indeed by increasing the pump power from 20 to 500 mW the position of the crossover frequency varies approximately as $(I)^{-1/2}$ as shown in Fig. 11.

The data discussed so far would indicate the bipolaronic nature of the excitations responsible for the photoinduced peaks of poly(CPDA). There is still an open problem to be solved relative to the fall off of the photoinduced signal according to $\omega^{-1/2}$ upon increasing chopper frequency. This type of decay has been quite generally observed for the photoexcitation bands of conjugated polymers which have been assigned to bipolarons, and has been interpreted in terms of a spread in recombination rates of photoexcited bipolarons.[17]

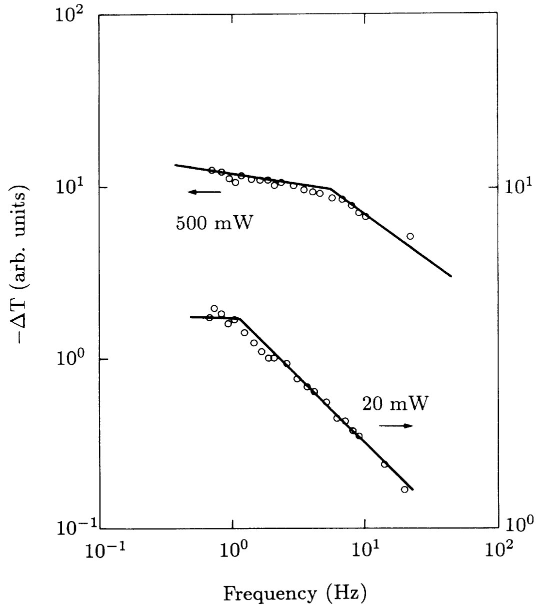

FIG. 10. Chopper frequency dependence in the low-frequency region of the 1.1-eV peak of poly(CPDA) for two different laser intensities; λ_{exc}= 488 nm, T = 80 K. For the discussion of the crossover region see text.

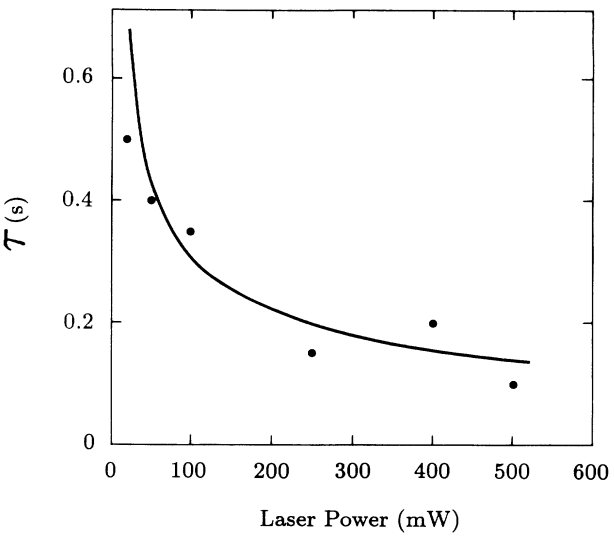

FIG. 11. Bipolaronic lifetimes as a function of the laser power (see text); λ_{exc}= 488 nm.

From the crossover of the high-frequency to low-frequency behavior in Fig. 10, we can give a rough estimate of the characteristic time for the decay of the longest-lived excitations at 80 K, $\tau \approx$ 0.1–0.5 sec. This long decay time is in agreement with long lived photoexcitations observed in several polydiacetylenes.[16,18] Other conjugated polymers show shorter decay times.[17,19,20] Also the temperature dependence shown in Fig. 7 is indicative of a recombination process characterized by low activation energy of the order of 10^{-2} eV. A similar value has been reported for the hopping rate of the charged bipolarons in PDA-9PA, $\{R = R' = (\mathrm{CH_2})_9\mathrm{OCOCH_2C_6H_5}\}$ and PDA-4BCMU $\{R = R' = (\mathrm{CH_2})_4\mathrm{OCONHCOO}(\mathrm{CH_2})_3\mathrm{CH_3}\}$ as derived from the temperature dependence of the photoinduced infrared active vibration modes in these polymers.[16]

IV. DISCUSSION

Experimental evidence gathered in the present work indicates that the long-lived photoexcitations in poly(CPDA) are charged bipolarons. A number of considerations support this interpretation. (i) Both the bands at 1.1 and 0.45 eV are asymmetric with a tail towards higher energies. This is indicative of transitions from localized states to a continuum, consistently with the formation of bipolarons rather than polarons as the main photoexcited species. Indeed, for a polaron only two of the three below gap absorptions are predicted to have appreciable intensity[11] but of these, one involves localized states and should therefore give rise to a symmetrical band. (ii) The observed dependence of the decay kinetics of the PA peaks on the square root of the laser intensity rules out a monomolecular generation mechanism. (iii) The observed dependence of the crossover region in the plot of $-\Delta T/T$ against the chopper frequency on the pump intensity confirms a bimolecular decay of the photoexcitations.

Our findings are in agreement with the conclusions reached by Pratt *et al.* on the basis of photoinduced absorption studies carried out on PDA-1OH $\{R = \mathrm{CH_3}, R' = \mathrm{CH_2OH}\}$.[18,21] For this polymer the two PA electronic bands of comparable intensity at 1.32 and 0.25 eV detected using different apparatus and excitation energies, are found to be consistent with photogeneration of bipolarons.

The identification of the photoexcitations in poly-CPDA as resulting from charged, spinless bipolarons is also consistent with the previously reported observations of photoinduced infrared-active vibrational modes in PDA-9PA, PDA-TS, PDA-4BCMU,[16] and in PDA-1OH,[21] and with the absence of any signal in light-induced electron spin resonance measurements.[16]

We would like to stress at this point that in other PDA's only one high-energy band has been observed. For PDA-TS in fact only a PA peak at 1.35 eV which has been assigned to a transition involving a triplet excitonic state in the gap has been found.[22] No indication of a low-energy band has been reported for this polymer.[21]

A possible explanation for the different origin of the PA peaks in the above PDA can be given by considering that, in polydiacetylenes, bipolarons are created through interchain charge transfer and coexist with intrachain singlet and triplet (neutral) excitations. Whether the main long-lived photogenerated defects are of interchain or intrachain nature will then depend on the efficiency of the interchain transfer which is related to the interchain distance. Since the polymer chains are more separated in PDA-TS than in PDA-1OH,[21] and presumably in poly(CPDA), we consider that poorer contact between chains in PDA-TS over those of other PDA prevents the formation of metastable charged defects.

The energy separation of the two subgap peaks ($2\omega_0$) in poly(CPDA), only 0.65 eV, is much smaller than that reported for PDA- 1OH (1.07 eV) and is comparable with the value 0.8 eV found in another nondegenerate ground-state conjugated polymer, namely polythiophene.[19] The size of the bipolaron is determined by the confinement parameter γ, which is function of the ratio $2\omega_0/E_g$.[11] By using a value of the energy gap from 2.2 to 2 eV we derive a value for $\gamma \approx 0.10$. For PDA-1OH a value of γ=0.23 can be evaluated from the data of Ref. 21. We note that the introduction of a carbazolyl group directly bound to the polymer backbone appears to reduce both the band gap and the confinement degree of the photoinduced defects, due to more extensive delocalization. A larger value for the confinement parameter is obtained for the polaron or polaron exciton. In this case the value for $2\omega_0$ is obtained from the energy of the photoluminescence[11] (1.8 eV) indicating a far larger splitting of the gap states for the polaron exciton than for the bipolaron.

In the presence of Coulomb interaction, the sum of the frequencies ω_1 and ω_2 of the two PA bands of the bipolarons is related to the band gap through[23]

$$\omega_1 + \omega_2 = E_g - 2U_B, \tag{6}$$

where U_B is the difference in Coulomb energy between the initial state (double charge) and the final state (single charge) with fixed lattice coordinates. From $\omega_1 + \omega_2 =$ 1.55 eV and $E_g \approx$ 2–2.2 eV, we find U_B= 0.22–0.32 eV and U_B/E_g=0.11–0.15. As already discussed by several authors,[19,24] this small value for U_B is consistent with the existence of bipolarons as the dominant charge excitation.

A more complete description of the photoexcitation dynamics of polydiacetylenes could be reached by comparing our results with those of the recent pump and probe experiment carried out on PDA-3BCMU $\{R = R' = \mathrm{(CH_2)_3OCONHCOO(CH_2)_3CH_3}\}$ and PDA-4BCMU using femtosecond laser pulses at 1.97 and 3.94 eV with probe energies ranging from 2.2 to 1.1 eV.[5] The main photoinduced absorption at 1.8 eV, observed with both the excitations, is assigned to singlet self-trapped excitons formed either from the initially photogenerated free ^1B_u excitons or from electron-hole pairs photogenerated by two-photon absorption. The decay of the PA peak depends only very weakly on the temperature, indicating that the thermal activation process of overcoming the potential barrier is not dominant in either the formation or the relaxation process of the self-trapped excitons. The weaker, longer-lived component of the photoinduced absorption at 1.5 eV, assigned to a triplet exciton, is generated by the 3.94-eV excitation and also by the two-photon absorption of the 1.97-eV laser pulse.

The results presented in the present work which refer to excitations possessing lifetimes of the order of the milliseconds to seconds, combined with those obtained in the femtosecond to picosecond regime previously sketched allow to draw the following scenario for the photoexcitations in PDA.

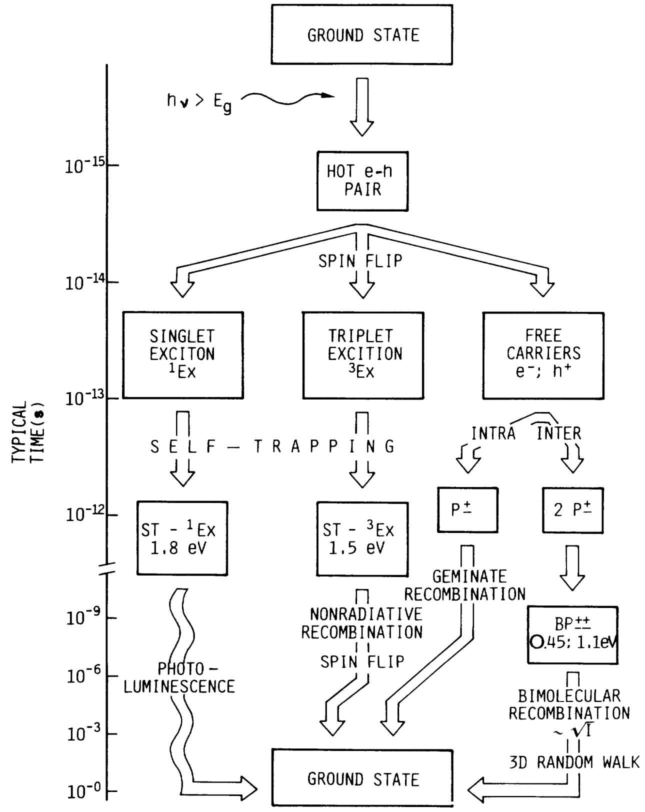

FIG. 12. Scheme of photoexcitations in polydiacetylenes.

When a photon with an energy corresponding to a singlet exciton is absorbed, it is quickly transformed into a trapped exciton (peak at 1.8 eV) which decays through radiative and nonradiative mechanisms.

For photons with energies above the interband gap E_g three decay pathways are possible for the photogenerated hot electron-hole pairs: (i) Most of them undergo geminate recombination and yield singlet excitons detected from the 1.8-eV peak seen in the picosecond range. (ii) A small fraction of the charged pairs will lose their spin memory and recombine into triplet states. Unlike singlet excitons which are detected only with the time resolved pump and probe technique, triplet excitons possess longer lifetimes and can be seen also in a steady-state experiment (photoinduced absorption).[5,22] (iii) The fraction of carriers escaping geminate recombination after thermalization will form polarons or, if charge separation between neighboring chains takes place, bipolarons. These latter excitations have usually long lifetimes and are easily seen in the photoinduced absorption experiments. Their motion is trap limited and therefore their recombination through bimolecular collision is temperature dependent as it is experimentally observed.

Possible photoexcitations pathways for above the gap absorption are described in the scheme depicted in Fig. 12.

ACKNOWLEDGMENTS

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[1] D.J. Sandman, G.M. Carter, Y.J. Chen, B.S. Elman, M.K. Thakur, and S.K. Tripathy, in *Polydiacetylenes*, edited by D. Bloor and R.R. Chance (Nijhoff, Dordrecht, 1985), p. 299.

[2] *Organic Materials for Non-linear Optics*, edited by R.A. Hann and D. Bloor (The Royal Society of Chemistry, London, 1989).

[3] P.A. Chollet, F. Kajzar, and J. Messier, Synth. Met. **18**, 459 (1987).

[4] K. Ichimura, T. Kobayashi, H. Matsuda, H. Nakanishi, and M. Kato, J. Chem. Phys. **93**, 5510 (1990), and references therein.

[5] T. Kobayashi, M. Yoshizawa, U. Stamm, M. Taiji, and M. Hasegawa, J. Opt. Soc. Am. **78**, 1558 (1990), and references therein.

[6] H. Bassler, in *Polydiacetylenes* (Ref. 1), p. 135.

[7] D. Bloor, in *Quantum Chemistry of Polymers—Solid State Aspects*, edited by J. Ladik, J.M. André, and M. Seel (Reidel, Dordrecht, 1983), p. 191.

[8] J. Orenstein, S. Etemad, and G.L. Baker, J. Phys. C **17**, L297 (1984).

[9] C. Cojan, G.P. Agrawal, and C. Flytzanis, Phys. Rev. B **15**, 909 (1977).

[10] H. Matsuda, H. Nakanishi, N. Minami, and M. Kato, Mol. Cryst. Liq. Cryst. **160**, 241 (1988).

[11] K. Fesser, A.R. Bishop, and D.K. Campbell, Phys. Rev. B **27**, 4804 (1983).

[12] Y. Okamoto and S.K. Kundu, J. Org. Chem. **35**, 4250 (1970).

[13] H. Matsuda, H. Nakanishi, T. Hosomi, and M. Kato, Macromolecules **21**, 1238 (1988).

[14] D. Bloor, Synth. Metals **21**, 71 (1987).

[15] G. Garbarino, C. Dell'Erba, C. Cuniberti, P. Piaggio, G.F. Musso, D. Comoretto, G. Lanzani, and G. Dellepiane, in *Optical and Electrical Properties of Polymers*, edited by J.A. Emerson and J.M. Torkelson, MRS Symposia Proceedings No. 214 (Materials Research Society, Pittsburgh, 1991), p. 149.

[16] Y. H. Kim, M. Nowak, Z.G. Soos, and A.J. Heeger, Synth. Met. **28**, D621 (1989).

[17] N.F. Colaneri, D.D.C. Bradley, R.H. Friend, P.L. Burn, A.B. Holmes, and C.W. Spangler, Phys. Rev. B **42**, 11 670 (1990).

[18] T. Hattori, W. Hayes, and D. Bloor, J. Phys. C **17**, L881 (1984).

[19] Z. Vardeny, E. Ehrenfreund, O. Brafman, M. Nowak, H. Schaffer, A.J. Heeger, and F. Wudl, Phys. Rev. Lett. **56**, 671 (1986).

[20] R.H. Friend, D.D.C. Bradley, and P.D. Townsend, J. Phys. D **20**, 1367 (1987).

[21] F.L. Pratt, K.S. Wong, W. Hayes, and D. Bloor, J. Phys. C **20**, L41 (1987).

[22] L. Robins, J. Orenstein, and R. Superfine, Phys. Rev. Lett. **56**, 1850 (1986).

[23] D.K. Campbell, D. Baeriswyl, and S. Mazumdar, Synth. Met. **17**, 197 (1987).

[24] Y.H. Kim, D. Spiegel, S. Hotta, and A.J. Heeger, Phys. Rev. B **38**, 5490 (1988).