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Photoinduced absorption of oriented poly[1,6-di(*N*-carbazolyl)-2,4-hexadiyne]

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We report the photoinduced absorption spectra of an oriented form of poly[1,6-di(*N*-carbazolyl)-2,4-hexadiyne] (polyDCHD) grown by molecular epitaxy. The polarized absorption spectra of the polyDCHD point out the high quality of the sample and the very high degree of alignment of the polydiacetylene chains. The millisecond photoinduced absorption spectrum shows the same features already observed in polycrystalline samples assigned to triplet excitons in addition to bipolarons. The study of the dependence of the photoinduced absorptions on the polarization of the laser beam confirms this assignment. After correction for the same number of absorbed photons in both polarizations, the photoinduced signal assigned to bipolarons is stronger by pumping with the electric field of the radiation perpendicular to the chain axis direction. This fact is indicative of the interchain nature of the generation process of these photoexcited species. On the other hand, such an effect is not observed for the photoinduced triplet-triplet transition according to its intramolecular nature. [S0163-1829(96)06924-X]

I. INTRODUCTION

The electronic, transport, and nonlinear optical properties of π-conjugated polymers have been intensively investigated for their applications in both electroluminescent flat displays[1] and photonic devices.[2] These properties are mainly due to the one-dimensional nature of the macromolecules that allows the delocalization of π electrons along the polymeric skeleton. However, the complete exploitation of the monodimensional character is usually prevented by the low degree of orientation of the polymer chains.

Several methods have been used to obtain oriented conjugated polymers such as mechanical stretching of either unoriented films[3] or polymers embedded in a suitable matrix,[4,5] and deposition of polymers on oriented substrates.[6] Among conjugated polymers, the polydiacetylenes (PDAs) represent unique systems since polymer single crystals can be obtained by topochemical polymerization of the monomer single crystals.[7] PDA single crystals show very large anisotropy of the linear and nonlinear optical properties.[8] It is, however, usually difficult to obtain large, defect-free single crystals. In addition, the processability of these materials is low. An improvement in the processability of PDAs, without losing the highly ordered structure typical of the crystalline form, is obtained by vacuum growth on suitable substrates of thin epitaxially ordered films of monomer that, after topochemical polymerization, retains the oriented structure.[9]

The availability of oriented polymeric samples could allow us to gain a deeper insight into the nature of the photoexcited states responsible for the high nonlinear optical response of the material. In a pump-and-probe experiment, the dependence of the photoinduced signal on the polarization of the pumping beam can provide information on the generation process of the excited states, while the dependence on the polarization of the probe beam can provide information on the orientation of the dipole moment of the photogenerated quasiparticles. Results reported in the literature for polyacetylene and polyparaphenylenevinylene[10] have shown that the response with a pump beam polarized perpendicularly to the chain direction is weaker than that with polarization parallel to the chain direction. However, after correcting for the same number of absorbed photons, the response with pump beam perpendicularly polarized results higher than that observed with parallel polarization. This effect is due to the intrinsic nature of the generation process of the photoexcitations. Similar results are also observed in the photoconductive response of oriented samples.[11] The following simple qualitative explanation has been offered for these results:

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when the pump is polarized perpendicularly to the chain axis, the interchain separation of some electron-hole pairs takes place and the interchain self-trapped electron-hole pairs so formed cannot recombine. Instead, for pump polarization parallel to the chain axis, the intrachain self-trapped electron-hole pairs easily recombine. As a consequence, interchain self-trapped pairs exhibit longer lifetimes than the intrachain ones and give rise to anisotropy of the photoinduced spectra. On this basis a quantitative model has been worked out to account for the observed anisotropy of the photoconductive response in oriented trans-polyacetylene where other factors like chain misalignment, sample heating effects, and bimolecular recombination have also been considered.[12] It has been established that a relatively small interchain coupling combined with laser heating effects accounts for the observed anisotropy if bimolecular recombination does not occur.[12]

Another way that is commonly used for the investigation of the long-lived excited states in these systems is the near-steady-state photoinduced absorption (PA) technique. Recently, we have applied this technique to the study of photoexcitations in several microcrystalline polycarbazolyldiacetylenes diluted in KBr.[13–18] Different types of photoexcited states have been detected, depending on the type of PDA and on the sample morphology. A common feature of all our experiments was, however, the presence of bipolarons. Poly[1,6-di(*N*-carbazolyl)-2,4-hexadiyne] (polyDCHD) was the only polymer for which, in addition, to bipolarons, another photogenerated band has been found which has been tentatively assigned to photogenerated triplet excitons.[15]

In the present paper we present the results of a study of the photoinduced spectrum of a film of polyDCHD oriented by molecular epitaxy carried out by using pump beam polarized parallel and perpendicular to the chain direction and unpolarized probe light. The anisotropy of the photoinduced bands allows us to gain a better understanding of the nature of the long-lived nonlinear excitations responsible for the PA spectrum.

II. EXPERIMENT

The oriented thin films of polyDCHD have been obtained by thermal polymerization of monomer films evaporated under a vacuum on a crystal of potassium acid phthalate (KAP). The details of the growth technique are described in Ref. 9. The DCHD molecules are characterized by the large carbazolyl side groups bonded to the conjugated backbone by a methylene spacer. The orientation of the monomer molecules is driven by the molecular insertion of the carbazolyl side groups between the KAP phenyl rings. The molecular matching is stabilized through π interactions between the aromatic groups of the monomer and those of the KAP substrate. The thickness of the polymeric film studied in the present work is of about 0.1 μm.

The polarized electronic absorption spectra have been recorded on a Cary 5*E* spectrophotometer operating in the range 300–2200 nm and equipped with Polaroid-type sheets; the resolution was ~1 nm. The photoinduced absorption spectra have been measured in the spectral range 0.6–2.4 eV every 0.01 eV with a homemade cw-photomodulation setup with lock-in detection (exciting wavelength of the 488-nm (2.54-eV) line of an argon-ion laser). The details of the experimental setup are given elsewhere.[15] The low-temperature measurements have been performed with a hydrogen-helium expansion cryostat.

III. THEORETICAL MODEL

The directly observed quantity in PA experiments is $-\Delta T/T$, the fractional change in sample transmission caused by absorption due to photoexcitation. This quantity is related to the total number of photoexcitations (N) created by a beam of section A through the energy-dependence optical absorption cross section σ of the photoexcited states:[19]

$$-\frac{(\Delta T)_{\parallel,\perp}}{T}=\sigma\frac{N_{\parallel,\perp}}{A}.$$

By using a pump beam polarized either parallel or perpendicular to the chain axis and an unpolarized probe light, the anisotropy of the PA signals is given by the ratio $N_\perp/N_\parallel$ derived as follows. The time dependence of the concentration of long-lived photoexcitations created with the polarization parallel ($n_\parallel$) and perpendicular ($n_\perp$) to the chain on a plane at a distance x from the illuminated surface is given by the following rate equations:[12,20]

$$\frac{dn_\parallel(x)}{dt}=g_\parallel\alpha_\parallel(1-R_\parallel)Ie^{-\alpha_\parallel x}-\frac{n_\parallel(x)}{\tau}-\beta n_\parallel^2(x), \qquad (1a)$$

$$\frac{dn_\perp(x)}{dt}=\{g_\parallel[\alpha_\parallel\sin^2(\delta)+\alpha_\perp^{1D}]+g_\perp\alpha_\perp^{3D}\}(1-R_\perp)Ie^{-\alpha_\perp x}-\frac{n_\perp(x)}{\tau}-\beta n_\perp^2(x), \qquad (1b)$$

where $g_\parallel$ and $g_\perp$ are the efficiencies of the generation of long-lived photoexcitations with parallel and perpendicular pump polarizations; I is the laser intensity; $\alpha_\parallel$ is the absorption coefficient along the chain axis; $\alpha_\parallel\sin^2(\delta)$ is the perpendicular absorption coefficient due to chain misalignment;[21] $\alpha_\perp^{1D}$ and $\alpha_\perp^{3D}$ are the perpendicular intrachain and interchain absorption coefficients, respectively; $\alpha_\perp=\alpha_\parallel\sin^2(\delta)+\alpha_\perp^{1D}+\alpha_\perp^{3D}$ is the overall perpendicular coefficient: and 1D and 3D denote one-dimensional and three-dimensional, respectively. R is the absolute reflectivity of the film, τ represents the lifetime of the photoexcitations under monomolecular decay, and β is the bimolecular recombination constant.

In the steady-state condition ($dn/dt=0$), Eqs. (1a) and (1b) can be integrated to yield the total number $N_\parallel$ and $N_\perp$ of long-lived photoexcitations for the two limiting cases of low photoexcitation density (linear recombination regime) and of high photoexcitation density (quadratic bimolecular recombination regime). For the linear regime, $n(x)\ll 1/(\beta\tau)$, $N_\perp/N_\parallel$ is given by

$$\frac{N_\perp}{N_\parallel}=\left[1-\frac{\alpha_\perp^{3D}}{\alpha_\perp}+\frac{g_\perp\alpha_\perp^{3D}}{g_\parallel\alpha_\perp}\right]\frac{(1-R_\perp)(1-e^{-\alpha_\perp d})}{(1-R_\parallel)(1-e^{-\alpha_\parallel d})}, \qquad (2)$$

where d is the sample thickness. For the quadratic bimolecular recombination regime, $n(x)\gg 1/(\beta\tau)$, the result is

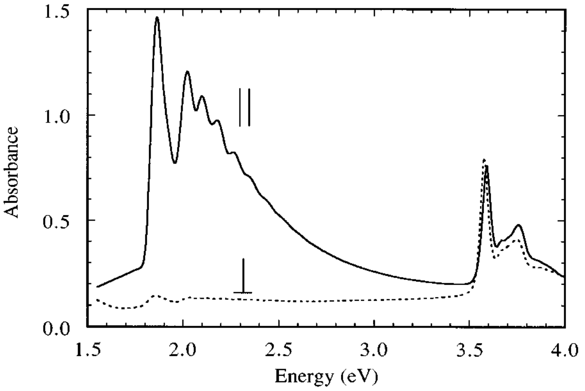

FIG. 1. Absorption spectrum of oriented polyDCHD at 4 K. Electric field of the radiation parallel (full line) and perpendicular (dashed line) to the chain axis.

$$\frac{N_\perp}{N_\parallel}=\sqrt{\frac{\alpha_\parallel(1-R_\perp)}{\alpha_\perp(1-R_\parallel)}}\sqrt{1-\frac{\alpha_\perp^{3D}}{\alpha_\perp}+\frac{g_\perp\alpha_\perp^{3D}}{g_\parallel\alpha_\perp}\frac{(1-e^{-\alpha_\perp d/2})}{(1-e^{-\alpha_\parallel d/2})}}. \tag{3}$$

If we define the intrinsic anisotropy $\mathcal{I}$ of the photoexcitation as

$$\mathcal{I}=1-\frac{\alpha_\perp^{3D}}{\alpha_\perp}+\frac{g_\perp\alpha_\perp^{3D}}{g_\parallel\alpha_\perp},$$

a value greater than one is obtained for those photoexcitations for which $g_\perp/g_\parallel \gg 1$ since, in general, $\alpha_\perp^{3D}/\alpha_\perp \ll 1$. The different efficiencies of the generation of long-lived photoexcitations in the two polarizations are evidence of the role played by the interchain interactions. When the pump beam is polarized perpendicularly to the chain direction some electron-hole pairs are directly generated on different chains and then, after the ultrafast self-trapping process, charged photoexcitations can be created. These photoexcitations do not easily recombine because they are located on different chains, thus giving rise with high efficiency to long-lived carriers. Instead, those photoexcitations created on the same chain quickly recombine and the generation efficiency of long-lived carriers in this case is very low.

IV. RESULTS

Figure 1 shows the electronic absorption spectra at 4 K of epitaxially grown polyDCHD for the electric vector of the radiation parallel and perpendicular to the chain direction. The low-energy side of the parallel component is dominated by the excitonic peak at 1.86 eV and by its well-resolved vibronic progression. The high-energy side shows the characteristic absorption bands of the carbazolyl group at 3.59 and 3.75 eV. The lack of any absorption in the intermediate spectral region, where short conjugated length defects are usually found,[17] is indicative of the high conjugation length of the polymer.

The apparent peak-to-peak anisotropy of the excitonic transition is about ten and that at 2.54 eV (energy of the exciting radiation used for PA measurements) is about five, but both become larger (~ 20) after subtracting the background of the substrate.[22] This high anisotropy ratio shows the very high degree of alignment of the polymeric chains.

As previously observed, the intensity of the corrected perpendicular absorption coefficient $\alpha_\perp$ could be due to three effects whose relative contributions can be evaluated in terms of chain orientation, zigzag structure of the backbone, and electronic interchain coupling. In oriented polyDCHD, chain misalignment turned out to be around 8°,[9] and the electronic interchain coupling was estimated to be of the order of 10 meV in PDA crystals.[23] We believe that in the oriented film this coupling should be even smaller on the basis of the following reasoning. The excitonic peak in Fig. 1 does not show any band splitting caused by interchain interactions which are then negligible relative to the exciton broadening parameter. From a fit of the absorption spectrum of Fig. 1 with an inverse square root line shape,[24] the broadening parameter turned out to be $\Sigma/2 \cong 20$ meV. Since band splitting is given by $2zt_\perp$,[4] where z is the number of interacting molecules ($z=2$) (Ref. 25) and $t_\perp$ is the interchain hopping integral, $t_\perp$ should be smaller than 5 meV. On the basis of these values, we believe that in polyDCHD the interchain interactions should not substantially affect the perpendicular absorption spectrum. The perpendicular absorption spectrum is then mainly originated by the chain misalignment and by the real structure of the backbone. Note, however, that $\alpha_\perp^{3D}$ may instead play a relevant role in the generation of photoexcited states and, in particular, in their intrinsic anisotropy[12] [see Eqs. (2) and (3)].

The absorption spectrum of oriented polyDCHD at 77 K (Ref. 26) is not so well resolved as the spectrum in Fig. 1 and the excitonic peak is shifted to 1.89 eV. Also, microcrystalline samples in KBr pellets show a similar absorption spectrum with the exciton at 1.86 eV (Ref. 26) with what may be considered as evidence of a high degree of order.

The PA spectrum of the oriented polyDCHD with unpolarized light at 77 K is reported in Fig. 2(a). In the same figure, the PA spectrum from the microcrystalline polymer in the KBr pellet is shown for comparison. Notice that photoinduced bands are observed at the same energies (0.81, 0.96, and 1.26 eV) in both spectra. Furthermore the same spectral behavior is observed with both in-phase and out-of-phase detection.[27] The small difference in the bleaching energies is consistent with the different energies of the excitonic transitions. We believe that the assignment of the PA spectrum previously performed on polyDCHD in KBr pellets[15,16] still holds for the oriented film. This is particularly true for the PA bands at 0.81 and 0.96 eV, which were previously assigned to long-lived bipolaronic excitations and their vibrational modes because both exhibit temperature [Fig. 2(b)], laser intensity [Fig. 3(a)], and chopper frequency[27] dependences similar to those previously observed in pellets. More questionable is the interpretation of the 1.26-eV peak which, from its behavior upon changing the experimental parameters, was tentatively assigned in the pellets to a triplet-triplet transition.[15] In the oriented sample this band shows a laser intensity dependence [Fig. 3(b)] similar to that observed in the microcrystalline form. In particular, at 20 K, a changeover from a $I^{0.72}$ to a $I^{0.57}$ law is found around 100 mW. This is indicative of the presence of both monomolecular and bimolecular recombination kinetics of the excitations. At 77 K, the bimolecular recombination process ($I^{0.48}$) is always dominant, probably because of a faster exciton diffusion. Fi-

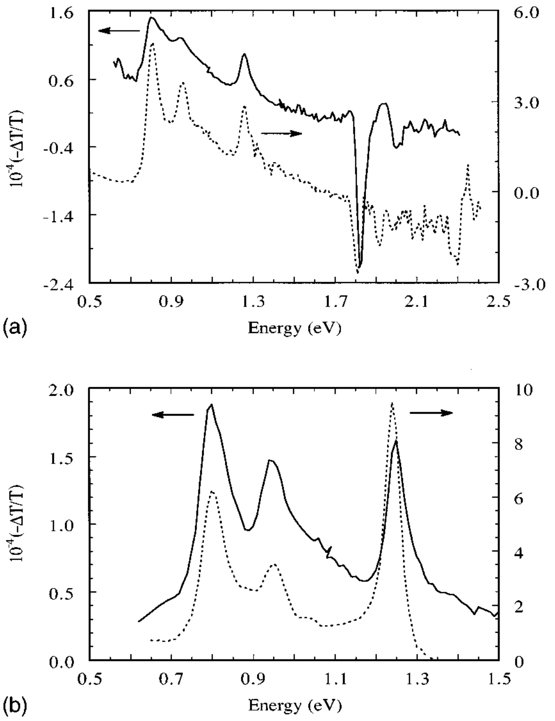

FIG. 2. (a) Photoinduced absorption spectra of polyDCHD at $T=77$ K, $\lambda_{\rm exc}=488$ nm, laser power 200 mW, and chopper frequency 13 Hz. Full line, oriented sample with unpolarized exciting radiation; dashed line, microcrystalline sample in KBr pellet. (b) The same as (a) but $T=20$ K.

nally, a lifetime lower than 10^{-3} s is inferred at 20 K from the chopper frequency dependence of this peak [Fig. 3(c)]. This result is again similar to that previously found in microcrystalline polyDCHD. The only noticeable difference between the oriented and microcrystalline samples may be found in the temperature effect on the peak intensity. In fact, more than a threefold increase is observed for the pellet but only a 50% increase is observed in the oriented sample on going from 77 to 20 K [Fig. 2(b)].

The photoinduced absorption spectra of oriented polyDCHD at 20 K obtained with pump polarization both parallel and perpendicular to the chain axis are reported in Fig. 4. The experimental anisotropy evaluated for each photoinduced signal is reported in Table I. In order to derive the values for the intrinsic anisotropy for the photoexcitation responsible for each peak, the experimental data must be corrected according to Eq. (3). Indeed, as shown in Figs. 3(a) and 3(b) bipolarons decay bimolecularly and triplet excitons at the laser power of 200 mW [Fig. 3(b)] decay nearly so. The measured reflectivity components at 2.54 eV are independent of the pump polarization[24] and measured absorbances $A_{\parallel}$ and $A_{\perp}$ are 0.43 and 0.021, respectively. By introducing these parameters into Eq. (3) one obtains for the intrinsic anisotropy of each band the values reported in the third column of Table I. It is interesting to note that the intrinsic response for bipolaronic peaks obtained with pump polarization perpendicular to the chain axis is stronger than that obtained with pump polarization parallel to the chain axis. One can deduce for these excitations $g_{\perp}/g_{\parallel} \gg 1$ as expected for the intermolecular generation of bipolaronic states. In agreement with the present model, the anisotropy

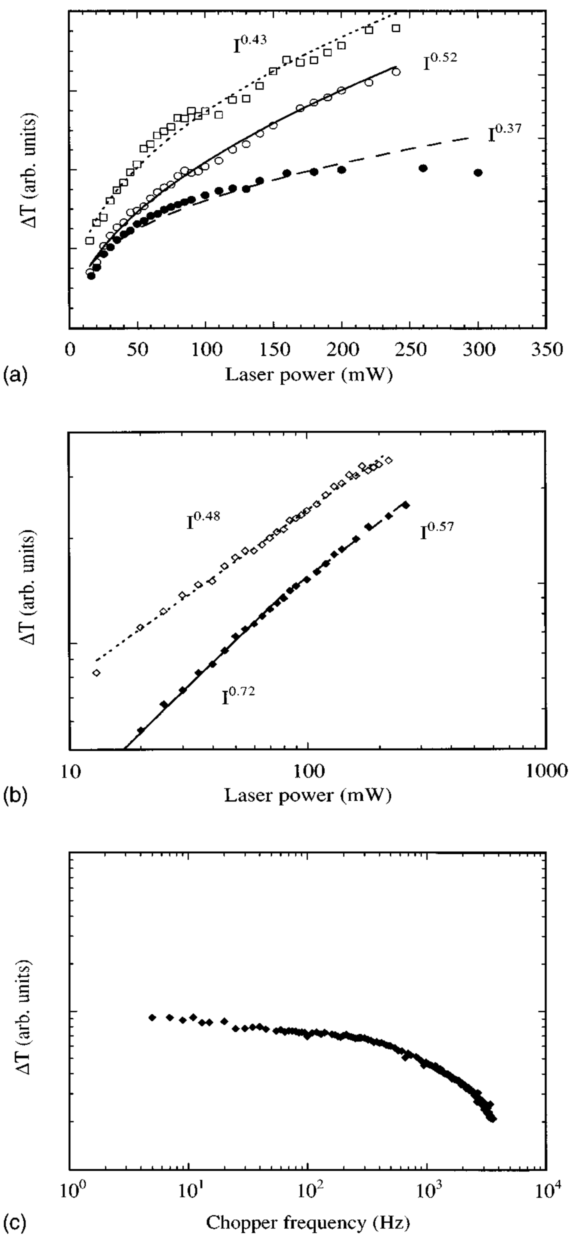

FIG. 3. (a) Laser power dependence of the 0.81- and 0.96-eV peaks of the oriented sample with unpolarized exciting radiation. Open squares, 0.96-eV band at $T=77$ K; open circles, 0.81-eV band at $T=77$ K; closed circles, 0.81-eV band at $T=20$ K. (b) Laser power dependence of the 1.26-eV peak of the oriented sample with unpolarized radiation. Open diamonds, 1.26-eV band at $T=77$ K; closed diamonds, 1.26-eV band at $T=20$ K. The lines are power-law fitting. (c) Chopper frequency dependence of the 1.26-eV peak of the oriented sample with unpolarized excitation radiation, $T=20$ K laser power 200 mW, $\lambda_{\rm exc}=488$ nm for all spectra.

of the bipolaronic signals does not change by varying the laser power in the range 50–200 mW as shown in Fig. 5 for the more intense 0.81-eV peak. An anisotropy of this order of magnitude has been observed both in pump and probe photoinduced absorption and in photoconductivity in other oriented conjugated polymers.[10–12] On the contrary, no anisotropy is practically observed for the 1.26-eV peak, in agreement with the expectations for intramolecular triplet ex-

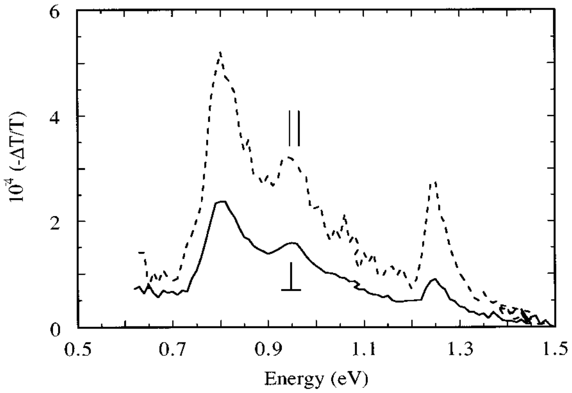

FIG. 4. Photoinduced absorption spectrum of oriented polyDCHD at 20 K, $\lambda_{exc}=488$ nm, laser power 200 mW, and chopper frequency 13 Hz. Dashed line, parallel pump polarization; full line, perpendicular pump polarization.

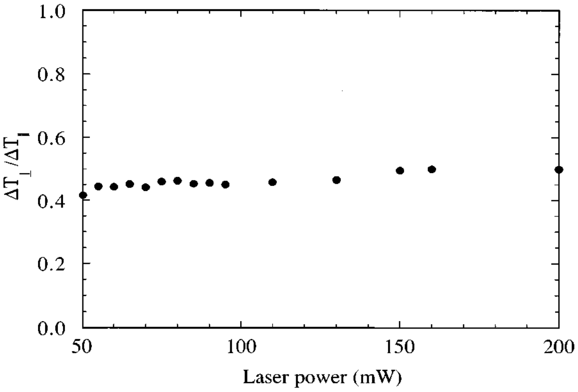

FIG. 5. Anisotropy of the 0.81-eV peak of oriented polyDCHD at different laser powers. $T=20$ K, $\lambda_{exc}=488$ nm, and chopper frequency 13 Hz.

citons ($g_\perp=0$). Note indeed that, being the triplet excitons formed via either intersystem crossing[28] or fusion and/or fission of intrachain singlet excitons,[29,30] they are intramolecularly generated.

We are not considering here the effects of thermal activation and of different recombination kinetics in the two polarization conditions on the observed anisotropy of the photoinduced signals. Thermal effects are due to the heating of the sample for intense laser pumping. When the pump-modulated thermal energy becomes larger than the activation energy of the photoexcitations, an increase in hopping conduction may occur with the consequence of a higher anisotropy of the PA signal. However, the heating of the sample can be revealed by the modulation of the bleaching. Since the photoinduced absorption spectra of polyDCHD recorded at different pump powers (50–200 mW) show only a slight modulation effect which has the same shape of the thermal modulated absorption,[24] it seems reasonable to disregard the thermal origin of the PA signals and their anisotropy.

Another possible but not intrinsic origin of the anisotropy of the PA spectra is that different recombination kinetics could occur with different pump polarization. We have accurately checked the intensity dependence of the PA signals and found for each peak the same behavior regardless of the polarization conditions. This indicates that recombination kinetics do not depend on pump polarization.

V. DISCUSSION

The presence of charged photoinduced states seems to be typical of polycarbazolyldiacetylenes.[13–18,26] This fact is quite surprising because in strongly correlated systems such as PDAs, triplet excitons are expected to be the main product of photoexcitation.[31,32] Experimental studies on other PDAs seem to confirm this point.[33,34] However, recent theoretical calculations based on the Pariser-Par-Pople model combined with the Su, Schrieffer, and Heeger (SSH) Hamiltonian for electron-lattice coupling and a Brazovskii-Kirova–type symmetry breaking energy[35] predict, in addition to triplet excitons, stable charged polarons (bipolarons) at low (high) doping levels.

TABLE I. Experimental and intrinsic anisotropy for the three peaks observed in the PA spectrum of oriented polyDCHD at 20 K.

Photoinduced peak (eV)	$(-\Delta T)_\perp/(-\Delta T)_\parallel$	$\mathcal{I}$
0.81	0.5	3.2
0.96	0.5	3
1.26	0.3	1.1

The origin of the interchain coupling in polyDCHD is, at present, unknown. The large interchain separation, ~7 Å ,[25] with respect to that of trans-polyacetylene (~4 Å) where strong evidence of interchain *e-h* pairs are reported,[10–12] seems to rule out a large interchain coupling between polymeric backbones. The dipole-dipole interactions between the carbazolyl side groups of different polymeric chains could be responsible for the observed effect. Once the photoexcitations are created, they can migrate on different chains via the photoconductive side groups and then bimolecularly recombine. Evidence of excitation migration from the side group to the polyDCHD backbone is, in fact, reported.[36] This possible interpretation could explain why in other PDAs charged photoinduced states are not observed. In our opinion the particular side group which characterizes the polycarbazolyldiacetylenes plays an active role in the photoexcitation mechanisms.

The observation of intrinsic anisotropy for the 0.81- and 0.96-eV photoinduced bands in oriented polyDCHD suggests an interchain nature of the photogeneration process for these excitations. On the contrary, the 1.26-eV band does not show any intrinsic anisotropy and this is indicative of the intrachain nature of its photogeneration process. These conclusions are in agreement with our previous assignment of the 0.81- and 0.96-eV bands as due to charged bipolarons and of the 1.26-eV band as due to neutral triplet excitons.

It is also interesting to compare the millisecond polarized PA data presented here with those relative to the femtosecond transient bleaching decay for the same sample.[37] In the case of ultrafast relaxation with excitation at 627 nm (1.98 eV) no difference was observed in the transient bleaching decay (monomolecular) for the two polarizations. This fact indicates that the dynamics is the same for both polarizations. It is difficult to believe that direct interchain separation takes place a long time after the photogeneration process. We suppose instead that the different behavior of the intrinsic anisotropy in the two experiments is due to the different energy of the pumping photons. In cw experiments polyDCHD was excited at 488 nm (2.54 eV), that is with an energy greater than the interband energy gap [2.35 eV (Ref. 38)]. In this case the creation of charged states via interband transitions due to interchain coupling is reasonable. The femtosecond transient bleaching decay measurements are performed with excitation at the main excitonic peak. Due to the intrachain nature of excitons in polyconjugated materials,[39] the interchain charge separation does not take place and no intrinsic anisotropy is observed because only intrachain perpendicular absorptions are activated with perpendicularly polarized beam. If this interpretation were correct, the measurements of the intrinsic anisotropy at different excitation wavelengths could be an important tool to investigate the nature of the excited states in oriented conjugated polymers.

In conclusion, the photoinduced absorption spectra of an oriented form of polyDCHD show nonlinear excitations similar to those previously observed in polycrystalline samples, that is bipolarons and triplet excitons. The study of the polarization dependence of the PA spectrum points out the interchain nature of the photogeneration processes associated with bipolarons and the intrachain generation of the triplet excitons. Different results for the pump polarization anisotropy at different excitation energies have been related to the different photophysics of the excited states of this conjugated polymer.

ACKNOWLEDGMENTS

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