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Triplet excitons in acyl- and alkyl-substituted polycarbazolyldiacetylenes: A spectroscopical and photophysical study

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Absorption, photoluminescence, and photoinduced absorption (PIA) spectra of films of red phase polycarbazolyldiacetylenes (polyCzDAs) carrying selected acyl (polyDPCHD) or alkyl (polyDCHD-HS) groups are reported. The absorption spectrum of polyDCHD-HS, which is almost independent of the temperature down to 20 K, shows an excitonic absorption followed by an inhomogeneously broadened vibronic progression. Very different is instead the case of polyDPCHD whose thin films show a very sharp excitonic transition and a vibronic progression with a lower electron-phonon (el-ph) coupling with respect to that of polyDCHD-HS. These peculiar characteristics allow the detection of additional features in the spectra, which are assigned on the basis of quantum chemical calculations to string modes of the backbone. As far as thick films of polyDPCHD are concerned, broad electronic spectra are observed. Raman spectroscopy studies suggest that this broadening is due to the presence of two forms of the polymer. Unlike other polydiacetylenes (PDA's) including polyDCHD-HS films, polyDPCHD films are also strongly luminescent, thus suggesting a different ordering of the dipole forbidden and allowed states. For these materials, the photoinduced absorption spectra are dominated by triplet excitons. Effects of different forms in acyl substituted polymers are observed also in the PIA spectra. The rise and decay of the triplet signal for polyDCHD-HS are accounted for through a dynamical model, which includes saturation effects in the monomolecular decay regime. A more complex kinetics is instead observed for polyDPCHD. From the study of the kinetics of the PIA spectra both the triplet generation efficiency and the density of traps are evaluated.

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INTRODUCTION

For several years our group has been interested in the preparation of diacetylenic monomers, their polymerization,[1,2] the study of their photophysical,[3–7] and electronic properties[8,9] as well as in the evaluation of their non linear optical (NLO) properties,[10–12] which are potentially suitable for photonic applications.[13] The nonlinear optical properties of these materials depend on the nature of the electronic excited states. Theoretical models of conjugated polymers show that four states, two of which are symmetry allowed and the other two symmetry forbidden, are essential for the evaluation of the NLO response of these materials.[14] It has also been shown that the lowest symmetry forbidden state plays a major role in the formation of triplet excitons,[7,15,16] which are the dominant photoexcitations in PDA's. On this basis, a wide investigation of the spectroscopical and photophysical properties of polyCzDAs becomes an important means not only for fundamental studies, but also in evaluating their possible performances as photonic materials. Moreover, since triplet excitons play a major role in electroluminescent/electrophosphorescent devices, PDA's are good model systems to study the photophysics of conjugated polymers.[17,18]

In this paper we report an extensive investigation of the optical and photophysical properties of the red phase of polyDPCHD and polyDCHD-HS (see Fig. 1). We first report a detailed spectroscopical characterization (absorption spectra at different temperatures, room temperature fluorescence, and Raman spectra) of the properties of the different films investigated. Preliminary studies have shown that polyDPCHD exhibits two different forms for thin and thick films, and that upon annealing thick films behave similar to the thin ones. This behavior, probably related to morphological and/or structural changes and never observed before in the red phase polyCzDAs films, will be investigated in more

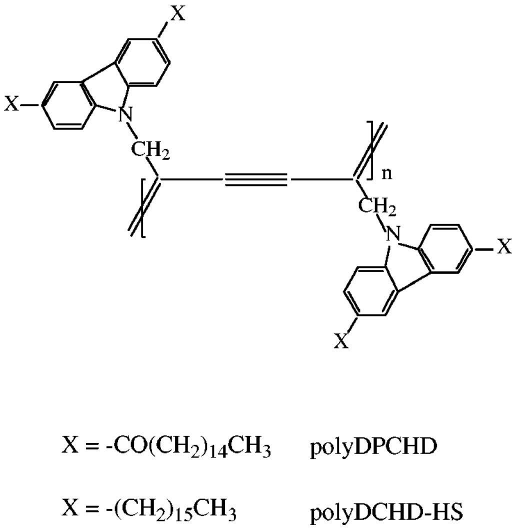

FIG. 1. Chemical structures of poly[1,6-bis(3,6-dipalmitolyl)-N-carbazolyl-2,4-hexadiyne] (polyDCPCHD) and poly[1,6-bis(3,6-dihexadecyl-N-carbazolyl)-2,4-hexadiyne] (polyDCHD-HS).

detail here. For thick annealed polyDPCHD and for polyDCHD-HS films (which do not show the changes just described for polyDPCHD) steady-state and microsecond time resolved photoinduced absorption spectra are reported, paying a particular attention to the possible photodamaging effects due to laser pumping. The PIA spectra are dominated by triplet excitons, whose pump-intensity-dependent dynamics is described in terms of different kinetics models which include saturation effects. From these models, the triplet generation efficiency and the trap density are deduced and compared with those found in other conjugated polymers.

EXPERIMENTAL

DPCHD and DCHD-HS monomers are synthesized according to Refs. 1 and 2. After polymerization and elimination of the residual monomer, toluene solutions of polyDCHD-HS are spin cast on glass substrates. Due to the lower solubility of polyDPCHD, thin films of this material were spin cast directly from the monomer solution on glass or fused silica substrates, then thermally polymerized at 115 °C for several hours. Thick films of polyDPCHD are obtained by repeated drop casting of monomer solutions and subsequent thermal polymerization.

Electronic absorption spectra are recorded with a double grating Varian model Cary 5E spectrophotometer equipped with a closed-cycle liquid helium Oxford model CCC1204 cryostat. The spectral resolution is one nanometer.

The long-lived photoinduced absorption spectra are recorded with a Bruker IFS 66/S Step-Scan FTIR spectrometer, equipped with Silicon and InSb detectors and with a homemade liquid nitrogen cryostat. Photoexcitation is provided by the 532 nm line of a Suwtech DPGL-2200 Nd:YAG duplicated laser (maximum power ~200 mW), and its modulation is obtained through an AA Opto-Electronics acusto-optical modulator model AA.MTS.110/A3-Vis. Continuous wave photoinduced absorption (CW-PIA) measurements are performed by running continuous scans with the laser light on and off, alternately. Several transmittance spectra are recorded and coadded for multiple cycles to provide a suitable signal-to-noise ratio (up to 10 000 total dark and light scans), with a spectral resolution of $8\ \mathrm{cm}^{-1}$. The CW-PIA spectra are then numerically calculated as $-\Delta T/T=(T_{\mathrm{off}}-T_{\mathrm{on}})/T_{\mathrm{off}}$, T_{off} and T_{on} being the transmittances recorded with the laser off and on, respectively.

Time resolved photoinduced absorption spectra (TR-PIA) are recorded in the step-scan mode[19] with $64\ \mathrm{cm}^{-1}$ spectral resolution. The fast data acquisition is provided by the 10 MHz, 16 bit analogical-digital-converter of the spectrometer. In our measurements, the modulation frequency of the laser is 1 KHz and the time interval between acquisitions 5 μs. For a number of co-additions for each interferogram point between 25 and 100, the time required for one measurement ranges between 30 and 60 min. Depending on the magnitude and on the temporal response of the PIA signal, the dc or ac signal from the detector preamplifiers can be used. In the dc mode, the time evolution of the transmission spectrum $T(t)$ is recorded and one spectrum prior to the laser turn-on T_{off} is used for deriving the TR-PIA as $[T_{\mathrm{off}}-T(t)]/T_{\mathrm{off}}$. In the ac mode, the time evolution of the differential transmittance $-\delta T(t)$ is recorded directly and a continuous-scan transmission spectrum with the laser light off T_{off} is used to calculate the time resolved TR-PIA as $-\delta T(t)/T_{\mathrm{off}}$.

Room-temperature Raman spectra with a resolution of $2\ \mathrm{cm}^{-1}$ are recorded with a Bruker FT spectrometer (FRS 100) equipped with a liquid nitrogen cooled germanium detector, where the excitation is provided by an Adlas 300 Nd:YAG laser (1064 nm).

Room-temperature photoluminescence (PL) spectra are measured by pumping the sample with the 514 nm line of a Coherent Innova 300 Ar+ ion laser. The emitted light is dispersed with a double grating Jobin & Yvon Mod. HG-25 spectrometer, and then recorded by a photomultiplier tube with spectral resolution $4-8\ \mathrm{cm}^{-1}$.

RESULTS AND DISCUSSION

Figure 2 shows the electronic absorption spectra at 20 K and room temperature of polyDPCHD [(a) thick, (b) thin] and polyDCHD-HS (c). Thick samples of polyDPCHD at room temperature show an excitonic absorption at 541 nm (2.29 eV) followed by vibronic replicas due to the CC double and triple bond stretchings at 501 (2.47) and 485 nm (2.56 eV). Below the main excitonic absorption, a well pronounced shoulder at 552 nm (2.25 eV), typical of thick samples, is observed. In addition, at higher energies, weak features (marked with an asterisk) are observed at 452 (2.74) and 438 nm (2.83 eV). Sample thickness and inhomogeneity affect the spectra by inducing light scattering effects due to the fact that these films are obtained by repeated drop casting of monomer solutions and subsequent polymerization. The usual tendency of monomer molecules to crystallize generates domains and defects giving rise to stronger light scattering effects with respect to the case of films grown from polymer solutions where a higher degree of homogeneity is present. These effects must not to be confused with the broadening due to conjugation lengths distribution, since here several spectral features are well resolved. Upon lowering the temperature down to 20 K, the spectrum redshifts and the low energy shoulder at 561 nm (2.21 eV) becomes more evident. The purely excitonic transition is now peaked at 543 nm (2.28 eV) and the vibronic replicas appear at 504 (2.46) and 487 nm (2.55 eV). The higher energy features are now detected at 454 (2.73) and 439 nm (2.82 eV).

The thinner films of polyDPCHD [Fig. 2(b)] show sharper absorption spectra, with negligible contribution from light scattering and with a ratio between the purely excitonic transition and the first vibronic replica much higher than that found for the thick polyDPCHD samples. Thick films of polyDPCHD after thermal annealing become similar to those of the thinner form, i.e., show absorption spectra very sharp and without the shoulder at 552 nm. The excitonic absorption for thin polyDPCHD at room temperature is observed at 537 nm (2.31 eV) with vibronic replicas at 498 and 487 nm (2.49, 2.55 eV) and with a high energy weak band at 454 nm (2.73 eV). These spectra are almost insensitive to temperature down to 20 K, the above features being shifted to 541 (2.29 eV), 500 and 488 (2.48 and 2.54), and 454 nm (2.73

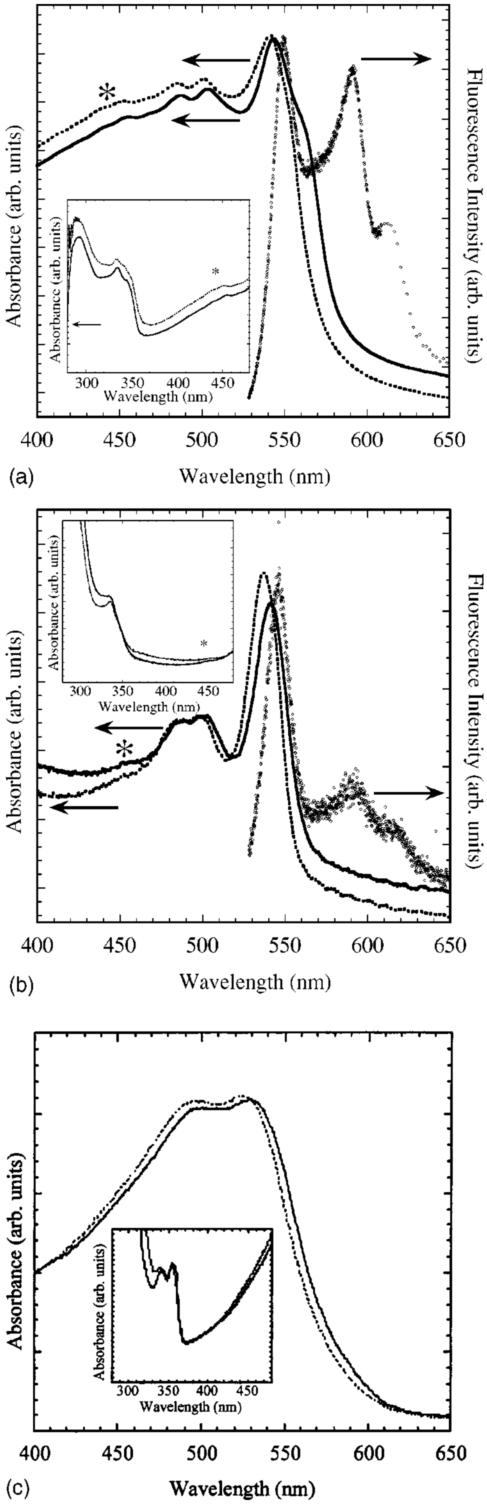

FIG. 2. Absorption spectra at room temperature (dashed line) and 20 K (full line). The asterisk labels the high energy band due to the string mode. The room temperature photoluminescence spectrum is also reported (dots). In the inset, the spectra in the absorption region of the side group are shown. (a) Thick polyDPCHD; (b) thin polyDPCHD; (c) polyDCHD-HS, for this polymer the photoluminescence spectrum is not reported due to its low intensity.

eV), respectively. The properties of the absorption spectra of thin (or thick annealed) films of polyDPCHD seem to be peculiar of acyl substituted polyCzDAs since they were also observed previously in a polymer with shorter acyl chains.[20]

Very different are the absorption spectra of polyDCHD-HS [Fig. 2(c)]. The excitonic transition in polyDCHD-HS is much broader than that in polyDPCHD due to a much wider distribution of conjugation lengths that partially masks the spectral resolution of the vibronic progression. The purely electronic transition at room temperature is located at 524 nm (2.37 eV) and only one broad band at 496 nm (2.50 eV) is detected, which is due to unresolved C═C and C≡C stretchings replicas.

Even for polyDCHD-HS, the temperature does not affect the spectral position of the main absorption features too much. As a matter of fact at 20 K the transitions occur at 529 and 498 nm, respectively. It is interesting to note that the poor sensitivity to temperature seems to be typical of the red forms of PDA's (Ref. 5) unlike to the blue ones.[4] This is due to the fact that in the films the red phase is the thermodynamically stable one in contrast to the blue metastable phase in crystalline (or polycrystalline) samples, where the long-range ordering of the chains can be easily removed by annealing.[21] In this respect it is interesting to note that the low energy shoulder observed only for thick polyDPCHD shows a remarkable temperature dependence. This fact suggests that this transition could have a very different origin with respect to those usually observed for the diacetylenic conjugated chains.

We would like to make some comments on the role of the el-ph coupling in acyl and alkyl substituted polymers. In this comparison we neglect the case of thick polyDPCHD films because, as observed before, the strong light scattering effects hamper an even qualitative evaluation of this interaction in the films. In spite of the better resolution of the vibronic progression in thin polyDPCHD with respect to polyDCHD-HS, the electron-phonon coupling appears larger in the alkyl-substituted polymer, as clearly indicated by the ratio between the purely excitonic absorption and the vibronic replicas. Only two other systems show a sharper excitonic peak accompanied by a lower el-ph interaction, namely, polyDCHD-HS in benzene solution at room temperature and very long isolated PDA chains embedded in their monomer single crystals.[22] Even though the reason for the sharpening of the excitonic transition is still not clear (polymer order, solvent interaction, polar side groups, polarization of the medium, nanoaggregates,....), this comparison suggests that the sharper the excitonic transition, the lower the electron-phonon coupling. Delocalization of π electrons along several microns, a small el-ph coupling and very a sharp transition have been recently reported for PDA chains embedded in their monomer crystals.[23] For the polyCzDAs here investigated the spectral position of the absorption maximum indicates that the average conjugation length in polyDPCHD is more extended than that of polyDCHD-HS. This fact is in full agreement with the reduced el-ph coupling observed in polyDPCHD with respect to polyDCHD-HS, being this interaction stronger in short conjugated segments.[24] However, in polyDCHD-HS the width of the distribution of

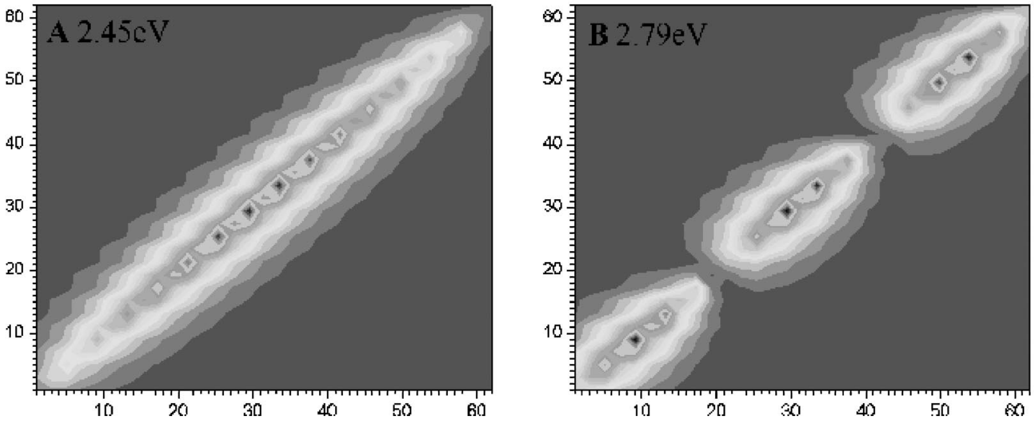

FIG. 3. Collective electronic oscillator plots relative to (a) the lowest electronic excitation at 2.45 eV and to (b) the first string mode at 2.79 eV for a 15 repeat units polydiacetylene isolated oligomer chain. The axes of the plots refer to the numbering of the carbon atom in the backbone.

the conjugated segments is such that we cannot exclude the existence in this sample of a limited amount of conjugated segments more extended than those in polyDPCHD.

Whatever the reasons for the different el-ph coupling in the two polymers, the side groups probably play some role, in particular when they are electronically active moieties such as the carbazolyl derivatives. In a previous paper,[25] we noted that the alkyl substitution of the carbazolyl group slightly affects the absorption spectrum of this chromophore by redshifting its transitions by a few nanometers without changing their shape. The absorption spectrum of an alkyl substituted carbazolyl group is reported in the inset of Fig. 2(c), where the typical pair of transitions around 350 nm are shown. Very different is the case of acyl substituted polymers [insets in Figs. 2(a) and 2(b)], where the low-energy transition of the doublet of the carbazolyl moiety seems to lose oscillator strength with respect to the high-energy one. This effect is related to the presence of the carbonyl group in the substituent, which affects the electron distribution of the carbazolyl ring. This fact could in principle affect the electron distribution on the backbone even in the presence of a CH_2 spacer between the carbazolyl group and the backbone. Quantum chemical calculations on the electronic properties of diacetylene oligomers having carbazolyl groups directly or indirectly (through a CH_2 spacer) attached to the backbones are in progress to elucidate this point.[26]

Quantum chemical calculations are also useful in the discussion of additional features in the absorption spectrum, which are related to the conjugated backbone. In a previous paper, the role of interchain interactions has been discussed.[8] Here, the same approach will be used for the assignment of fine details in the spectra, such as the very weak band observed around 450 nm only for the polymers where a small el-ph interaction allows the observation of the even weakest features. Calculations based on the collective electronic oscillator (CEO) method for a 15 repeat unit neutral oligomers (see Ref. 8 for details) showed that the main absorption of the diacetylenic backbone is located at 2.45 eV, followed by other transitions of much lower oscillator strengths, of which the first allowed one is located at 2.79 eV. The analysis of these modes shows that the excitations of a linear conjugated chain resemble the vibrations of a string. In Fig. 3(a) we observe that the lowest excitation is delocalized over the whole chain, and that the maximum separation of the electron-hole pair, defined as the largest distance between two symmetric nonzero off-diagonal terms, is about five repeat units around the middle of the chain. The symmetry of the off-diagonal terms means that this excitation does not have any charge transfer character. In Fig. 3(b) the CEO mode is drawn for the next allowed transition. The excitation is fragmented into three different sections of the chain (each of them being five repeat units long), and for each section the exciton is about four units wide and centered in the middle of the segment. A similar situation is found for the higher energy allowed transitions, which are not reported here. These plots show the analogy with the string vibrations, and it could be easily proved that allowed (forbidden) transitions must have an even (odd) number of nodes, with oscillator strengths approximately proportional to the inverse square of the latter. The spectral position of the weak band and its low intensity compare favorably with the predictions of our calculations, thus suggesting its assignment to the first string mode of the conjugated backbone.

We have so far discussed the unusual differences observed in the absorption spectra of a selected acyl and alkyl substituted polyCzDA. In what follows we will discuss the large differences found in the fluorescence properties of the two polymeric films. We first notice that, while acyl substituted polymers are luminescent [Figs. 2(a) and 2(b)], in polyDCHD-HS films the photoluminescence emission is almost negligible. However, for polyDCHD-HS in benzene solution, i.e., when sharp absorption features and low el-ph coupling are observed, the emission efficiency increases up to about 1%.[27] The different efficiency is probably related to the ordering of the first excited states for the polymers in different environments. An extensive investigation of the excited states of polyDCHD-HS allowed us to show that in the solid state, when the polymer is nonfluorescent, the first excited state of $2A_g$ symmetry[10,11] lies about 0.2 eV below the $1B_u$ state while in benzene solution, where luminescence is detected,[28] the lowest excited state of $1B_u$ symmetry lies

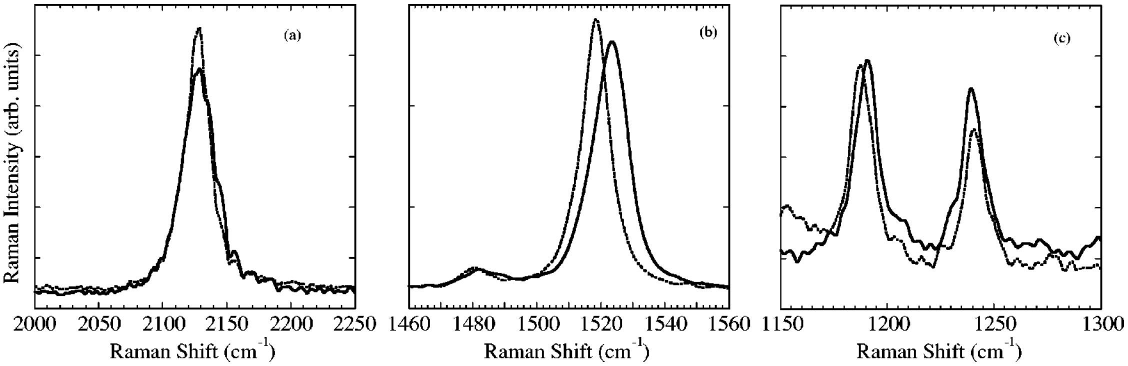

FIG. 4. Raman spectra for thick (dashed line) and thick annealed (full line) polyDPCHD in the spectral regions of (a) C≡C, (b) C═C, and (c) C—C stretching modes.

about 0.03 eV below the $2A_g$ state, thus explaining its unusual emission properties. Not yet fully understood is the case of the acyl substituted polymers, where the ordering of the electronic excited states has not been measured. The only available data are provided by the third harmonic generation (THG) measurements, which showed that a 3ω transition is observed almost resonant with the main electronic mode detected in the linear absorption.[29] Unfortunately THG is not sensitive to the symmetry of the transition, thus not providing an unambiguous assignment of the excited states. However, the large photoluminescence detected for films of the acyl substituted polymers suggests that the ordering of the symmetry forbidden/allowed excited states is similar to that found for polyDCHD-HS in benzene solution. These facts could have important consequences on the nature and intensity of the photoinduced absorption spectra of the polymers, because the $2A_g$ excited states play an important role in the generation of triplet excitons through the singlet fission process.[7,15,16] It can be recalled that the $2A_g$ level goes below the $1B_u$ one as a result of a lattice relaxation connected to el-ph coupling.[30–32] When the latter effect is negligible, the $2A_g$ level sets above the $1B_u$ one.[33]

As observed before, a relatively high luminescence efficiency is present only in those PDA's showing narrow electronic transitions, i.e., reduced el-ph coupling and extended electronic delocalization. This fact seems to be in contrast with the polyene picture, which is widely used to discuss the photophysical properties of conjugated polymers, in which for eight or more π electrons the symmetry forbidden state is located below the first allowed state.[34] Probably the interchain distance, the nature of the side groups and the polarization effect of the medium play an important role in the ordering of the excited states, as has been recently observed in di-phenyl substituted polyacetylene.[8,35,36]

Coming back to the spectral emission properties of the acyl-polymers reported in Fig. 2 (not corrected for self-absorption) we can note that the 0-0 emissions for thick and thin polyDPCHD were detected at 548.0 (2.257) and 546.0 nm (2.269 eV), respectively, followed by the 0-1 bands at 591.6 and 589.0 nm, and by the 0-2 emissions at about 613 and 610 nm. For thick polyDPCHD films self-absorption plays a major role on the intensity by smoothing the 0-0 band, while for thin films a remarkably mirrorlike symmetry between absorption and emission is observed. The Stokes shift for thin polyDPCHD is small (40 meV) and an even smaller value (16 meV) was found for another polyCzDAs having shorter acyl chains,[20] thus suggesting a small geometrical relaxation in the excited states.

The energy separation in the vibronic progression both for absorption and emission is related to the vibrational modes of the excited and fundamental electronic states respectively. The latter modes can be detected by Raman spectroscopy, and in Fig. 4 we show the Raman spectra of the thick and thick annealed polyDPCHD. Notice that the Raman spectra of thin films cannot be measured with our apparatus, but since the electronic absorption of thin and thick annealed films are identical, we assume the same to be true also for their Raman spectra. The most typical normal modes of the red phase polydiacetylenes are those of the triple (around 2100 cm^{-1}) and double (around 1500 cm^{-1}) bond stretchings. More difficult is the assignment of the bands observed below 1300 cm^{-1}. In fact, they strongly depend on the nature of the substituents and on the polymerization degree,[37] but we can roughly assign the backbone bending mode at about 950 cm^{-1}, the C—C stretching mode around 1200 cm^{-1}, and a mode with strong contributions from the side groups or by the residual monomer at about 1250 cm^{-1}.[37,38]

In the triple bond region [Fig. 4(a)] a single band at 2128 cm^{-1} is observed for both forms of polyDPCHD. Very differently behaves the C═C stretching region, where the thick and thick annealed films show peaks at 1518 and 1523 cm^{-1} respectively [Fig. 4(b)]. In Fig. 4(c) bands for the thick annealed (thick) films are detected at 1191 (1187) and 1240 (1239) cm^{-1}. We note that the vibrations showing different frequencies in thick and thick annealed (thin) films are those related to the single and double bonds, i.e., to the bonds geminal to the side groups. This fact, previously observed also in polyDCHD-HS benzene solutions upon thermal activation of a phase transition,[27] suggests that two polymeric structures with different side groups arrangement could be present in the two forms of polyDPCHD films, namely, in thick and thin films.[39] The Raman frequencies of the two forms, obtained with excitation at 1064 nm, indicate a more extended conjugation for thick films, in apparent disagreement with the results of the above discussion. However, we note that in this case the low energy tail of the absorption spectrum is more pronounced due to the presence of the shoulder at 560 nm which provides an enhanced resonant Raman condition with respect to the case of thin films, where only a very sharp absorption at 537 nm is observed. The fact that thick annealed films show the same optical and spectroscopical properties as the thinner ones suggests that some sort of irreversible phase transition can be thermally activated in this case. On the other hand the observation that different polar side groups orientations could affect the electronic and Raman spectra of PDA's is not new. In fact in PDA-TS a well characterized high order reversible phase transition was observed and assigned to the change in the arrangement of the polar side groups.[40]

In the past we studied the photophysical properties of blue- and red-phase PDA's as a function of their supramolecular structure.[4,5,41] For the red phase of PDA's only triplet excitons were detected, while in the blue phase the photogeneration of triplet and charged photoexcitations, whose relative efficiency depends on the interbackbone spacing, was observed. The noticeable differences observed in the absorption spectra of alkyl and acyl substituted polyCzDAs strongly suggest that different properties could occur in their excited states too. For this reason we carefully investigated the properties of the excited states of these polymers by means of the CW-PIA and the FTIR step scan time resolved (TR-PIA) techniques, which allow for the study of the rise and decay evolution of the excited states in the microsecond time domain by probing their absorption change upon photoexcitation.

In previous papers we reported on a preliminary investigation of CW-PIA spectra in these polymers,[20,42] which we will extend here. Figure 5(a) shows the CW-PIA spectra upon increasing the pumping power of thick annealed films of polyDPCHD, which behave similarly to the thin ones.[20,42] The spectra are asymmetrical with a high-energy tail, and are dominated by a quite sharp peak at $11\,330\ \mathrm{cm}^{-1}$ ($11\,380\ \mathrm{cm}^{-1}$) for low (high) pump intensity. In the low-energy side of the peak a shoulder at about $10\,300\ \mathrm{cm}^{-1}$ is observed. As it was shown before,[20] this shoulder depends on the thickness and on the thermal treatments of the films. For comparison, the CW-PIA spectrum of nonannealed thick polyDPCHD films is reported in the inset of the same figure. In this case the shoulder is much more evident and takes the form of a true satellite peak. Its pump-intensity dependence was shown to be similar to that of the main peak, and its spectral position coincident with that of the very weak absorption band which is almost negligible in thin or thick annealed films.[20,42]

The intensity dependence of the CW-PIA spectrum is quite complex. Upon increasing the pumping power from 1 to 45 mW (over a spot of about 2 mm diameter), the signal increases sublinearly ($I^{0.3}$) showing complicated kinetics. At higher pumping power the signal decreases, indicating a modification of the properties of the sample. This modification is also confirmed by the fact that by reducing the power down to 5 mW, it is impossible to recover the signal initially observed at the same power.

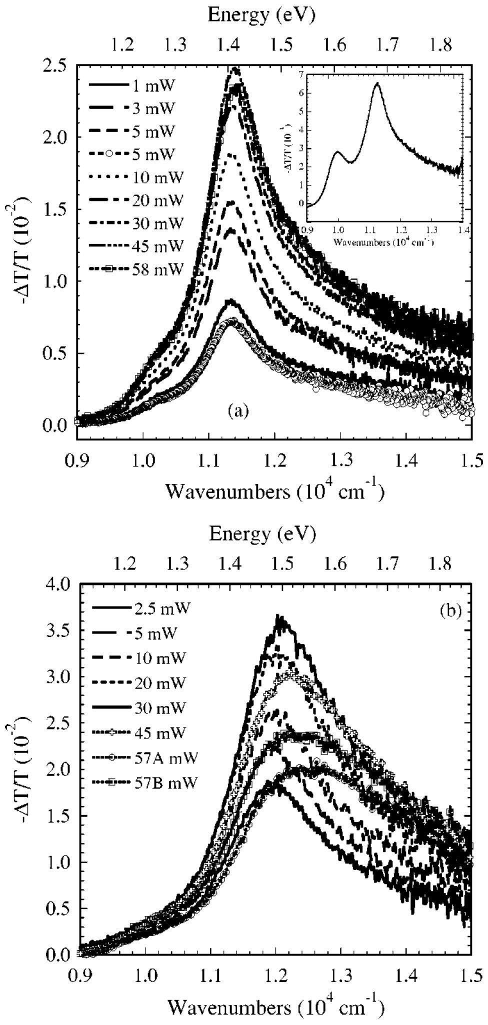

FIG. 5. CW-PIA spectra at different pump intensities for thick annealed polyDPCHD (a) and polyDCHD-HS (b) films. In the panel (a) inset, the CW-PIA spectrum of thick polyDPCHD is reported for comparison. $T = 77$ K.

Even more complicate is the case of polyDCHD-HS. In Fig. 5(b) the pump-intensity dependence of the CW-PIA spectra for this polymer is reported. Up to 30 mW the spectral position is almost unchanged and the intensity dependence ($I^{0.3}$) is similar to that observed for polyDPCHD. For higher pumping intensities, the peak shifts toward higher energies and its intensity strongly decreases, indicating deep modifications to take place inside the film. Moreover, a small shoulder appears at about $10\,000\ \mathrm{cm}^{-1}$ (1.24 eV). It is also interesting to note that by leaving the sample in the dark after an extended exposition (each CW-PIA spectrum requires a laser exposition between three and four hours) the PIA spectrum often recovers part of its intensity, as can be observed, e.g., in the spectrum 57B of the same figure. We cannot then exclude the possibility of sample modification and/or damaging under illumination. In addition, in view of the possible application of these PDA's in photonic devices working under intense light fluxes, and to understand their intrinsic photophysical properties, a careful characterization of their photochemical and photophysical stability is desirable. The already investigated photodamaging and photopatterning of polyDCHD-HS and polyDPCHD under UV-lamp illumina-

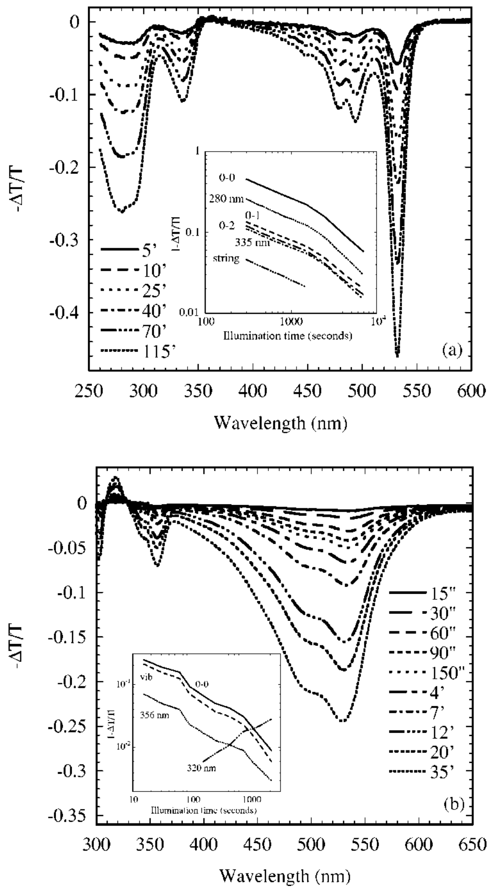

FIG. 6. Effect of the irradiation with 532 nm laser light on the normalized transmittance variation of polyDPCHD (a) and polyDCHD-HS (b) in standard laboratory conditions. In the inset, the illumination time evolution of the main features observed in the spectra, is reported (0-0, 0-1, 0-2, string mode at 450 nm, side group absorption at 280 and 335 nm).

tion[43] and of polyDCHD-HS solution irradiated by 1064 nm laser radiation[44] suggest that great care must be used in studying their properties in standard laboratory conditions. Before studying the photophysical properties of these polymers we have accordingly decided to characterize the effect on these samples of an intense 532 nm laser irradiation in standard laboratory conditions and in void.

Figure 6(a) shows the negative transmission difference between the irradiated and nonirradiated thick annealed polyDPCHD film, normalized to the transmission of the nonirradiated one for a different light exposure. A selective bleaching of the absorption spectrum is observed, indicating that photo-oxidation of the conjugated skeleton, side groups, and residual unreacted monomer takes place. The bleaching is not uniform and preferentially occurs for the 0-0 transition, giving rise to a progressive deformation of the absorption spectrum. The time evolution for the most important transitions (0-0, 0-1, 0-2, string mode at 450 nm, side group absorption at 280 and 335 nm) is very similar [inset of Fig. 6(a)].

Different is the case of polyDCHD-HS [Fig. 6(b)]. Again the bleaching in the spectra of the conjugated backbone is observed with a rate somewhat higher than that of polyDPCHD. However in the spectral region of the side groups absorption, a new absorption feature grows in addition to the bleaching upon irradiation at 320 nm. As an effective purification procedure of this polymer from unreacted monomers was used,[2] the new UV feature cannot be due to photodamaging of the monomer molecules, but is to be probably assigned to carbazolyl rings changes.[45]

When the experiments for both polymers are repeated in void (10^{-4} Torr), no modifications in the absorption spectra are detected upon exposition to the laser light up to one hour. This fact rules out any photo-oxidation effect to be responsible for the changes of the CW-PIA spectra after extended laser illumination. A careful investigation of the damaging effects in the PIA spectral region (both in air and in void) does not show any effect and no new absorption features arise there, thus indicating that the modifications of the PIA spectra are related to some photoexcitation process under very high photon flux and not to the generation of defect states. Heating of the sample is a possible effect of long-time illumination in the absorbing region. In this case changes in morphology and/or phase of the samples associated with spectroscopical properties modifications could occur. This is particularly true for the satellite band/shoulder observed in thick polyDPCHD films, which disappears after several measurements and could be assigned to an intrinsic state for this particular form of the polymer.

Let us now turn our attention to the main photoexcited species in the CW-PIA spectra, the triplet excitons. Triplet dynamics in conjugated polymers and organic semiconductors is an important factor for both light emitting devices and fundamental studies. Triplet exciton generation is detrimental for light emitting diodes based on the recombination of singlet excitons, but is important for devices based on phosphorescent emission. On the other hand, the generation of triplet excitons can be driven by several factors such as hyperfine interactions,[46] spin-orbit coupling,[47] charge recombination,[17] or singlet fission.[7,15,16,30,48] In our previous work on a red form of alkyl substituted polycarbazolyldiacetylenes[7] we showed the fission process of the first symmetry forbidden excited state o be the source of the triplet excitons. This is due to the fact that the wavefunction of that state describes a pair of triplets coupled to resultant zero spin.[48] This picture has been also confirmed by Schott and co-workers, who observed a similar dynamics in blue form PDA's,[16] by the Vardeny's group in poly-p-phenylene-vinylene derivatives,[15] and in photosynthetic antennas.[49] Even though these processes are in general ultrafast, taking place in the femtosecond time domain, complicated triplet dynamics occurs also in longer time domains.[3,50–52] For these reasons we started an investigation of the microsecond (μs) triplet exciton dynamics in our samples. In these measurements the laser light exposition is much reduced with respect to the CW-PIA ones, thus allowing for the investigation of triplet dynamics without running into the previously described case of extended illumination observed in the CW-PIA spectra.

The three-dimensional plots in Fig. 7 show the μs PIA spectra for thick annealed polyDPCHD (a) and polyDCHD-HS (b) films with their time evolution as mea-

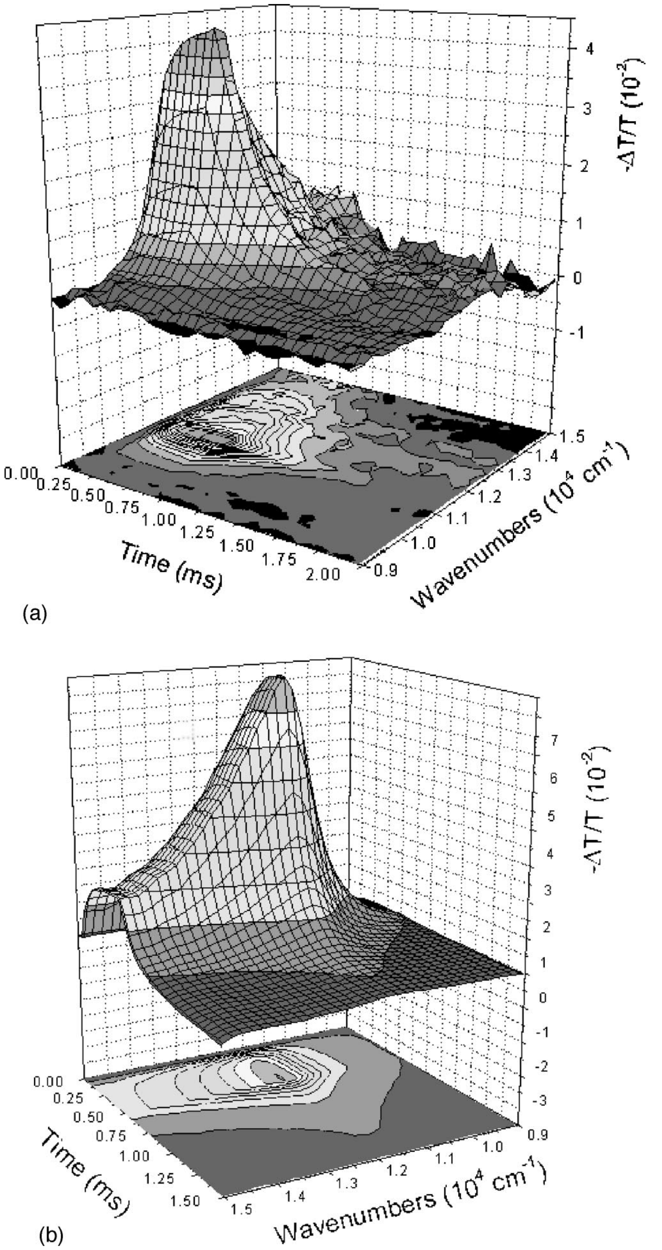

FIG. 7. Three-dimensional plot of TRS-PIA signal vs time and wave numbers for polyDPCHD thick annealed films (a) and polyDCHD-HS (b). At the bottom, the corresponding contour plot points out the temporal evolution of the triplet state.

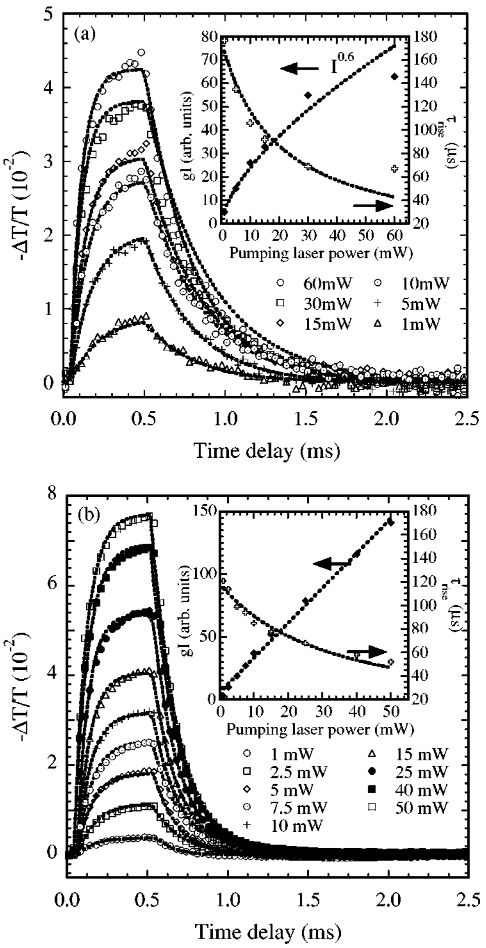

FIG. 8. Symbols: time evolution of the TRS-PIA spectra at the maximum of the triplet signal for 500 μs pumping time at different pump intensities for thick annealed polyDPCHD (a) and polyDCHD-HS (b). Lines: fit with Eqs. (2) and (4). In the insets, the intensity dependence of the fit parameter gI and τ_{rise} is also reported.

sured upon a 750 μs pumping time. Similar results are obtained for different pumping times. In the $-\Delta T/T$-time plane, the rise and decay traces are reported, as are the PIA spectra in the $-\Delta T/T$-wavelength plane. In the time-wavelength plane the level curves corresponding to different intensities of the PIA signal are displayed. The TR-PIA spectra show the same features previously detected in the CW-PIA ones, but with lower spectral resolution. The time slices show that the PIA signal for both polymers is not "instantaneously" generated, but slowly increases showing saturation effects during the pumping time. In fact no variation of the spectral shape is observed in the time domain investigated, and the time dependence of the signal is similar for all wave numbers, thus indicating that a single excited species is observed. As discussed before, the generation of triplet excitons in conjugated polymers takes place in a much shorter time domain than the one here investigated. Thus these results indicate that the triplet species here observed are trapped, and that their signal grows up until complete saturation of all the trap sites has been reached. The saturation is also confirmed by the intensity dependence of the PIA peak, which follows a strongly sublinear law ($I^{0.3}$).

To better investigate the dynamics in the two polymers, we report in Fig. 8(a) [8(b)] a typical slice displaying the polyDPCHD (polyDCHD-HS) rise and decay curves as measured at their PIA spectral peaks upon increasing the pumping power. It is apparent that the decay times for the triplet signals of the two polymers are very different, the longer ones being observed for the acyl-substituted polycarbazolyldiacetylene. Moreover, the rise and decay lifetimes for each polyCzDA are different and the signals show sublinear intensity dependence. The fitting with a single exponential function of the data recorded at various pumping powers for the *separate* rise and decay processes provides some preliminary

TABLE I. Values of the fitting parameters for the rise and decay curves at different excitation intensity in polyDPCHD and polyDCHD-HS. The values of n_0 are deduced from Ref. 54.

	PolyDPCHD				PolyDCHD-HS			
Intensity (mW)	g	τ (μs)	τ_{rise} (μs)	n_0 (10^{17} cm^{-3})	g	τ (μs)	τ_{rise} (μs)	n_0 (10^{17} cm^{-3})
1	0.73	302	177	2.1	0.44	126	121	8.9
2.5					0.59	178	114	3.2
5	0.44	302	135	3.7	0.56	158	99	5.1
7.5					0.53	183	94	5.2
10	0.38	346	106	4.0	0.54	168	85	6.4
15	0.32	348	92	4.2	0.51	164	78	7.8
25					0.46	165	68	9.1
30	0.27	388	69	4.6				
40					0.43	167	58	10
50					0.41	163	52	11
60	0.15	307	67	5.4				

information. The rise time for polyDPCHD (polyDCHD-HS) regularly decreases from 360 to 310 μs (180 to 110 μs) upon increasing the laser power, while the decay time does not show a regular dependence on the intensity, being scattered in the range 60–130 μs (70–113 μs). A simple monomolecular rise and decay kinetics cannot reproduce the observed data, due to the difference between the rise and decay time constants, the intensity dependence of the rise time and the sublinear pumping power dependence. We then worked out a kinetic model to take into account at least the most significant effects. This model, which has been successfully used to study the kinetics of polarons in blue phase PDA's (Ref. 6) and sexithiophene,[53] predicts the trap sites to be responsible for the saturation of the signal, which is expected to cause the sublinear intensity dependence. The density of the triplet photoexcitations bound to traps (n) is described by the following rate equation:

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

where τ is the decay time, g the generation efficiency of trapped triplets, I the pump intensity, and n_0 the trap sites density. The analytical solution of this differential equation for the rising process is given by

$$n_{\mathrm{rise}}(t)=gI\tau_{\mathrm{rise}}[1-e^{-t/\tau_{\mathrm{rise}}}],\quad n_{\mathrm{rise}}(0)=0, \tag{2}$$

where

$$\frac{1}{\tau_{\mathrm{rise}}}=\frac{1}{\tau}+\frac{gI}{n_0} \tag{3}$$

while for the decay

$$n_{\mathrm{decay}}(t)=n_{\mathrm{rise}}(t^*)e^{(t^*-t)/\tau},\quad n_{\mathrm{decay}}(t^*)=n_{\mathrm{rise}}(t^*) \tag{4}$$

where the beginning of the decay curve and the end of the rise one is fixed at t^*. For this kinetics, τ_{rise} is seen to decrease upon increasing the pump intensity, as experimentally observed. On the contrary, the decay time is not affected by the traps, since they are active only under photoexcitation and not during the dark period. Moreover, the signal is proportional to $gI\tau_{\mathrm{rise}}$, thus having an intrinsically sublinear intensity dependence. The data in Fig. 8 for both the rise and decay processes can be *simultaneously* fitted with Eq. (1), the fitting parameters being reported in Table I (see Ref. 54 for details). A detailed check of the fitting quality is provided by the intensity dependence of the gI and τ_{rise} parameters reported in the insets of Fig. 8. Unfortunately for polyDPCHD the agreement is not fully satisfactory, since gI still shows a sublinear intensity dependence (suggesting an efficiency g depending on the pumping flux) and τ_{rise} shows a poor agreement with Eq. (3). On the contrary for polyDCHD-HS we found a full agreement with the prediction of the kinetic model, since gI is linear in the intensity and τ_{rise} almost perfectly matches Eq. (3). We tried to improve the fit for polyDPCHD by including in the rate equation two possible alternative or cumulative bimolecular channels, one for the decay and the other for the saturation:

$$\frac{dn}{dt}=-\frac{1}{\tau}n-\beta n^2+gI\left[1-\frac{n}{n_0}-\delta\left(\frac{n}{n_0}\right)^2\right], \tag{5}$$

where β is the bimolecular recombination constant and δ a second order saturation coefficient. Also in this case the rate equation has an analytical solution,[55] but the fitting results are still not satisfactory for polyDPCHD. We conclude that other mechanisms should contribute to the saturation effects for this polymer. A sublinear intensity dependence of the photoinduced absorption is often reported in the literature.[3–5,36,46,50–53,56–61] We have to disentangle among the possible reasons for this behavior, e.g., bimolecular recombination, dispersive transport, and true saturation effects. Bimolecular recombination can be easily detected due to the dependence of the lifetime from the inverse square root of the pump intensity.[3] In our case we can exclude this mechanism to take place since the decay time results to be almost independent on I. Dispersive transport occurs in disordered solids when the excitation hops from different sites with different probabilities which are related to the site energies. These phenomena have been widely investigated in low mobility solids such as inorganic amorphous[62] and organic semiconductors.[63] In this mechanism the recombination constant becomes $\tau=(t/t_0)^{1-\alpha}$, where t_0 is the hopping time in a crystalline structure (no disorder) and α $(0\leqslant\alpha<1)$ is the dispersion parameter related to the width of the Gaussian energy distribution among the different sites.[63] By using this recombination rate, the anomalous modulation frequency and intensity dependences of the PIA spectra recorded by the lock-in technique,[50] triplet exciton migration,[51] and polaron recombination[64] have been accounted for. In our case, the pure exponential decay of the signal indicates that the dispersive transport does not play a major role. Then to interpret our data for polyDPCHD we must invoke some additional saturation effect acting on g. Since we are investigating on a photophysical process including multiple steps, e.g., photon absorption, triplet formation, and triplet decay, the saturation process could in principle occur at different levels. For example, in semiconductor quantum wells, a saturation process takes place in the ground-excited state transition, thus limiting the absorption of the excited states.[65] In conjugated polymers the saturation process has been sometimes observed[53,56,66,67] but never fully described. For instance, in Ref. 56, even though a sophisticated kinetics is used for the interpretation of the time evolution of charged carriers in a wide time domain ranging from femtoseconds to milliseconds, the saturation effects in the secondary generation processes are quantitatively explained only using an *ad hoc* ansatz $[1-\exp(-\phi/\phi_{\mathrm{sat}})]$ for the pump fluence (ϕ) dependence. On the contrary, in the model here discussed the saturation effects naturally come from the kinetic equation and account for the observed data for triplets in polyDCHD-HS. Notice that a similar equation has been used to describe the saturation process due to transient triplet hole burning in ladder-type conjugated polymers.[65] In that case, the saturation value of the triplet density is equal to that of the chromophores, i.e., nearly all chromophores run into their triplet states and the absorption of the sample approaches zero. Since in our experiments we cannot monitor the transient change of the ground state, we prefer to interpret our data in the framework of the trap density which has been successfully used in the past.[6,53]

The estimated value of g for polyDCHD-HS in the μs time regime is about 0.5 (see Table I), similar to the values obtained for other conjugated polymers,[56,68] and much higher then those obtained for highly luminescent polymers.[69] This value of g for triplet excitons indicates that half of the photoexcitation density follows different decay pathways. Since polyDCHD-HS is not fluorescent in the solid state, radiative recombination cannot be responsible for such decays. Part of the triplet excitons possibly undergo a much faster recombination, while part of the primary photoexcitations (excited singlet states) recover the ground state through tunneling processes.[70] In the case of polyDPCHD, even though the proposed model does not reproduce the full set of data with the same accuracy as for polyDCHD-HS, g appears to be lower than in polyDCHD-HS. This is compatible with the efficient radiative decay observed for this polymer.

We turn now our attention towards the physical nature of the traps (n_0) in PDA's. In our previous studies we showed that they could be either the chain ends [in the blue form of PDA-4BCMU (Ref. 6)] or some chain twistings [breakdowns of conjugation within the macromolecule, as in polyDCHD-S (Ref. 71)]. The chain density for polyDCHD-HS can be estimated in the following way. A chain length of about 60 nm and a diameter of 3.84 nm were determined for the rodlike structure of the polymer.[2,72] The resulting chain volume is about 10^{-18} cm^3, and the chain density 10^{18} cm^{-3}, in good agreement with the n_0 value obtained from the fittings. No further speculations can be made about the possible presence of chain twistings whose density should however, be low due to the abovementioned rodlike structure of polyDCHD-HS. Consequently, the chain ends should play a role in the trapping process of triplet excitons in PDA's.

In conclusion, we have shown that acyl and alkyl substituted polycarbazolyldiacetylenes have different spectroscopical properties. They indeed exhibit different el-ph couplings which strongly modify not only the shape of the absorption spectra but also the relaxation of the excited states and the emission properties associated with different orderings of the excited states. The very sharp features observed in polyDPCHD thin films allow for the observation and assignment of a new weak absorption feature due to a string mode of the backbone. The Raman spectra show that the arrangement of the polar side groups is responsible for the difference observed in thick and thin (or thick annealed) films of polyDPCHD. The main photoexcited species in the μs time domain for these PDA's are the triplet excitons, but their generation efficiency is greater in polyDCHD-HS where the competing fluorescence process is absent. The rise and decay kinetics of triplet excitons is affected by the presence of traps. Triplets accommodate on trap sites, possibly chain ends, with a dynamics accounted for by a properly developed model.

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[1] D. Cavallo, M. Alloisio, C. Dell'Erba, C. Cuniberti, D. Comoretto, and G. Dellepiane, Synth. Met. **127**, 71 (2002).

[2] B. Gallot, A. Cravino, I. Moggio, D. Comoretto, C. Cuniberti, C. Dell'Erba, and G. Dellepiane, Liq. Cryst. **26**, 1437 (1999).

[3] G. Dellepiane, C. Cuniberti, D. Comoretto, G. F. Musso, G. Figari, A. Piaggi, and A. Borghesi, Phys. Rev. B **48**, 7850 (1993).

[4] D. Comoretto, I. Moggio, C. Dell'Erba, C. Cuniberti, G. F. Musso, G. Dellepiane, L. Rossi, M. E. Giardini, and A. Borghesi, Phys. Rev. B **54**, 16 357 (1996).

[5] D. Comoretto, I. Moggio, C. Cuniberti, G. Dellepiane, M. E. Giardini, and A. Borghesi, Phys. Rev. B **56**, 10264 (1997).

[6] D. Comoretto, I. Moggio, C. Cuniberti, G. F. Musso, G. Dellepiane, A. Borghesi, F. Kajzar, and A. Lorin, Phys. Rev. B **57**, 7071 (1998).

[7] G. Lanzani, G. Cerullo, M. Zavelani-Rossi, S. De Silvestri, D. Comoretto, G. F. Musso, and G. Dellepiane, Phys. Rev. Lett. **87**, 187402 (2001).

[8] M. Ottonelli, G. Musso, D. Comoretto, and G. Dellepiane, Phys. Chem. Chem. Phys. **4**, 2754 (2002).

[9] M. Ottonelli, I. Moggio, G. F. Musso, D. Comoretto, C. Cuniberti, and G. Dellepiane, Synth. Met. **119**, 611 (2001).

[10] D. Grando, G. Banfi, D. Comoretto, and G. Dellepiane, Chem. Phys. Lett. **363**, 492 (2002).

[11] F. D'Amore, A. Zappettini, G. Facchini, S. M. Pietralunga, M. Martinelli, C. Dell'Erba, C. Cuniberti, D. Comoretto, and G. Dellepiane, Synth. Met. **127**, 143 (2002).

[12] E. Giorgetti, G. Margheri, S. Sottini, G. Toci, M. Muniz-Miranda, L. Moroni, and G. Dellepiane, Chem. Phys. Lett. **4**, 2762 (2002).

[13] A. Boyle and W. J. Blau, in *Handbook of Advanced Electronic and Photonic Materials and Devices*, edited by H. S. Nalwa, Vol. 9 of Nonlinear Optical Materials (Academic Press, New York, 2001), p. 309; G. I. Stegeman and A. Miller, in *Photonics in Switching*, edited by J. E. Midwinter (Academic Press, Orlando, 1992), Vol. I, p. 81.

[14] S. N. Dixit, D. Guo, and S. Mazumdar, Phys. Rev. B **43**, 6781 (1991); D. Guo, S. Mazumdar, S. N. Dixit, F. Kajzar, F. Jarka, Y. Kawabe, and N. Peyghambarian, *ibid.* **48**, 1433 (1993).

[15] O. J. Korovyanko, I. I. Gontia, Z. V. Vardeny, T. Masuda, and K. Yoshino, Phys. Rev. B **67**, 035114 (2003); M. Wohlgenannt, W. Graupner, G. Leising, and Z. V. Vardeny, Phys. Rev. Lett. **82**, 3344 (1999); R. Osterbacka, M. Wohlgenannt, M. Shkunov, D. Chino, and Z. V. Vardeny, J. Chem. Phys. **118**, 8905 (2003).

[16] B. Kraabel, D. Hulin, C. Aslangul, C. Lapersonne-Meyer, and M. Schott, Chem. Phys. **227**, 83 (1998).

[17] A. Kohler, J. S. Wilson, and R. H. Friend, Adv. Mater. (Weinheim, Ger.) **14**, 701 (2002), and references therein.

[18] A. P. Monkman, H. D. Burrows, L. J. Hartwell, L. E. Horsburgh, I. Hamblett, and S. Navaratnam, Phys. Rev. Lett. **86**, 1358 (2001).

[19] R. A. Palmer, J. L. Chao, R. M. Dittmar, V. G. Gregoriou, and S. E. Plunkett, Appl. Spectrosc. **47**, 1297 (1993); P. Chen and R. A. Palmer, *ibid.* **51**, 580 (1997).

[20] D. Comoretto, M. Ottonelli, G. F. Musso, M. Alloisio, D. Cavallo, C. Cuniberti, C. Dell'Erba, G. Dellepiane, C. Soci, A. Rastelli, and F. Marabelli, Synth. Met. **138**, 75 (2003).

[21] A. J. Campbell and C. K. L. Davies, Polymer **36**, 675 (1995).

[22] C. Lapersonne-Meyer, J. Berrehar, M. Schott, and S. Spagnoli, Mol. Cryst. Liq. Cryst. **256**, 423 (1994).

[23] M. Schott, Synth. Met. **139**, 739 (2003); T. Guillet, J. Berréhar, R. Grousson, J. Kovensky, C. Lapersonne-Meyer, M. Schott, and V. Voliotis, Phys. Rev. Lett. **87**, 087401 (2001).

[24] G. Dellepiane, R. Tubino, and C. Cuniberti, Croat. Chem. Acta **61**, 347 (1988); G. Dellepiane, in *Molecular Electronics, Proceedings of the 4th International School on Condensed Matter Physics*, edited by Borissov (World Scientific, Singapore, 1987), p. 371.

[25] C. Colombi, D. Comoretto, C. Cuniberti, G. F. Musso, P. Piaggio, and G. Dellepiane, Macromol. Chem. Phys. **197**, 1241 (1996).

[26] M. Ottonelli, G. F. Musso, and G. Dellepiane, Appl. Surf. Sci. **226**, 99 (2004); M. Ottonelli, G. F. Russo, D. Comoretto, and G. Dellepiane, J. Am. Chem. Soc. (to be published).

[27] M. Alloisio, A. Cravino, I. Moggio, D. Comoretto, S. Bernocco, C. Cuniberti, C. Dell'Erba, and G. Dellepiane, J. Chem. Soc., Perkin Trans. 2 **2**, 146 (2001).

[28] L. Moroni, P. R. Salvi, C. Gellini, G. Dellepiane, D. Comoretto, and C. Cuniberti, J. Phys. Chem. A **105**, 7759 (2001).

[29] F. D'Amore, S. M. Pietralunga, M. Martinelli, M. Alloisio, D. Cavallo, C. Cuniberti, C. Dell'Erba, and G. Dellepiane, Synth. Met. **138**, 363 (2003).

[30] G. F. Musso, D. Comoretto, F. De Melas, C. Cuniberti, and G. Dellepiane, Synth. Met. , (1999).

[31] D. K. Campbell, J. Tinka Gammel, H.-Q. Lin, and E. Y. Loh, Jr., Synth. Met. **49-50**, 631 (1992).

[32] Z. G. Soos, S. Ramasesha, and D. S. Galvao, Phys. Rev. Lett. **71**, 1609 (1993).

[33] A. Race, W. Barford, and R. J. Bursill, Phys. Rev. B **67**, 245202 (2003); **64**, 035208 (2001); M. Yoshizawa, A. Kubo, and S. Saikan, *ibid.* **60**, 15 632 (1999).

[34] B. S. Hudson, B. E. Kholer, and K. Schulten, in *Excited States*, edited by E. C. Lim (Academic, New York, 1982), Vol. 6.

[35] I. Gontia, S. V. Frolov, M. Liess, E. Ehrenfreund, Z. V. Vardeny, K. Tada, H. Kajii, R. Hidayat, A. Fujii, K. Yoshino, M. Teraguchi, and T. Masuda, Phys. Rev. Lett. **82**, 4058 (1999).

[36] I. I. Gontia, Z. V. Vardeny, T. Masuda, and K. Yoshino, Phys. Rev. B **66**, 075215 (2002).

[37] D. N. Batchelder and D. Bloor, *Resonance Raman Spectroscopy of Conjugated Macromolecules, in Advances in Infrared and Raman Spectroscopy*, edited by R. J. H. Clark and R. E. Hester (Wiley, Chichester, 1984), Vol. 11.

[38] T. Chen, A. Vierheiling, W. Kiefer, and A. Materny, Phys. Chem. Chem. Phys. **3**, 5408 (2001); A. Vierheiling, T. Chen, P. Waltner, W. Kiefer, A. Materny, and A. H. Zewail, Chem. Phys. Lett. **312**, 349 (1999).

[39] Since thick films are obtained through repeated monomer depositions, we conjecture that at the interface between the different deposited layers the interdigitation of the long acyl chains could be different from the single deposition case. This different chain entanglement could modify the arrangement of the carbazolyl moieties, which could then cause stresses on the conjugated backbone. Thermal annealing provides a relaxation of the stresses by making the thick film more uniform.

[40] *Polydiacetylenes*, edited by H.-J. Cantow (Springer-Verlag, Berlin, 1984); R. Zielinski and J. Kalinowski, J. Phys. C **20**, 177 (1987).

[41] G. Dellepiane, D. Comoretto, and C. Cuniberti, J. Mol. Struct. **521**, 157 (2000).

[42] D. Comoretto, M. Ottonelli, G. F. Musso, G. Dellepiane, C. Soci, and F. Marabelli, Synth. Met. **139**, 889 (2003).

[43] D. Cavallo, M. Alloisio, C. Dell'Erba, C. Cuniberti, D. Comoretto, and G. Dellepiane, Synth. Met. **127**, 71 (2002).

[44] D. Comoretto and E. Giorgetti (unpublished).

[45] Notice that this new band in photodamaged samples occurs at the onset of the glass substrate absorption. We cannot then exclude the glass transparency to be affected by the extended laser irradiation. Even though this effect is not important for the PIA spectra discussed in this paper, further work on this point will be performed with films grown on different substrates.

[46] *Organic Photovoltaics*, edited by CJ. Brabec, V. Dyakonov, J. Parisi, and N. S. Sariciftci (Springer-Verlag, Berlin, 2003).

[47] B. Kraabel, D. Moses, and A. J. Heeger, J. Chem. Phys. **103**, 5102 (1995).

[48] P. Tavan and K. Schulten, Phys. Rev. B **36**, 4337 (1987); K. Schulten and M. Karplus, Chem. Phys. Lett. **14**, 305 (1972); G. F. Musso, D. Comoretto, F. De Melas, C. Cuniberti, and G. Dellepiane, (unpublished).

[49] C. C. Grandinaru, J. T. M. Kennis, E. Papagiannakis, I. H. M. van Stokkum, R. J. Cogdell, G. R. Fleming, R. A. Niederman, and van Grondelle, Proc. Natl. Acad. Sci. U.S.A. **98**, 2364 (2001).

[50] O. Epshtein, Y. Eichen, E. Ehrenfreund, M. Wohlgenannt, and Z. V. Vardeny, Phys. Rev. B **90**, 046804-1 (2003).

[51] C. Rothe and A. P. Monkman, Phys. Rev. B **68**, 075208 (2003).

[52] Y.-H. Cha, Y. Furukawa, M. Tasumi, T. Noguchi, and T. Ohnishi, Chem. Phys. Lett. **273**, 159 (1997).

[53] P. A. Lane, X. Wei, Z. V. Vardeny, J. Poplawski, E. Ehrenfreund, M. Ibrahim, and A. J. Frank, Synth. Met. **76**, 57 (1996).

[54] The efficiency g can be obtained by remembering that $-\Delta T/T=\sigma dn$, where σ is the triplet absorption cross section (10^{-15} cm^2) and d is the penetration depth (about 10^{-4} cm for a resonant absorption in an unoriented conjugated polymer). Then, n_0 can be easily obtained from the fitting parameters g, τ, and $\tau_{\rm rise}$ [Eq. (3)] when you convert the pumping power (P, measured in mW) to the density of absorbed photons per unit time (I, measured in cm^{-3} s^{-1}). According to Ref. 6, $I=P\lambda_{\rm exc}A/hcV$, where $A=1-R-T\approx 0.8$ (R is the reflectance and T the transmittance), and V is the film volume corresponding to the laser spot (2 mm diameter with penetration depth $\approx 10^{-4}$ cm). For $P=1$ mW, we get $I=8.84\times 10^{17}$ cm^{-3} s^{-1}. Notice that the values of the fit parameter for low pumping power are less reliable due to the reduced sensitivity of our power meter below 10 mW.

[55] By rearranging Eq. (5) it assumes the form $dn/dt=An^2+Bn+C$, where $A=-\beta-\delta gI/n_0^2$; $B=-1/\tau_{\rm rise}$; $C=gI$, i.e., a Riccati's differential equation, which can be solved with standard procedures giving rise to $n(t)=2C\tanh[(\sqrt{\Delta}/2)t]/\sqrt{\Delta}-B\tanh[(\sqrt{\Delta}/2)t]$, where $\Delta=B^2-4AC$.

[56] C. Silva, D. M. Russel, AS. S. Dhoot, L. M. Herz, C. Daniel, N. C. Greenham, A. C. Arias, S. Setayesh, K. Mullen, and R. H. Friend, J. Phys.: Condens. Matter **14**, 9803 (2002).

[57] R. A. J. Janssen, N. S. Sariciftci, and A. J. Heeger, J. Chem. Phys. **100**, 8641 (1994).

[58] Y. V. Romanovskii, V. I. Arkhipov, and H. Baessler, Phys. Rev. B **64**, 033104 (2001).

[59] M. Westerling, R. Osterbacka, and H. Stubb, Phys. Rev. B **66**, 165220 (2002).

[60] K. A. Coplin, A. L. Habakuk, and D. T. Glatzhofer, Synth. Met. **124**, 271 (2001).

[61] C. Rothe, S. Hintschich, A. Monkman, M. Svensson, and M. R. Anderson, J. Chem. Phys. **116**, 10503 (2002).

[62] H. Scherr and E. W. Montroll, Phys. Rev. B **12**, 2455 (1975).

[63] G. Schnönherr, H. Baessler, and M. Silver, Philos. Mag. B **44**, 47 (1981); F. Stolzenburg, B. Ries, and H. Baessler, J. Mol. Electron. **3**, 149 (1987).

[64] A. F. Nogueira, I. Montanari, J. Nelson, A. R. Durrant, C. Winder, N. S. Sariciftci, and C. Brabec, J. Phys. Chem. B **107**, 1567 (2003).

[65] C. V. Shank, R. L. Fork, R. F. Leheny, and J. Shah, Phys. Rev. Lett. **42**, 112 (1979); D. A. B. Miller, D. S. Chemla, D. J. Eilenberg, P. W. Smith, A. C. Gossard, and W. T. Tsang, Appl. Phys. Lett. **41**, 679 (1982); D. S. Chemla and D. A. B. Miller, J. Opt. Soc. Am. B **2**, 1155 (1985); S. Schmitt-Rink, D. S. Chemla, and D. A. B. Miller, Adv. Phys. **38**, 89 (1989).

[66] See, for instance, D. W. McBranch and M. B. Sinclair, in *Primary Photoexcitations in Conducting Polymers*, edited by N. S. Sariciftci (World Scientific, Singapore, 1996), p. 587.

[67] Yu. V. Romanovskii, H. Baessler, and U. Scherf, Chem. Phys. **276**, 321 (2002).

[68] J. S. de Melo, H. D. Burrows, M. Svensson, M. R. Andersson, and A. P. Monkman, J. Chem. Phys. **118**, 1550 (2003).

[69] M. A. Loi, C. Gadermaier, E.. J. W. List, G. Leising, W. Graupner, G. Bongiovanni, A. Mura, J.-J. Pireaux, and K. Kaeriyama, Phys. Rev. B **61**, 1859 (2000).

[70] T. Kobayashi, in *Primary Photoexcitations in Conducting Polymers*, edited by N. S. Sariciftci (World Scientific, Singapore, 1996), p. 430.

[71] G. Lanzani, S. Stagira, G. Cerullo, S. De Silvestri, D. Comoretto, I. Moggio, C. Cuniberti, G. F. Musso, and G. Dellepiane, Chem. Phys. Lett. **313**, 525 (1999).

[72] C. Cuniberti (unpublished).