SPECTROSCOPICAL AND PHOTOPHYSICAL INVESTIGATIONS ON POLYDIACETYLENES WITH DIFFERENT ORDERING OF THE A_g AND B_u EXCITED STATES

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Absorption, photoluminescence and photoinduced absorption spectra of polycarbazolyldiacetylenes (polyCzDAs) carrying selected acyl (polyDPCHD) or alkyl (polyDCHD-HS) groups are reported. The absorption spectrum of polyDCHD-HS films, which is almost independent of the temperature, 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.

Unlike other polydiacetylenes (PDAs), the polyCzDAs which exhibit narrow spectral features and reduced el-ph coupling, such as polyDPCHD films and polyDCHD-HS in benzene solutions, are luminescent thus suggesting a different ordering of the dipole forbidden and allowed states. This interpretation is confirmed by two-photon spectroscopic data.

The ordering of the A_g and B_u excited states also affects the generation of triplet excitons, which are the main long-living excited states of PDAs. The rise and decay of the triplet signal for polyDCHD-HS are accounted for through a dynamical model, based on a monomolecular decay regime including saturation effects. 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.

Keywords: polydiacetylene, conjugated polymer photophysics, A_g , B_u ordering

1. INTRODUCTION

Since several years our group has been interested in the preparation of diacetylenic monomers, their polymerization [1,2], the study of their photophysical [3,4,5,6,7] and electronic properties [8, 9] as well as in the evaluation of their non linear optical (NLO) properties [10, 11, 12]. Among the different polydiacetylenes (PDAs), we have been interested in those having at least one photoconductive carbazolyl moiety as a side group. The main photophysical properties of these PDAs can be summarized as follows:

- In addition to triplet excitons, charged photoexcited states can be generated in the blue form of the polymers.
- The relative intensity of charged states (presumably polarons [13]) with respect to triplet excitons depends on the interbackbone separation, which is modulated by the supramolecular structure of the polymeric chains. The larger the interchain separation, the lower is the signal of charged states as compared with that of triplet excitons [5,6].
- In red phase PDAs, only triplet excitons are photogenerated through a singlet fission process of the lowest excited A_g state [7]. Notice that the A_g forbidden states are also essential for the evaluation of the NLO response of these materials [14].

More recently, a new puzzling result has been obtained. Some of our PDAs in the red form may exhibit a non negligible luminescence [1,15]. This fact has stimulated an extensive work on the investigation of their spectroscopical and photophysical properties.

In this paper, we report a detailed spectroscopical characterization (absorption, fluorescence, Raman and photoinduced absoprtion spectra) of the properties of red phase polyDPCHD and polyDCHD-HS (see Fig. 1).

Preliminary studies have shown that polyDPCHD exhibits two different forms for thin and thick films, and that upon annealing thick films behave like the thin ones [16]. This behavior, which has never been observed before in the red phase polyCzDAs films, is here investigated in more detail in particular in relation to its photophysical properties. For the thick annealed polyDPCHD and for the polyDCHD-HS films, which do not show any thickness dependent change,

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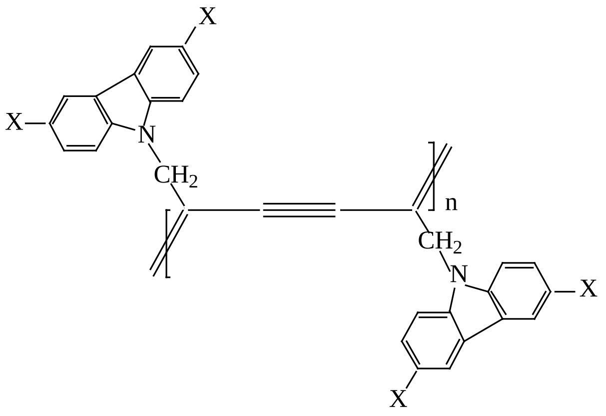
microsecond time resolved photoinduced absorption spectra are discussed. Particular attention to the possible photo-damaging effects due to laser pumping have been already discarded [16]. The PIA spectra are dominated by triplet excitons, whose pump-intensity dependent dynamics is described in terms of a kinetic model including saturation effects. Triplet generation efficiency and the trap density are deduced and compared with those found for other conjugated polymers.



X=-CO(CH$_2$)$_{14}$CH$_3$	polyDPCHD
X=-(CH$_2$)$_{15}$CH$_3$	polyDCHD-HS

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).

2. 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.

Time resolved photoinduced absorption spectra are recorded with a Bruker IFS 66/S Step-Scan FTIR spectrometer as previously described [16]. A detailed description of the Raman, photoluminescence (PL) and absorption spectra has been also previously reported [16].

3. RESULTS AND DISCUSSION

Fig. 2 shows the room temperature electronic absorption spectra of polyDPCHD (both thick and thin) and polyDCHD-HS. Thick samples of polyDPCHD 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 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.

The thinner films of polyDPCHD 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 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 except for the 552 nm shoulder, which is observed only in thick films [16]. 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 previously observed in a polymer carrying shorter acyl side chains [17].

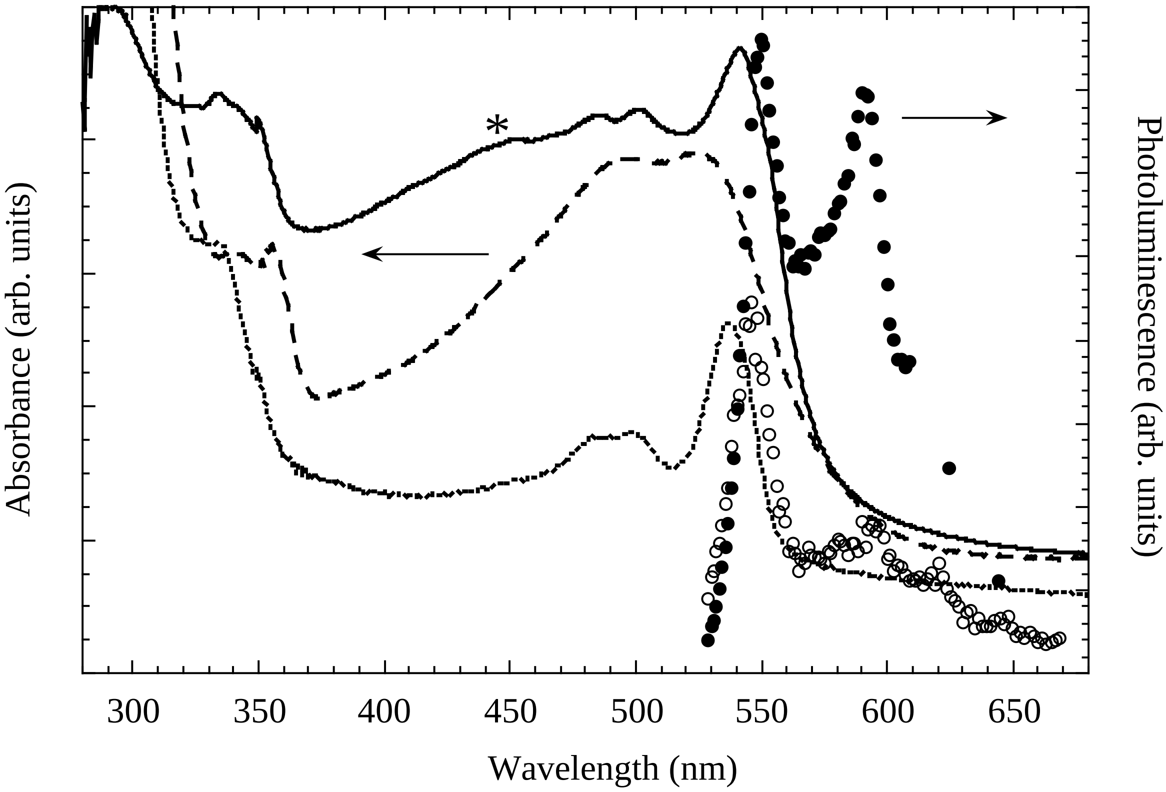


Fig. 2. Room temperature absorption and photoluminescence spectra for thick polyDPCHD (full line, full circles), thin polyDPCHD (dotted line, open circles), and polyDCHD-HS (dashed line). For the latter polymer the PL spectrum is too weak to be recorded. The asterisk labels the high energy band due to the string mode (see text).

Very different is the absorption spectrum of polyDCHD-HS. 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 too much the spectral position of the main absorption features. It is interesting to note that the poor sensitivity to temperature seems to be typical of the red forms of PDAs [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 [18]. In this respect it is interesting to note that the low-energy shoulder observed at 552 nm only for thick polyDPCHD shows a remarkable temperature dependence [16]. This fact suggests that this transition could have a very different origin with respect to those usually observed for the diacetylenic 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* [15] and *very long isolated PDA chains embedded in their monomer single crystals* [19]. Even though the reason for the sharpening of the excitonic transition is still not clear, this comparison suggests that the sharper the excitonic transition, the lower the electron-phonon coupling. Delocalisation 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 [20]. 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 [21].

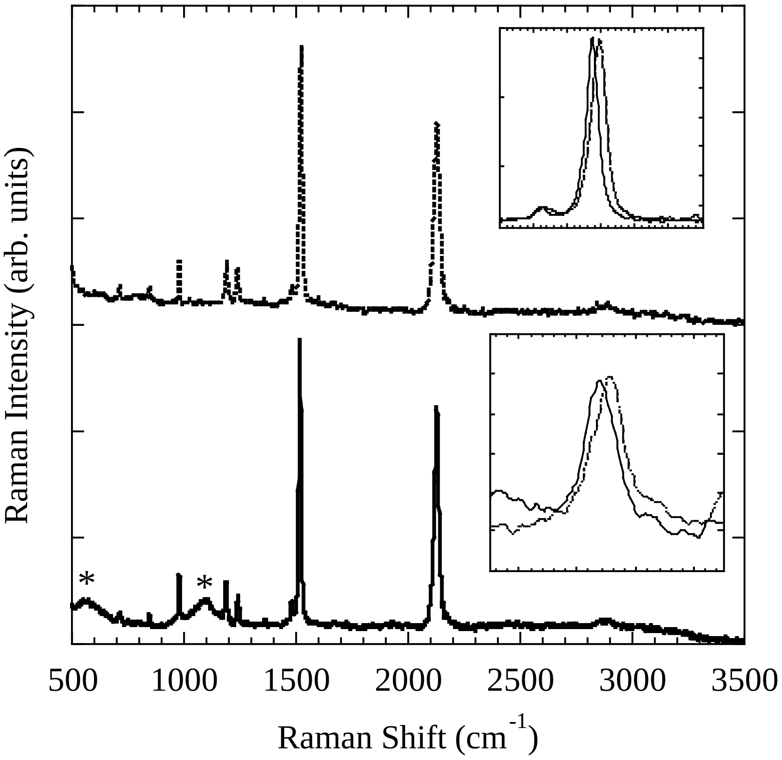


Fig. 3. Raman spectra for thick (dashed line) and thick annealed (full line) polyDPCHD. The insets show C=C (top), and C-C (bottom) stretching modes spectral regions. The asterisks label substrate modes.

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. They 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. Indeed, 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 surprisingly show a strong interaction between carbazolyl moiety and backbone π-electrons in spite of the presence of the CH_2 spacer [22]. It is interesting to note that Raman spectroscopy seems to support the role of sidegroups on the different properties shown by thin and thick polyDPCHD. In Fig. 3 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 [23], 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} [23,24].

In the triple bond region 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 (inset Fig. 3 top). In Fig. 3 (bottom), bands for the thick annealed (thick) films detected at 1191 (1187) and 1240 (1239) cm^{-1}, respectively, are reported (see enlarged view in the bottom inset of the same figure). We note that the vibrations showing different frequencies in thick and thick annealed (thin) films are those related to the single and double bonds (see insets), 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 [15], suggests that two polymeric structures with different side groups arrangement are present in the two forms of polyDPCHD films, namely in thick and thin films. 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 PDAs 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 [25].

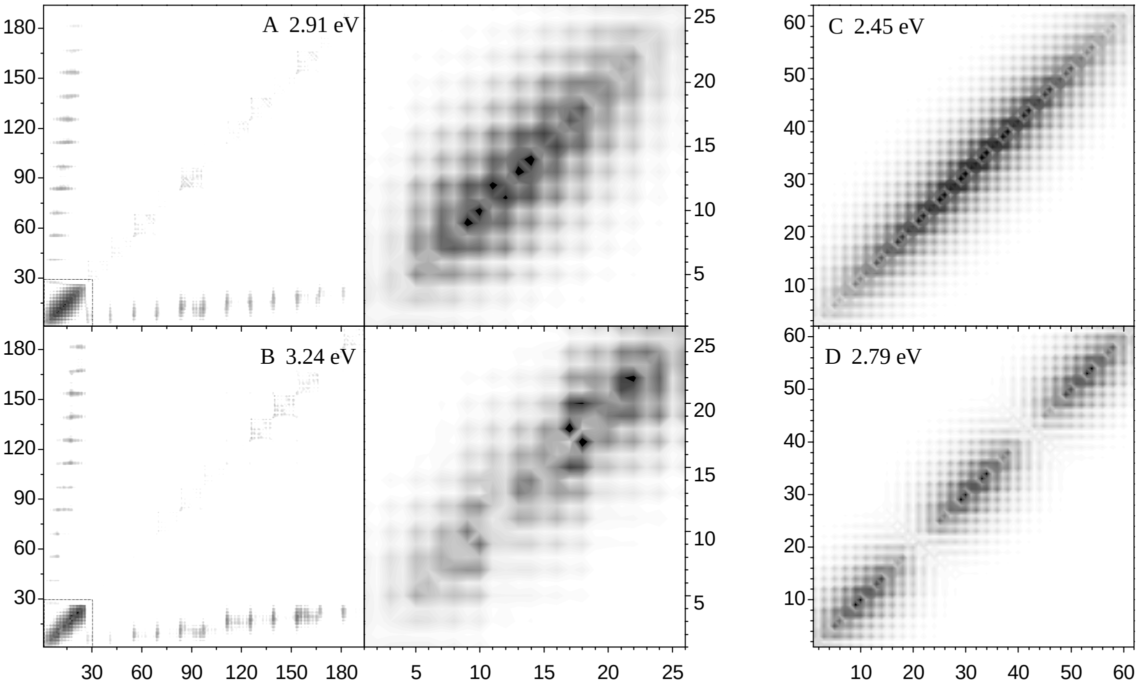


Fig. 4. Plots of the collective electronic oscillator modes for the n = 6 oligomer of Fig. 1 with X = H (left) and for a 15-unit unsubstituted oligodiacetylene (right). The lowest electronic excitations at 2.91 eV (A) and 2.45 eV (C) and the first string mode at 3.24 eV (B) and 2.79 eV (D) are depicted. For the A and B cases full modes are reported in logarithmic scale to in an effort to highlight the very small contributions of the carbazolyl terms, while details of the backbone region (bottom left) are reported in the panels attached on the right. The axes of the plots refer to the numbering of the heavy atoms in each molecule [27].

The absorption spectra of polymers having very sharp electronic transitions allow to evidence fine details in the spectra, such as the very weak band observed around 450 nm only for thin polyDPCHD and polyDCHD-HS benzene solutions [15]. A quantum mechanical approach can be used for the assignment of the above features, based on the Collective Electronic Oscillator (CEO) method [26]. In Figure 4 the one-electron transition density matrices (the collective electronic oscillator modes, in a CEO language) are depicted for the first and second allowed transitions of (i) a carbazolyl-substituted n = 6 oligomer (which we call CHD_6) of the polymers in Figure 1, where we have only put X = H for computational reasons, and (ii) an unsubstituted 15-unit oligodiacetylene (D_{15}). For CHD_6 (D_{15}) the lowest and main absorption is located at 2.91 (2.45) eV, while the next (and weak) transition occurs at 3.24 (2.79) eV. The analysis of the CHD_6 transitions density matrices (Fig. 4, left) shows that these excitations are practically localized over the backbone, only a very small interaction with the carbazolyl moieties being present. To highlight the contributions of the latter, the full representation of each mode is reported in logarithmic scale. These results imply that, at least for low transition energies, this molecule can be considered as formed by non interacting backbone and carbazolyl moieties. Details of the CHD_6 backbone excitations are depicted in Figure 4 (A and B) and can be compared with the corresponding features relative to D_{15} (Figure 4, C and D). For the latter oligomer the electronic transitions [see ref. 8 for details] can be well described referring to the model of the vibrating string (a one-dimensional system) which implies that allowed (forbidden) transitions must carry an even (odd) number of nodes, and their oscillator strengths are approximately proportional to the inverse square of the node number. For example, the second allowed excitation (D) shows two nodes and the global matrix elements (which are proportional to the oscillator strength of the transition) are substantially smaller that in case C. For CHD_6 the situation is slightly different because in this case the backbone does not adopt a perfect trans-planar structure [27], some deviations being induced by the presence of the carbazolyl groups. Notice that despite this fact conjugation along the backbone is maintained due to the “bridge” effect of the π-electrons of the triple bonds. For the lowest transition, which corresponds to the main absorption peak, the excitation is seen to be delocalized over the whole chain in both cases, and the extension of the electron-hole pair is about 4/5 repeat units. Instead for the next allowed transitions some difference occurs in the shape of the modes, which reflects the fact that for CHD_6 the simple string analogy is not completely adequate, as shown by the absence of any nodes. This fact could be easily understood in terms of the already referred distortion from the perfect trans-planar structure, which implies that the coupling terms can no longer be assumed to be equal, as was for the linear case.

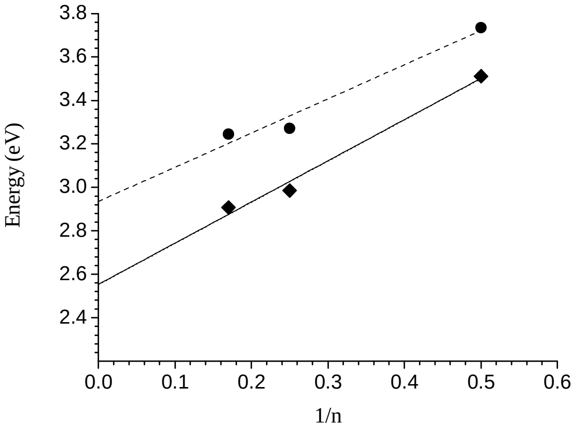


Fig. 5. Computed CEO excitation energy for the lowest (diamonds) and second (circles) allowed transitions of CHD_n (n = 2, 4, 6).

The trend of the two optical excitations is shown in Figure 5 for three CHD_n oligomers (n = 2,4,6) versus 1/n, and the linear fit gives as extrapolated values 2.55 and 2.93 eV for the lowest and the second optical excitation respectively. These quantities are in good agreement with the observed value of about 2.30 eV for the excitonic absorption, and with the high energy weak band observed around 2.70 eV in the polymers. This suggests that the “pseudo first string mode” of the conjugated backbone can be assigned to the observed high energy weak band.

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 (Fig. 2), 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% [15, 16]. The spectral emission properties of the acyl-polymers (not corrected for self-absorption) are also reported in Fig. 2. 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 mirror-like 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 [17], thus suggesting a small geometrical relaxation in the excited states.

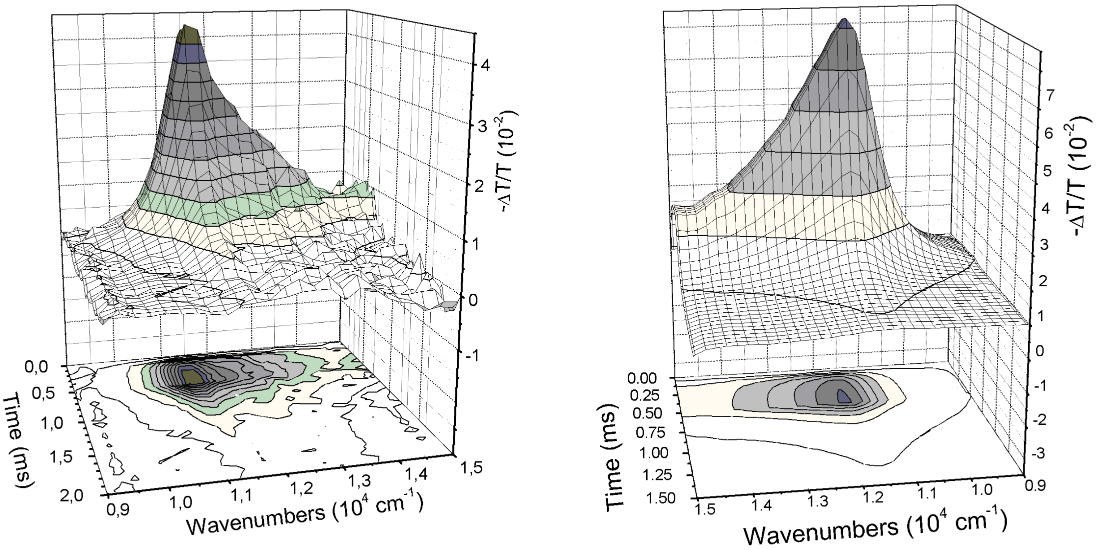


Fig. 6. Three-dimensional plot of TR-PIA signal vs time and wavenumbers for polyDPCHD thick annealed films (a) and polyDCHD-HS (b). At the bottom, the corresponding contour plot points out the temporal evolution of the triplet state.

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 to show that in the solid state, when the polymer is non fluorescent, 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 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]. 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, 31, 32]. When the latter effect is negligible, the $2A_g$ level sets above the $1B_u$ one [33].

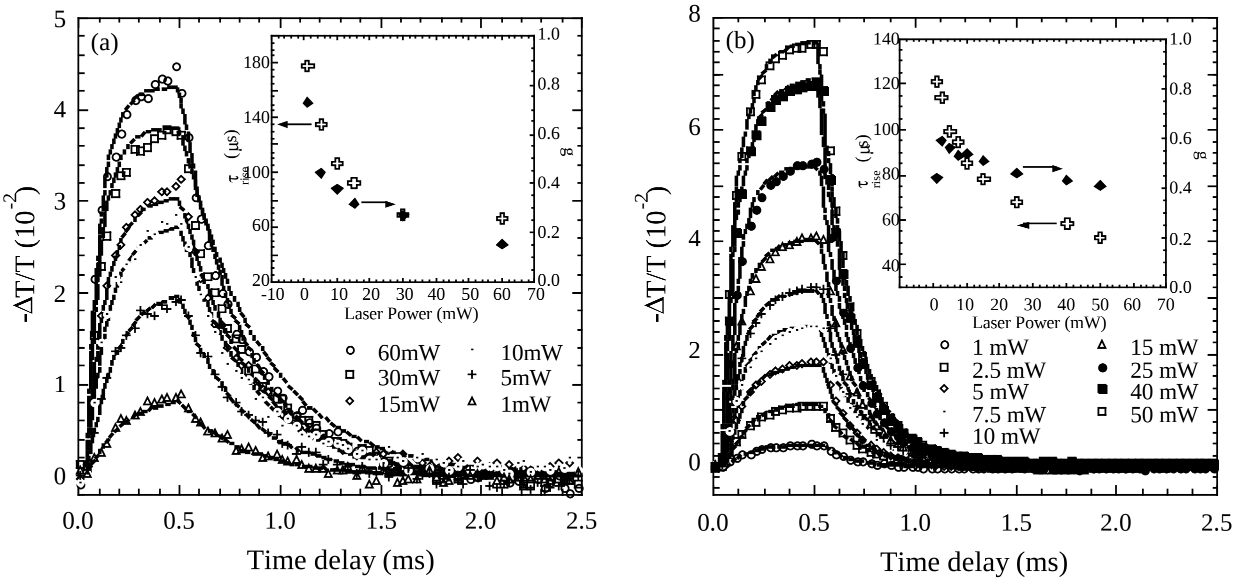


Fig. 7. Symbols: time evolution of the TR-PIA spectra at the maximum of the triplet signal at different pump intensities for thick annealed polyDPCHD (a) and polyDCHD-HS (b). Lines: fit with Equations 2 and 4. In the insets, the intensity dependence of the fit parameter g and τ_{rise} is also reported.

As observed before, a relatively high luminescence efficiency is present only in those PDAs 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].

In the past we studied the photophysical properties of blue- and red-phase PDAs as a function of their supramolecular structure [4,5,37]. For the red phase of PDAs 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 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.

The main photoexcited species in the PIA spectra are 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 [38], spin-orbit coupling [39], charge recombination or singlet fission [7,40]. 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 to 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 [40]. Even though these processes are in general ultrafast, taking place in the femtosecond time domain, complicated triplet dynamics occurs also in shorter time domains [3, 41, 42]. For these reasons we started an investigation of the microsecond (µs) triplet exciton dynamics in our samples.

The three-dimensional plots in Fig. 6 show the µs PIA spectra for thick annealed polyDPCHD (a) and polyDCHD-HS (b) films with their time evolution as measured upon a 750 µs pumping time. In the –ΔT/T-time plane, the rise and decay traces are reported, as are the PIA spectra in the –ΔT/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 wavenumbers, 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.

To better investigate the dynamics in the two polymers, we report in Fig. 7a (7b) 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 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 PDAs [6] and sexithiophene [43□] predicts 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 [16]:

$$n_{rise}(t) = gI\tau_{rise}\left[1-e^{-\frac{t}{\tau_{rise}}}\right],\ n_{rise}(0) = 0 \tag{2}$$

where

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

while for the decay

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

being the beginning of the decay curve and the end of the rise one 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 $gI\tau_{rise}$, thus having an intrinsically sublinear intensity dependence. The data in Fig. 7 for both the rise and decay processes can be *simultaneously* fitted with Eq. 1, being the fitting parameters reported in Table I. A detailed check of the fitting quality is provided by the intensity dependence of the g and τ_{rise} parameters reported in the insets of Fig. 7. Unfortunately for polyDPCHD the agreement is not fully satisfactory, since g 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 good agreement with the prediction of the kinetic model, since g is almost constant with the intensity and τ_{rise} almost perfectly matches Eq. 3. We conclude that other mechanisms should contribute to the saturation effects for polyDPCHD.

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 [44], and much higher then those obtained for highly luminescent polymers [45]. 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 [46]. 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.

TABLE I

	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				

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 according to Ref.16.

We turn now our attention towards the physical nature of the traps (n_0) in PDAs. In our previous studies we showed that they could be either the chain ends (in the blue form of PDA-4BCMU [6]) or some chain twistings (breakdowns of conjugation within the macromolecule, as in polyDCHD-S [47]). 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, 48]. 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 shold however be low due to the above mentioned rod-like structure of polyDCHD-HS. Consequently, the chain ends should play a role in the trapping process of triplet excitons in PDAs.

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 PDAs 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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