

On the nature of long-lived photoexcited states in polydiacetylenes: the photoinduced absorption spectra of PDA-4BCMU*

D. COMORETTO^{1,2}, I. MOGGIO², M. ALLOISIO², C. CUNIBERTI², G.F. MUSSO^{1,2}, M. OTTONELLI¹, G. DELLEPIANE^{1,2}, F. KAJZAR³ and A. LORIN³

¹INFM – Istituto Nazionale per la Fisica della Materia, 24 Corso Perrone, I-16 152 Genova, Italy

²Dipartimento di Chimica e Chimica Industriale, Università degli Studi di Genova, 31 via Dodecaneso, I-16146 Genova, Italy

³Commissariat à l'Énergie Atomique, Direction des Technologies Avancées, LETI, DEIN/LPEM, CEA/Saclay, 91191 Gif Sur Yvette, Cedex, France

We report the results of steady-state photoinduced absorption experiments on PDA-4BCMU grown and oriented on silica substrate. A high degree of axial order, checked by linear and nonlinear optical dichroism and correlated with X-ray measurements was found. Polycrystalline films were obtained with a preferential orientation of crystallites. Unlike the solution cast films exhibiting the so called "red form" only, the deposited films are blue thus showing a better π -electron conjugation than in the former case due to a better planarity of polymer chains. The films were used to perform steady-state photoinduced absorption experiments. Three photoinduced absorption bands at 0.82, 0.95, and 1.39 eV were observed. The 0.82 and 0.95 eV absorption features are assigned to charged states while the 1.39 eV peak is originated by triplet excitons. The photogeneration in PDA-4BCMU of both charged and neutral states is discussed and compared with the results obtained in polydiacetylenes having carbazolyl groups as substituents. The relative weight of one excited species over the other one is dictated by the molecular and supramolecular organization of the polymer.

Keywords: polydiacetylenes, conjugated polymers, non-linear optics, oriented thin polymeric films

1. Introduction

Among the conjugated systems, the polydiacetylenes (PDAs), $(=CR-C\equiv C-CR'=)_n$, have attracted particular attention because they can be prepared in the form of macroscopic single crystals through solid-state topochemical polymerization of the corresponding monomers. In addition, the possibility of changing the substituents of the polymer backbone allows to obtain a variety of materials with properly designed optical and electronic properties. For practical applications, PDAs grown on suitable substrates by the epitaxial technique or, when soluble, cast from so-

lution are usually considered. Polymerization of diacetylenic crystals usually leads to polymers in the blue phase characterized by a well defined singlet excitonic peak around 620 nm. However, thermochromic [1] and solvatochromic [2] phase changes are possible and in this condition a red form characterized by an absorption band around 540 nm is obtained. The study of different forms of PDAs, because of their different conjugation length, provides additional information on the photophysics of these polymers.

The nature of excitations in p-conjugated polymers has been extensively studied by the continuous wave photoinduced absorption (PA) technique. The PA spectra of PDAs, so far reported by other authors, usually deal with their blue form. A strong PA peak

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around 1.4 eV has been observed for PDA-TS ($R = R' = -CH_2SO_3C_6H_4CH_3$) [3,4] and attributed to neutral photoexcitations on the basis of the results of the study of its decay in the presence of an applied magnetic field [5,6]. For the same polymer no evidence of photoexcited charged states in the NIR region is reported. On the contrary the presence of PA signals associated only with the charged photoexcitations has been found in PDA-1OH ($R = -CH_3$, $R' = -CH_2OH$) and PDA-9PA ($R = R' = -(CH_2)_9OCOCH_2C_6H_5$) [4,7,8]. In these cases the assignment has been substantiated by the presence in the low frequency region of the PA spectrum of infrared activated vibrational (IRAV) modes which are associated with the charged states. To make this picture more confused, IRAV modes are reported to be present also in PDA-TS and PDA-4BCMU ($R = R' = -(CH_2)_4OCONHCH_2COOC_4H_9$) [7,8]. In all these cases, no light induced electron spin resonance (LESR) signals were detected suggesting the photogeneration of doubly charged spinless bipolarons [8]. The presence of triplet excitons in the blue form of PDA-4BCMU [9] and PDA-3BCMU ($R = R' = -(CH_2)_3OCONHCH_2COOC_4H_9$) [10] has been detected around 1.4 eV with picosecond PA spectra for probe energies above 1.2 eV.

For the red form of PDAs only a few experimental data are available for PDA-4BCMU [9,11] and PDA-ClCin22 [poly(bis-p-chlorocinnamate,10,12-docosadiyn-1,22-diol)] [11]. The PA peak observed at 1.4–1.5 eV is attributed to neutral excitations (triplet excitons).

In the last few years we have been interested in the study of a class of polydiacetylenes having the carbazolyl group attached directly or indirectly, through a CH_2 spacer, to the main chain [12]. Our interest in the polycarbazolyldiacetylenes (PCzDAs) is dictated by the particularly high value of the third-order polarizability [13,14] and enhanced photoconductive response [15] observed for polyDCHD ($R = R' = -CH_2NC_{12}H_8$) as well as by the unusual excitation profile of the photocurrent [16] in polyCPDO ($R = -NC_{12}H_8$, $R' = -CH_2OH$). The large dipole moment and the photoconducting property of the carbazolyl ring seem to affect to some extent the properties of the polydiacetylene backbone.

The results of PA studies carried out on these polymers are the following ones. Only the charged photoexcitations are detected for those PCzDAs having one carbazolyl substituent, directly attached to the polymer backbone. On the contrary, neutral triplet excitons as well as charged photoexcitations have

been observed for a series of blue PCzDAs symmetrically substituted with carbazolyl groups attached to the polymer backbone via one CH_2 spacer. By increasing the interbackbone distance in these polymers through the insertion of long aliphatic chains on the carbazolyl side group like in polyDCHD-S [$R = R' = -CH_2-(3,6-H_3C-(CH_2)_{11}NC_{12}H_8$] and in polyDCHD-HS [$R = R' = -CH_2-(3,6-H_3C-(CH_2)_{15}NC_{12}H_8$] neutral triplet excitons become the dominant photoexcitations while the charged species are strongly depressed. The red forms of the PCzDAs reveal PA features at 1.5 eV (polyDCHD), at 1.45 eV (polyDCHD-S), and at 1.47 eV (polyDCHD-HS) [17] attributed to triplet excitons on the basis of their lifetimes and the lack of the IRAV modes.

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

The understanding of the mechanisms that favour the photogeneration of one of the excitations over the other one could greatly help in the design of the supramolecular architecture necessary to achieve a desired property. It is well known indeed that both neutral and charged photoexcitations are important in different fields of application. When the dominant excitations are triplet excitons, nonlinear optical properties are particularly favourable. On the other hand, when charged states dominate the PA spectra, the conjugated polymers are promising for photovoltaic applications. In order to propose a possible application for PDAs it is necessary to establish whether the presence of both neutral and charged excitations is observed only for the polycarbazolyldiacetylenes like polyDCHD and its modified forms or it is a general feature of the PDA chain. For this reason we have carried out PA experiments on the blue form of a PDA-4BCMU film on a silica substrate. The results of such a study will be here reported and discussed.

2. Experimental

Oriented thin films of PDA-4BCMU were obtained by vacuum epitaxy of monomers. First, a very thin layer (10–15 nm) was deposited by vacuum evaporation on a cleaned silica substrate. The film was polymerized with UV light and the obtained polymer oriented by rubbing. Then a thicker film was grown by high vacuum deposition of the same diacetylene monomer. The epitaxially grown thin film was again poly-

merized with UV light. Well oriented thin films with the thickness up to 300 nm can be obtained in this way [19]. The film studied in the present paper has a total thickness of about 150 nm. The PDA-4BCMU system is soluble in some organic solvents and solution cast films are red. The thin films obtained, as here described, are instead blue. The synthesis of the PCzDAs is reported in previous works [12].

The electronic absorption spectra have been recorded using a Cary 5E spectrophotometer, operating in the range 180–3300 nm, equipped with both a liquid nitrogen and a hydrogen-helium expansion cryostat; the spectral resolution of all spectra was ~1 nm. Non linear optical dichroism was measured and texture studies by X-rays were performed as described in Ref. 19.

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

3. Results and discussion

Before discussing the data obtained on the oriented PDA-4BCMU we will report the electronic and PA spectra of some PDAs belonging to different classes of polycarbazolyldiacetylenes. Figure 1 reports chemical structures of the polymers discussed in the present work. The nature of the excited states of each PCzDA will be here briefly discussed and a detailed study of their photoexcitations has been already published.

Figures 2 and 6 show the electronic absorption and PA spectra of polyCPDO, polyDCHD, oriented polyDCHD, polyDCHD-S (blue form) and polyDCHD-S (red form), respectively. All these PCzDAs have been studied as microcrystalline pellets and polyethylenes blends except of polyDCHD studied as oriented epitaxially grown film. In this latter case the PA spectrum shows nonlinear excitations

similar to those observed in polycrystalline samples but the study of the polarization dependence of the PA bands allows gaining a more complete picture of the photoexcitations.

The electronic spectrum of polyCPDO exhibits the features quite different from those of other PCzDAs reported here. Direct bonding of the carbazolyl group to the PDA skeleton clearly forbids the appearance of the well-defined singlet excitonic transition observed in the PCzDAs having a spacer between the two conjugated groups. The PA spectrum of this polymer (Fig. 2), whose unresolved absorption edge falls at 1.5 eV, shows two bands unambiguously assigned to the charged species as also confirmed by the appearance in the MIR of IRAV bands.

The very well resolved electronic absorption spectra of polyDCHD (blue form) show both in the microcrystalline sample (Fig. 3) and in the oriented film (Fig. 4) a strong excitonic peak at about 1.86 eV followed by its vibronic progression. The measured peak-to-peak anisotropy of the purely excitonic transition for the oriented sample is about ten but becomes about 20 after subtracting the background of the anisotropic substrate. This high anisotropy ratio shows the very high degree of alignment of the polymeric chains. The PA spectrum of both samples (Figs. 3 and 4) shows the bands at 0.81, 0.96 eV, and 1.26 eV. The analysis of these bands and the study of the anisotropy of each PA signal allows the assignment of the two lower energy peaks to charged states and of the 1.26 eV band to neutral triplet excitons. Indeed, after correction for the same number of absorbed photons in both polarizations, the low-energy photoinduced signals in Fig. 4 are stronger by pumping with the electric field of the radiation perpendicular to the chain axis direction. This fact is indicative of the interchain nature of the generation process of these photoexcited species (charged species). On the other hand, such an effect is not observed for the PA triplet-triplet transition at 1.26 eV, according to its intramolecular nature [20]. The presence of the charged states is also confirmed by appearance in the MIR of IRAV, bands detected as Fano windows, due to the interaction between the electronic and vibrational states.

The electronic spectrum of polyDCHD-S (blue form, Fig. 5) is very similar to that of polyDCHD. In addition, the Raman lines of the two polymers fall at about the same vibrational frequencies, indicating chains of about the same conjugation length. But, quite different is the PA spectrum of polyDCHD-S shown in the same figure when compared to that of

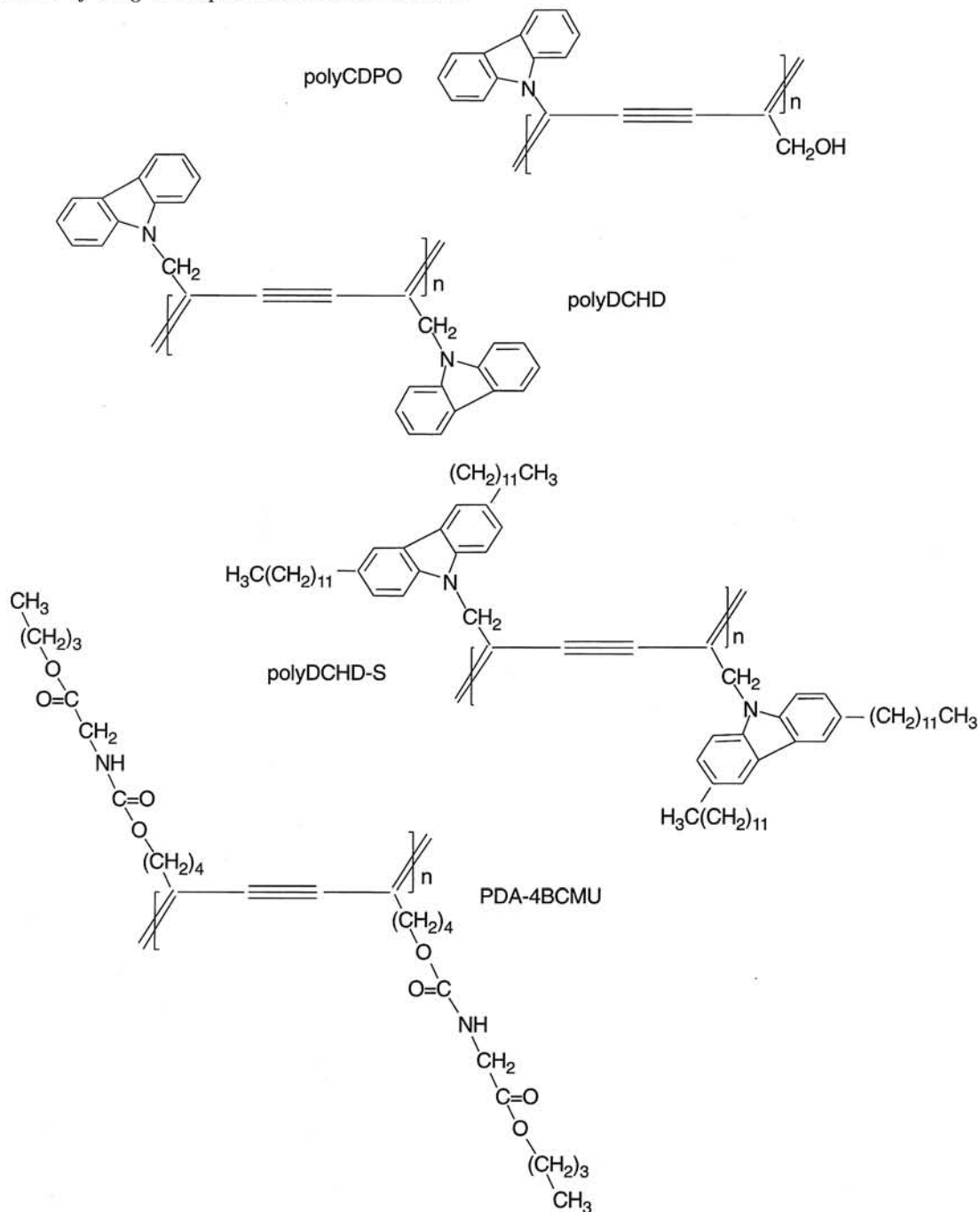


Fig. 1. Chemical structures of the PDAs.

polyDCHD. In blue polyDCHD-S the PA spectrum is dominated by a peak at 1.45 eV that was assigned to a triplet-to-triplet transition. In addition, extremely small signals associated with charged states were detected at about 0.8–1 eV (see inset Fig. 5). It is interesting to notice that the relative intensity of the signals originated by charged states with respect to that of the triplet-to-triplet transition is strongly influenced by the presence of the long alkyl groups on the substituents. The different supramolecular structures of the two polymers yield to different relaxation processes for the possible photoexcitations. Both charged

and neutral non-linear excitations are photogenerated but their decays are driven by the interchain hopping which depends on the interbackbone separation. For polyDCHD-S X-ray diffraction studies provided a value of 2.95 nm for the longest axis of the elementary cell [21], much larger than that for polyDCHD (1.7 nm) [22]. In the former polymer the lack of interbackbone decay routes forces the triplets to be deep trapped and limit the formation of photoexcited charged states. These states indeed can be created only if an electron is transferred from one chain to another one.

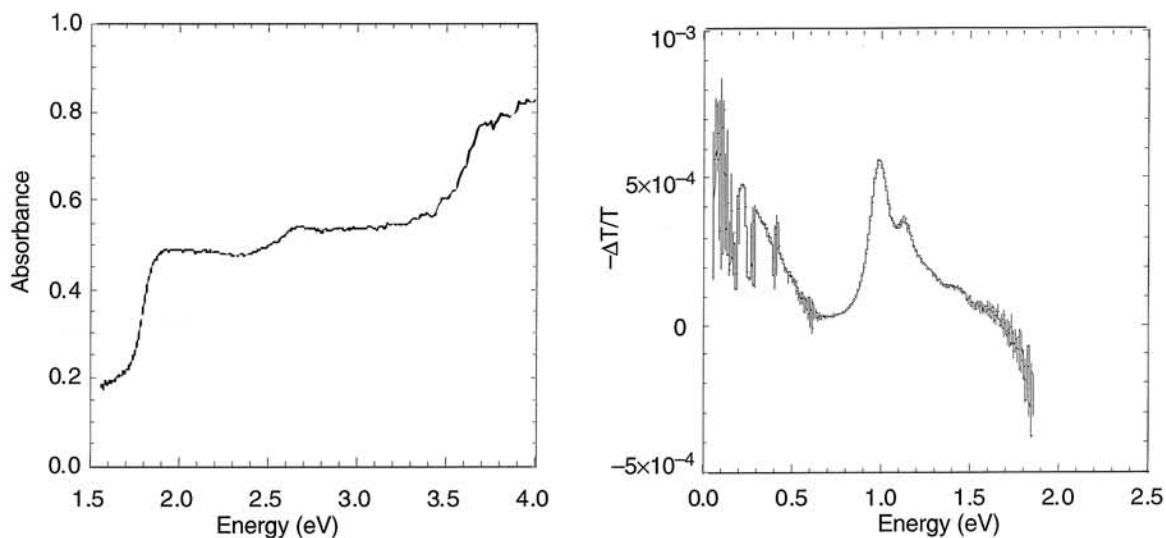


Fig. 2. Left: electronic absorption spectrum of polyCPDO. Right: long time PA spectrum of polyCPDO.

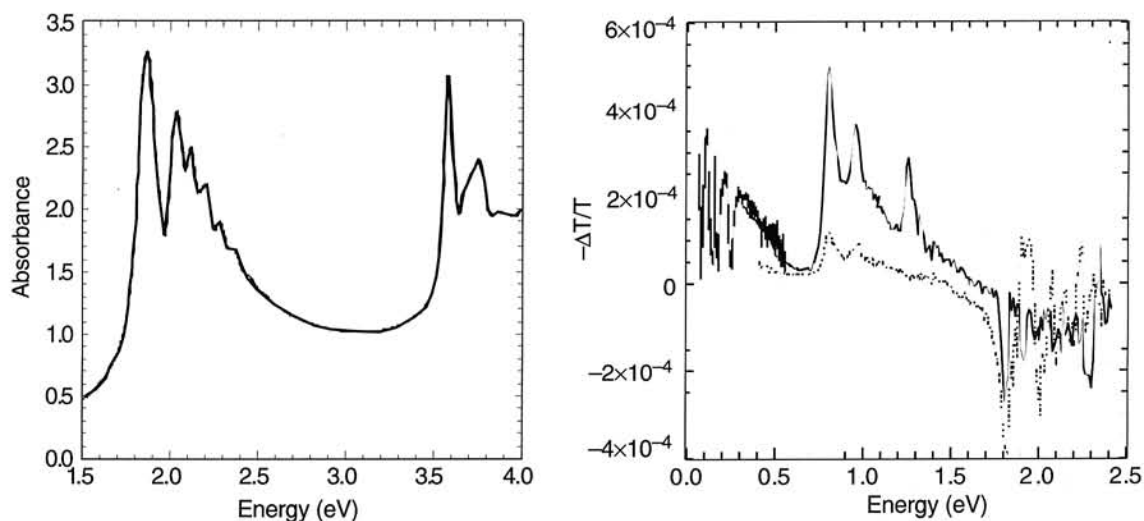


Fig. 3. Left: electronic absorption spectrum of polyDCHD. Right: PA spectrum of polyDCHD for in-phase (full line) and out-of-phase (dotted line) detection.

Figure 6 shows the electronic absorption of the red form of polyDCHD-S. When compared with the blue form, the spectra of the red form are indicative of a shorter effective conjugation length accompanied by a broadening of its distribution. The reduction of the effective conjugation length of the red form is also confirmed by the values of the Raman frequencies that are at higher wavenumbers with respect to those of the blue form. The PA spectrum of the red polymer shows only a PA signal at 1.4 eV. This band appears at about the same energy of the PA peak of the blue form but its shape is more asymmetrical, with no evident shoulder in its low-energy side. Moreover, unlike the blue polymers, no signals due to long-lived charged excitations could be detected here.

These results suggest that for red polyDCHD-S the formation of charged states is completely inhibited. This fact could be explained by the electron transfer mediated by interchain coupling and then strictly related to the overlap of the p_z orbitals of adjacent chains. Because the chain conformation of PDAs in the red phase is somewhat twisted from the planar conformation typical for the blue form (presumably due to the non perfect alignment of the side groups that reduces the long range interchain order) the already small overlap between the backbone orbitals of different chains is further reduced. The similarity of either the 1.4 eV signal of the red form and the 1.45 eV peak of the blue form allows to assign the 1.4 eV signal of the red form to a triplet-to-triplet transition, as already proposed for the 1.45 eV peak of the blue form.

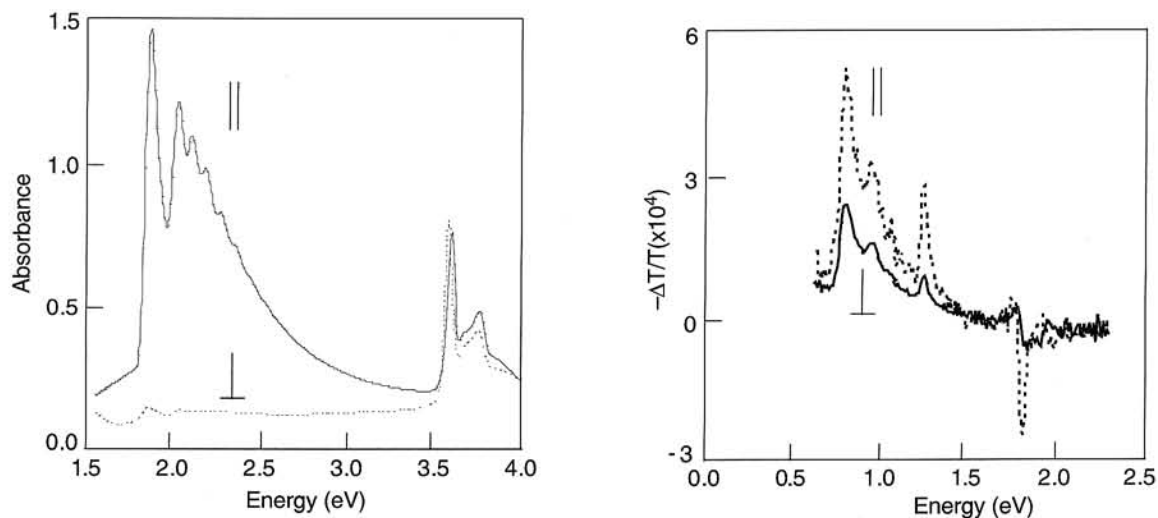


Fig. 4. Left: absorption spectrum of oriented polyDCHD for the electric field of the radiation parallel (||) and perpendicular (⊥) to the chain axis. Right: modulus of the PA spectrum of oriented polyDCHD with parallel (||, dotted line) and perpendicular (⊥, full line) pump polarization.

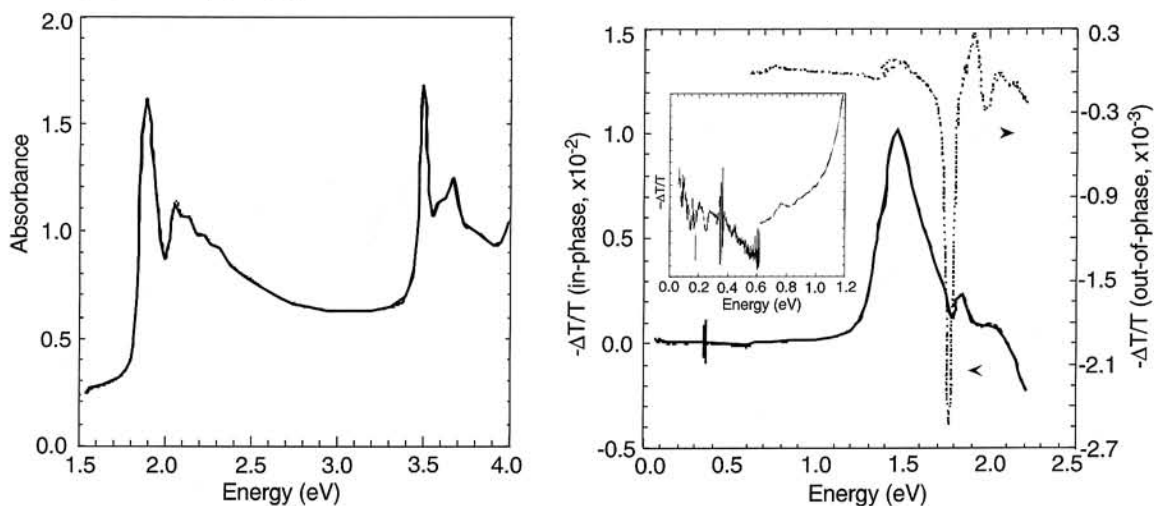


Fig. 5. Left: electronic absorption of blue polyDCHD-S. Right: in-phase (full line) and out-of-phase (dashed line) detection; inset: IRAV signals.

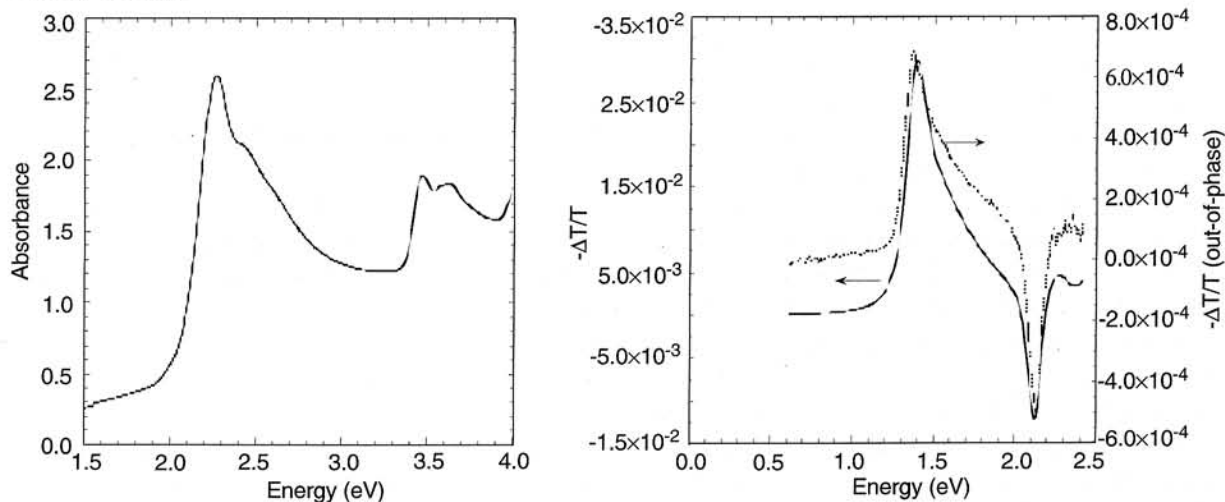


Fig. 6. Left: electronic absorption spectrum of red polyDCHD-S. Right: PA spectrum of red polyDCHD-S for in-phase (full line) and out-of-phase (dashed line) detection.

The similarity of the PA data for the blue and the red forms of polyDCHD-S clearly indicates that the conjugation length is not a unique parameter which determines spectral features and properties of the PA spectra. The main difference between the PA spectra of polyDCHD and polyDCHD-S is that in the former the blue form can accommodate an almost-free triplet photoexcitation, while in the latter the blue form (although with the same effective conjugation length) gives rise to a trapped exciton. The triplet excitons of the red forms are trapped for both polymers. The cause for the different behaviour of the blue form of the two polymers is most likely related to the supramolecular organisation that controls the extension of the triplet excitons, their dynamics and their interactions. The photoexcited triplets observed in the time scale region of the PA experiments are most likely trapped on the conformational defects. The depth of the traps depends on the difference between the configurational structure of the defect and the structure of the regular chain. Then, different depth of the traps in the two polymers could then be related to more relevant changes, required to accommodate the photoexcitations in the backbone of the polymer that exhibits larger substituents.

Figure 7 shows the polarized electronic absorption spectra of the film of oriented PDA-4BCMU. The component of the absorption spectrum parallel to the chain axis exhibits at 1.94 eV the excitonic absorption band followed by its vibronic progression. The component of the absorption spectrum perpendicular to the chain axis shows essentially the same features but with reduced intensity due to the misalignment of the crystallites in the film. The peak to peak anisotropy is about 4, indicating that a substantial degree of orientation is obtained with the growth technique used. Further information on the degree of chain order for this sample has been obtained by using nonlinear optical dichroism and X-ray texture studies [19]. In particular, a detailed knowledge of the chain orientation distribution has been provided by the angular variation of the intensity in third harmonic generation measurements with the incident light polarization parallel to the thin film surface (Fig. 8).

The photoinduced absorption spectra of PDA-4BCMU show three peaks at 0.82, 0.95 and 1.39 eV of comparable intensity (Fig. 9). The structure of these PA spectra is very similar to the previously reported for the blue form of PCzDAs previously discussed [12]. The comparative analysis among the PA spectra, here presented, suggests us to assign the PDA-4BCMU PA peaks at 0.82 and 0.95 eV (LE

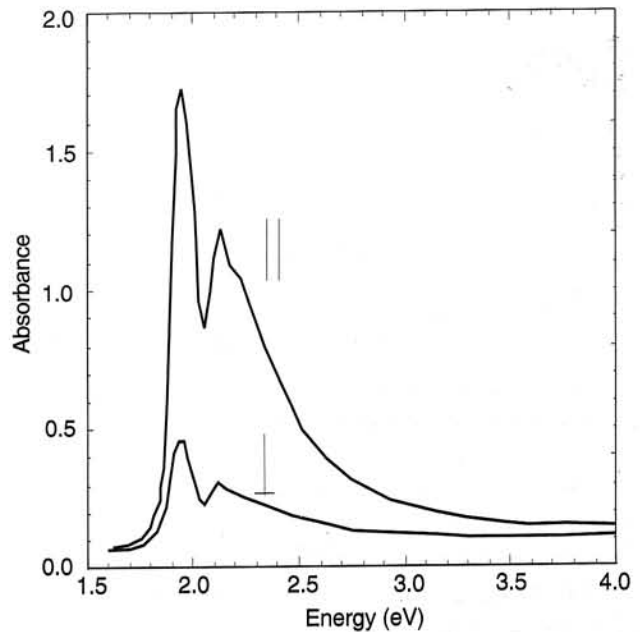


Fig. 7. Absorption spectrum of PDA-4BCMU for the electric field of the radiation parallel and perpendicular to the chain axis.

band) to photoexcited charged states (polarons or bipolarons) and the 1.39 eV peak (HE band) to a transition between photoexcited triplet excitonic states. This assignment has been substantiated by a detailed analysis of the dependence of the PA spectra on the experimental parameters [12].

The PA spectra, here reported, suggest us another interesting observation. The HE band, due to a triplet-to-triplet exciton transition, is located at 1.39 eV in the blue form of PDA-4BCMU, and is shifted to 1.5–1.6 eV [5,6,9–11] or to 1.7–1.8 eV [6] for the same polymer in the red or yellow forms, respectively. This energy shift could be related to the different conjugation length in the different forms as observed in controlled length oligothiophenes [23]. However, more interesting is the comparison with other PDAs. In polyDCHD we detected a triplet exciton transition at 1.26 eV and in its soluble derivative (polyDCHD-S) at 1.45 eV for the blue form and at 1.4 eV for the red form, thus, showing that the conjugation length is not the only parameter affecting the transition energy. It is possible that the nature and depth of the traps affect this energy but we cannot exclude that the detailed characteristic of the excited states of these polymers can be dependent on the nature of the side groups and on the supramolecular order. Models for the electronic states, concerning the conjugated skeleton alone, cannot be adequate for the description of these materials.

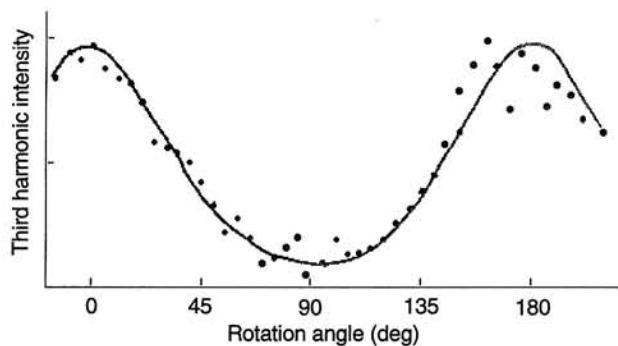


Fig. 8. Rotation angle dependence of third harmonic intensity for a PDA-4BMCU oriented thin film.

The most interesting features of the spectra, here reported, are the LE peaks of PDA-4BMCU. The comparison with the behaviour of the PA spectra of the PCzDAs, unambiguously assigns these peaks to photoexcited charged states. This is an absolutely new feature for PDA-4BMCU. Even though this polymer was greatly studied in the past, and in particular with ultrafast spectroscopes [5,6,9,11], which more directly probe the intrinsic photoexcited states, the PA spectrum of this polymer for probe energies between 0.5 and 1 eV was never reported. The experience gained in the study of PCzDAs suggests that charged states for the blue form of these polymers appear in this spectral region. The fact that no photoinduced charge transfer to C₆₀ was detected in PDA-4BMCU [11] as instead found for other conjugated polymers could be due to the use of the red form of the poly-

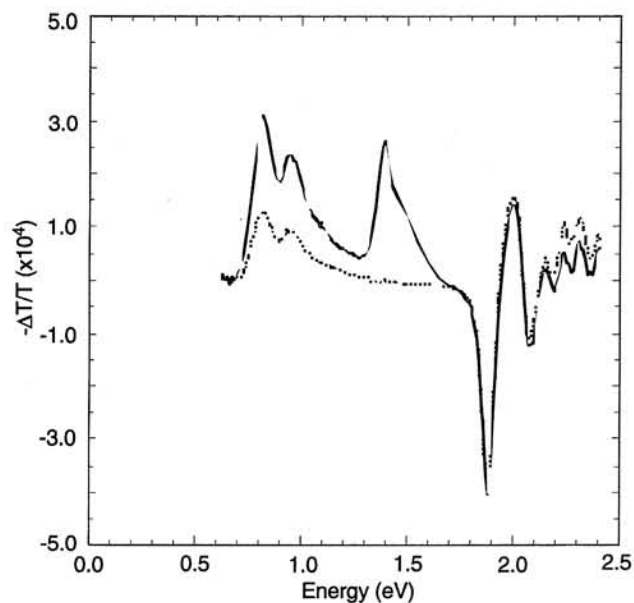


Fig. 9. PA spectrum of PDA-4BMCU for in-phase (full line) and out-of-phase (dashed line) detection. The pumping light is polarized parallel to the chain.

mer. Indeed, the red forms of PDAs do not give rise to photoexcited charged states, as demonstrated by their PA spectra where only triplet excitons are detected. We notice that instead in the blue forms of the same polymers also charged states (polarons or bipolarons) are observed. The fact that charged states are a quite general feature of blue PDAs open new possibilities for molecular engineering. In fact the electronic properties of blue PDAs can be modified to allow charge transfer process with other systems. This possibility is of great importance for realisation of photovoltaic devices because (joined with the great order and consequent high mobility of the carriers in blue PDAs) an increase in the energy conversion of these devices could be obtained.

Acknowledgements

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