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The photophysics of triplet excitons in substituted polycarbazolyldiacetylenes

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Abstract

Absorption and photoinduced absorption (PIA) spectra of thin films of polycarbazolyldiacetylenes carrying alkyl (polyDCHD-HS) or acyl (polyDPCHD) substitutions are reported. The absorption spectra are dominated by an excitonic absorption followed by a vibronic progression, and are quite insensitive to the temperature. The PIA spectra show the typical spectral feature of a triplet excitation whose rise and decay times are different. The PIA signal shows a strong sublinear pumping intensity dependence, which also affects the rise time.

Keywords: Photoinduced absorption; Polydiacetylenes; Triplet excitons

1. Introduction

Since several years, we have been interested in the preparation of diacetylenic monomers, their polymerization and in the study of the photophysical properties of the polymers, which are potentially suitable for photonic applications [1]. The non-linear optical properties depend on the nature of the electronic excited states, thus making a wide investigation of the spectroscopical and photophysical properties of these materials an important means in evaluating their possible performances [2]. Moreover, the photoinduced absorption (PIA) spectra of these materials are dominated by triplet excitons, which in turn are created by singlet fission taking place in few tenths of femtoseconds [3]. Since triplet excitons may play a major role in electroluminescent/electrophosphorescent devices, polydiacetylenes (PDAs) are good model systems to study the photophysics of conjugated polymers [4].

In this paper we report an extensive characterization of the optical and photophysical properties of the red form of polycarbazolyldiacetylenes carrying both alkyl (polyDCHD-HS) or acyl (polyDPCHD) substitutions in the 3,6 positions of the carbazolyl rings (see inset of Fig. 4 below). To this end, low temperature absorption and photoinduced absorption spectra are reported and discussed.

2. Experimental

DCHD-HS and DPCHD monomers are synthesized according to [5]. 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, the thin films of this material are spin cast directly from the monomer solution on glass or fused silica substrates, then thermally polymerized at 115 °C for several hours.

The absorption spectra are recorded with a double grating Varian mod. Cary 5E spectrophotometer equipped with a closed-cycle liquid helium cryostat. The long-lived photoinduced absorption spectra are recorded with a Bruker IFS 66/S step-scan FT-IR spectrometer equipped with silicon and InSb detectors and with an home-made liquid nitrogen cryostat. The photoexcitation is provided by the 532 nm line of a Suwtech DPGL-2200 Nd:YAG duplicated laser, and its modulation is obtained by an AA Opto-Electronics acusto-optical modulator mod. AA.MTS.110/A3-Vis. Continuous scans with light on and off are alternatively recorded and co-added for several cycles to provide a suitable signal-to-noise ratio (up to 10,000 total dark and light scans), with a resulting 8 cm^{-1} resolution. The transmittance spectra with light on and off are then used to numerically obtain the $-\Delta T/T$ photoinduced absorption spectra. Time resolved photoinduced absorption spectra with 64 cm^{-1} spectral resolution are recorded with the step-scan option of the spectrometer employing the internal 16 bit ADC for fast data acquisition.

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3. Results and discussion

In Fig. 1 the 80 K absorption spectra of thin polyDPCHD and polyDCHD-HS films are reported and compared. The purely electronic transition is located at 2.34 eV (2.29 eV) for polyDCHD-HS (polyDPCHD). The excitonic transition in polyDCHD-HS is much broader than that in polyDPCHD due to a wider distribution of conjugation lengths. This inhomogeneous broadening partially masks the spectral resolution of the vibronic progression. In fact, in polyDPCHD two vibronic replicas (at 2.47 and 2.55 eV) due to the CC double and triple bond stretchings are observed, while in polyDCHD-HS only one broad replica (at 2.49 eV) is detected. In spite of the better resolution of the vibronic progression in polyDPCHD with respect to polyDCHD-HS, the intensity of the electron–phonon coupling appears larger in the alkyl-substituted polymer, as clearly indicated by the ratio between the purely excitonic and the 0–1 bands. As previously pointed out, the relatively low intensity of the vibronic progression in polyDPCHD allows for an investigation of minor details in its absorption spectrum such as the very weak band at 2.74 eV, which could be assigned to the second mode of a string vibration [6]. It is also interesting to note that the comparison between the spectra here reported and those at room temperature [5,6] shows an almost negligible temperature dependence of the spectral position, which indicates an hindered chain conformation. A further difference between the two polymers is in the shape of their absorption spectra. In polyDPCHD the latter is strongly dependent on the preparation and thickness of the film [6], while this is not the case for polyDCHD-HS where the thickness simply affects intensity without any shape modification. This fact is probably related to the different substituents carried by the carbazolyl groups in the two polymers as it is also suggested by the strong difference of the absorption spectra in the spectral region of the carbazolyl group (above 3.4 eV).

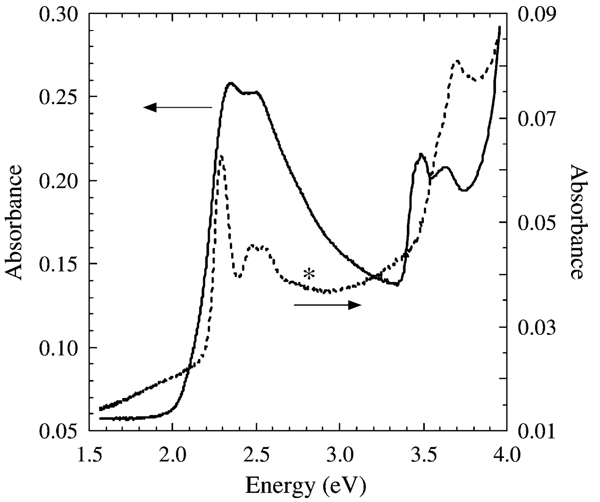

Fig. 1. A 80 K electronic absorption spectra of thin films of polyDCHD-HS (full line) and polyDPCHD (dashed line). The asterisk marks the small feature described in the text.

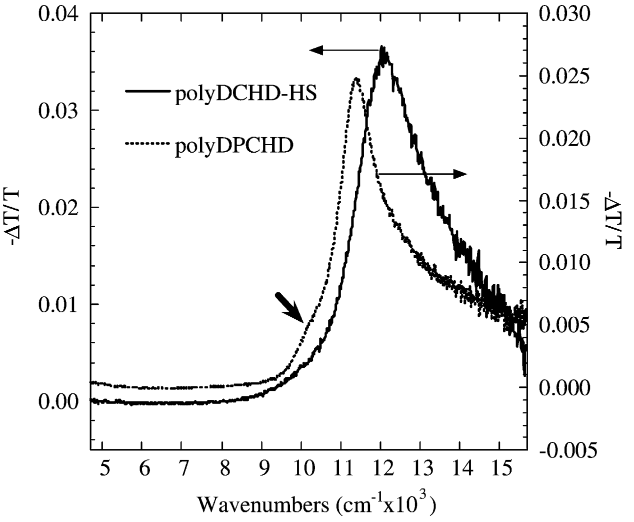

Fig. 2. Steady-state photoinduced absorption at 80 K of polyDCHD-HS (full line) and polyDPCHD (dashed line). The bolded arrow indicates the shoulder whose intensity depends on the degree of irradiation and/or damaging.

We are currently carrying out an AFM study to investigate the possible existence of morphological differences in the films of the two materials.

In view of the possible application of these polymers in photonic devices working under intense light flux, a careful characterization of their photochemical and photophysical properties has been carried out. The photo-damaging and photo-patterning of polyDCHD-HS and polyDPCHD under UV-lamp illumination has been previously reported [7] and suggests that a great care must be used in studying their properties. Moreover, photophysical studies are further stimulated by the promising values of their third-order susceptibilities [1,8]. In this respect we recall that the dominant photoexcitation of the red phase polydiacetylene is the triplet exciton [6].

The steady-state photoinduced absorption spectra of the two polymers are reported in Fig. 2. In a thin film of polyDPCHD a sharp PIA band is observed at about 11,300 cm^{-1} (1.40 eV), with an additional shoulder at 10,000 cm^{-1} (1.24 eV) whose intensity has been previously shown to depend on the sample thickness and irradiation [6] In polyDCHD-HS the PIA spectrum shows only a band at 11,700 cm^{-1} (1.45 eV) independent on the film thickness. We notice that under intense and continuous illumination with the green laser the PIA spectrum of polyDCHD-HS evolves towards a more complicated shape, with an overall intensity reduction and the appearance of a shoulder in the 10,000–11,000 cm^{-1} spectral range, similar to that observed in polyDPCHD. The characterization of this process, as well as the study of the damaging of this polymer after irradiation with the 532 nm laser will be reported in a forthcoming publication [9].

The PIA bands recorded for the two polymers are assigned to the triplet-to-triplet transition typical of PDAs. Their

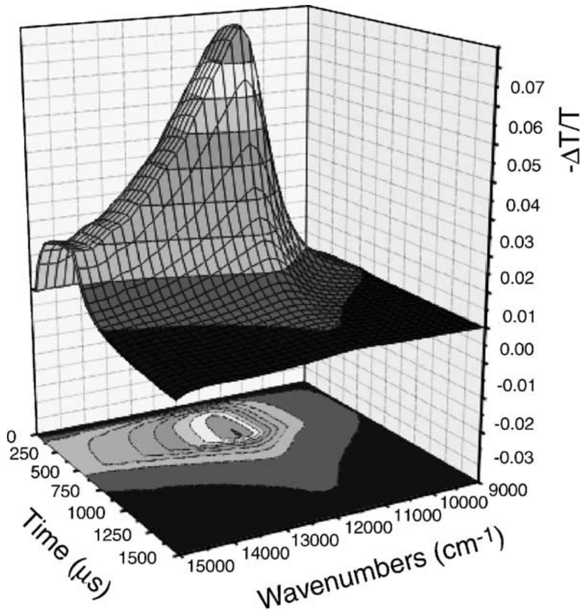

Fig. 3. Three-dimensional plot of photoinduced absorption vs. time and wavenumbers for polyDCHD-HS. At the bottom, the corresponding contour plot points out the temporal evolution of the triplet state.

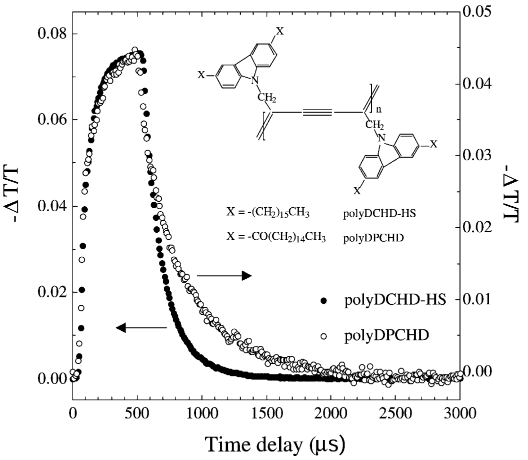

Fig. 4. Rise and decay of the photoinduced peak signal for polyDCHD-HS and polyDPCHD. In the inset, the chemical structure of the two polymers is reported.

dynamics can be investigated with the step-scan option of the Fourier Transform instrumentation, which also allows the simultaneous detection of the time evolution of the PIA spectrum in the μs domain. The three-dimensional plot in Fig. 3 shows the μs PIA spectrum for polyDCHD-HS with its temporal evolution as measured upon a 750 μs pumping time. 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 which correspond to different intensity of the PIA signal are displayed. These results indicate that the PIA spectrum of polyDCHD-HS has no structure and that its intensity shows saturation effects versus pumping time. In fact, no variation of the spectral shape is observed by slicing the plot along the time axis, and the same time dependence is observed in the different slices. Moreover, the intensity dependence of the peak in the PIA spectrum follows a strongly sublinear law ($I^{0.3}$) as also previously observed for polyDPCHD [6]. To better investigate the dynamics of the two polymers, we report in Fig. 4 a typical slice displaying their rise and decay curves as measured at their PIA spectral peaks. It is apparent that the decay times for the triplet signals of the two polymers are very different, the longer one being observed for the acyl-substituted polycarbazolyldiacetylene. Moreover, the rise and decay lifetimes are different, indicating that a simple monomolecular kinetics cannot be responsible for the observed behaviour, as also suggested by the sublinear intensity dependence. However, the fitting with a single exponential function of the data recorded at various pumping powers for the rise and decay processes separately provides some preliminary information. In the available range of laser power (2.5–60 mW), the rise (decay) time for polyDCHD-HS ranges between 110 and 180 μs (70–113 μs), the corresponding values for polyDPCHD being 310–360 μs (60–130 μs). To explain the difference in the rise and decay times we are currently working out a model which includes an additional decay pathway, which is active only under illumination and is related to the presence of traps. This model, which has been successfully used to study the kinetics of polarons in blue phase PDAs [10], predicts the traps to be responsible for the saturation of the signal, which causes the $I^{0.3}$ intensity dependence [6].

The preliminary data here reported indicate that even in the red and more stable form polycarbazolyldiacetylenes show unusual behaviours that strongly affect their photophysical properties, and which have to be considered when these materials are used for photonic applications.

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