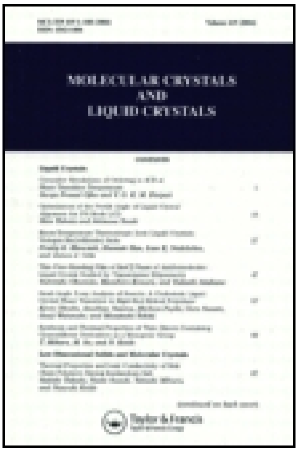

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Polydiacetylene Chains Diluted in Their Single Crystal Monomer Matrix: Towards the Isolated Conjugated Chain

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Version of record first published: 04 Oct 2006.

To cite this article: C. Lapersonne-meyer , J. Berréhar , M. Schott & S. Spagnoli (1994): Polydiacetylene Chains Diluted in Their Single Crystal Monomer Matrix: Towards the Isolated Conjugated Chain, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 256:1, 423-430

To link to this article: http://dx.doi.org/10.1080/10587259408039272

Mol. Cryst. Liq. Cryst. 1994, Vol. 256, pp. 423–430
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POLYDIACETYLENE CHAINS DILUTED IN THEIR SINGLE CRYSTAL MONOMER MATRIX: TOWARDS THE ISOLATED CONJUGATED CHAIN

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Abstract : Absorption, fluorescence and resonant Raman spectra at 2 or 5 K of polydiacetylene poly4BCMU chains diluted in their single crystal monomer matrix are studied, and discussed in terms of the single conjugated polymer chain electronic properties. Two new electronic transitions are observed below the intense exciton one. Absorption lines are very narrow (≤ 30 cm^{-1} hwhm).
Fluorescence is dominated by emission from the intense exciton state and its origin coincides with that of the absorption. Emission from the two other levels is also detected.

1. INTRODUCTION

Polydiacetylenes (PDAs) are good model systems for the study of conjugated polymers, since they can be obtained as macroscopic single crystals by solid-state topochemical polymerization of the corresponding diacetylene (DA) monomer crystal [1,2]. In crystals where the polymer content x is very low, polymer chains are expected to be very weakly interacting; such a crystal may then be a good approximation of isolated conjugated chains all having the same geometry. This is the motivation for our study.

For this purpose, we have chosen the DA known as 4BCMU (R-C≡C-C≡C-R, with R: $(CH_2)_4$-OCO-$NHCH_2$-COO-C_4H_9). This DA shows no significant thermal polymerization, so the polymer content in a crystal stays constant over time. It can be totally polymerized by γ-rays and it is known that polymer chains grow to very long length (1 to 10 μm), even at low polymer contents [3]. The monomer crystal shows no absorption up to 30000 cm^{-1} (3.7 eV), and any visible absorption is that of the polymer present in the crystal. The room temperature absorption spectra of polymer chains diluted in the monomer and of the bulk polymer are identical: chain absorption peaks at ν_0 = 15900 cm^{-1} (1.97 eV) with hwhm Γ_0 = 380 cm^{-1} and the dichroïc ratio is 120±20 [4]. Isolated chains are then representative of those of the bulk polymer (this is not the case for instance for the well-studied PDA known as pTS [5]).

This study mainly concerns monomer crystals in which the spectroscopically measured polymer content is $\lesssim 3\ 10^{-4}$ in weight. In a separate paper [4], it was shown that the polymer exciton energy and the $\nu_{C=C}$ stretch Raman frequency decrease considerably as temperature decreases. Two first order structural transitions of the monomer crystal show up as discontinuities in the chain spectroscopic properties near 320 and 220 K. So, these chains behave as probes of the monomer structural changes. We present and discuss here further results on low temperature spectroscopic properties of these chains.

2. LOW-TEMPERATURE ABSORPTION SPECTRUM

An absorption spectrum taken at 5K for light polarized parallel to the polymer chains is presented in Fig. 1. It shows:

- an intense narrow exciton line ν_0 at 14580 cm^{-1} (1.81 eV) implying very low energy dispersion, if any, of the chain electronic transition. A homogeneously broadened line of that width corresponds to a lifetime of ~ 175 fsec, which is therefore the lowest limit for the unrelaxed exciton lifetime.
- two weak narrow lines ν_a and ν_b, 220 and 590 cm^{-1} (27 and 73 meV) below the main exciton line respectively. They are ~30 times less intense than the main line in all studied samples. This means either that a single chain presents several electronic transitions or that there are three chain populations each with a well-defined conformation.
- several other lines which can be assigned to vibronic states of the exciton.

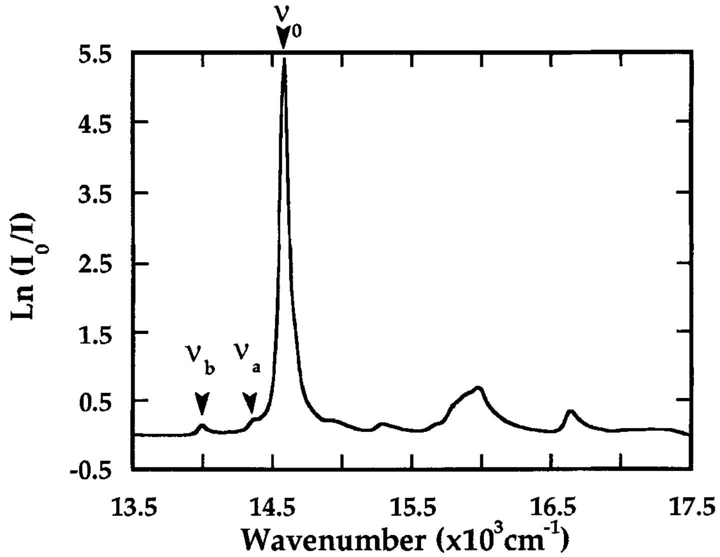

Figure 1 : Optical density at 5K of polymer chains in a 100 μm thick 4BCMU monomer crystal (x=0.03%)

The same kind of spectrum is obtained for 3BCMU - a DA with side groups differing from those of 4BCMU by the presence of $(CH_2)_3$ instead of $(CH_2)_4$ near the polymer chain - i.e. two weak narrow lines 550 and 700 cm^{-1} below the main exciton line at 15340 cm^{-1} or 1.90 eV (Figure 2). This indicates that these features are not specific to 4BCMU.

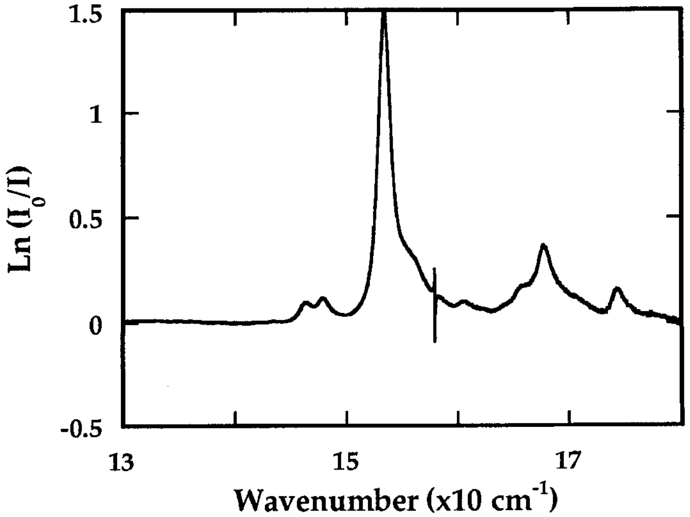

Figure 2 : Optical density at 5K of polymer chains in a 56 μm thick 3BCMU monomer crystal (x=0.01%)

3. LOW TEMPERATURE FLUORESCENCE

Fluorescence is absent or extremely weak at room temperature. Figure 3 shows an emission spectrum at 2K, excited at 514,5 nm (19430 cm^{-1} or 2.41 eV), far above the absorption energy, to minimize the overlapping of Raman spectrum, leaving only third or higher order overtones and combinations as possible contributions. It was checked that the emission spectrum is not specific of this excitation range.

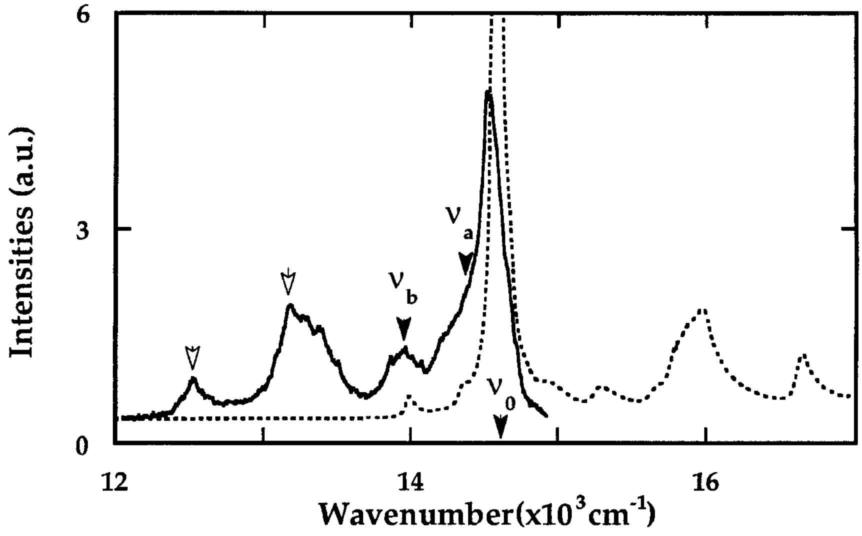

Figure 3 : Emission spectrum at 2K of polymer chains in a 4BCMU monomer crystal excited at 514.5 nm (full line). (dotted line : corresponding absorption spectrum)

This spectrum looks like the mirror image of the absorption spectrum shown in Fig. 1, except for the main line which is weakened and distorted by reabsorption. The emission origin energy was estimated as follows: the vibronic lines corresponding to one C=C or one C≡C stretch quantum are observed in Fig. 3 (see arrows) at 13180±10 cm^{-1} (1.634 eV) and 12530±10 cm^{-1} (1.553 eV) respectively. The corresponding ground state vibration frequencies known from the Raman spectrum were added, leading to an origin energy of 14600±20 cm^{-1}, equal to the main exciton energy ν_0 to the accuracy of this determination. This spectrum is dominated by the main exciton emission with its corresponding vibronic lines.

The question arises of a possible emission from the two lower energy levels ν_a and ν_b. Upon excitation at 14000 or 14360 cm^{-1}, a weak emission is observed extending ~150 cm^{-1} below excitation, suggesting that there is indeed fluorescence emission from these two states.

A determination of the fluorescence decay time was attempted using 20 ps pulses at 15300 or 15980 cm^{-1}, choosing an emission wavenumber out of any Raman line. A slight broadening of the corresponding emission pulses is observed, showing that the emission decay time is a few ps at most. A convolution of the instrumental function by a single exponential leads to an estimated lifetime of 1.5 ps. However, this value should be taken as an order of magnitude only. Subpicosecond time-resolved fluorescence study is in progress.

4. LOW TEMPERATURE RESONANCE RAMAN SPECTROSCOPY

We report here preliminary results. The RRS spectra at 2 K show much more lines than usual in PDAs especially in the low frequency region <400 cm^{-1} [6]. In this paper, only the regions around 1450 cm^{-1} (C=C stretch) and 2100 cm^{-1} (C≡C stretch) will be discussed. In each region up to five lines are observed. The respective excitation spectra of these five lines were studied between 13850 and 14700 cm^{-1}, i.e. in the region of the three electronic transitions (see Fig. 1). The excitation frequencies ν_{max} at which each Raman line has a maximum intensity are given in Table I.

ν_{max} (cm^{-1})	$\nu_{C=C}$ (cm^{-1})		$\nu_{C\equiv C}$ (cm^{-1})	
14600 ($\approx\nu_0$)	1420	(23)	2066	(20)
	1427	(100)	2076	(100)
	1451	(4)	2105	(4)
14000 ($\approx\nu_a$)	1435		2088	
14500		(8)		(8)
14350 ($\approx\nu_b$)	1441		2096	
14600		(4)		(3)

TABLE I : Frequencies ν_{max} at the maxima of excitation spectra for each observed Raman line in the $\nu_{C=C}$ and $\nu_{C\equiv C}$ regions. Relative intensities at 14600 cm^{-1} are indicated in brackets.

To each $\nu_{C=C}$ line corresponds a $\nu_{C\equiv C}$ one with the same excitation spectrum. In all excitation spectra, there is a maximum at ν_0 except for the pair 1435-2088 cm^{-1}, for which the maximum is near 14500 cm^{-1} rather than at ν_0. Batchelder and Bloor [6] invoked a Fermi resonance to explain a line splitting in the $\nu_{C=C}$ region, but the identity of the patterns observed for both $\nu_{C=C}$ and $\nu_{C\equiv C}$ ranges excludes such an explanation here.

5. DISCUSSION

The present study has shown that three nearby electronic states are observed, leading to one very intense absorption (at ν_0) and two weak ones. Fluorescence originates mainly from ν_0.

The positions and intensities of the two weak absorption lines ν_a and ν_b, relative to the main absorption ν_0 are the same for all monomer crystals studied. We have also studied crystals containing up to a few percent polymer content with no significant changes in these relative positions and intensities. Interchain interactions cannot therefore be invoked to account for ν_a and ν_b. These observations are also against the existence of three chain populations with different conformations since their relative concentrations should then be the same in all samples. This suggests that one is dealing with three electronic transitions of the same chain.

Another fact in favor of this hypothesis is that, as mentioned above, 3BCMU shows three very similar transitions: the 3BCMU and 4BCMU polymer chains seem to have very similar electronic properties although their surrounding matrices are different. For instance, as shown in Fig. 4, the temperature dependences of the polymer absorption, and the monomer phase transitions are not the same. The monomer crystal structures, as far as they are known, are also different.

If, in the 4BCMU crystal, all polymer chains are equivalent with the same electronic transitions, the usual assumption that the 1-D unit cell of PDA chains contains a single C_4 repeat unit may not be valid here. Each electronic or vibrational transition would then be split into two or more states leading to separate absorption or Raman lines of different intensities if respective symmetries are different. For instance, the two weak absorption lines might correspond to the splitting of an A_g state. Such a state has been reported in a diacetylene oligomer [7]. To go further into the interpretation of absorption and resonance Raman data together, more work is in progress.

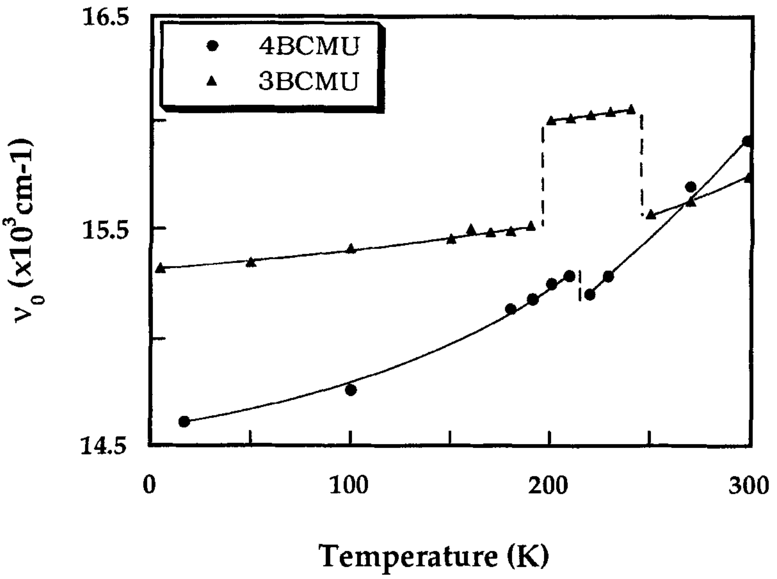

Figure 4: Temperature dependences of the peak absorption energy of 3BCMU and 4BCMU polymer chains in their respective monomer matrix (lines are guides for the eye).

The exciton fluorescence decay time is not longer than a few psec. The room temperature exciton lifetime of an isolated chain is not known, but a lifetime $\lesssim$ 2 psec (attributed to a self-trapped exciton [8]) has been measured in the non fluorescent bulk polymer [8-11]. This suggests that the observation of chain fluorescence at 2 K is not associated to a lengthening of the non radiative exciton decay time, which indeed does not increase in the bulk polymer at low T [8,12]. Subpicosecond study of fluorescence decay should bring information about the excited states relaxation to be discussed in comparison with previous results on bulk polydiacetylenes.

In conclusion, it should be stressed that in the system studied here, chains are isolated in the sense that interchain interaction is minimized, but these chains are still within the periodic potential of the surrounding monomer crystal which influences the chain conformation and properties.

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