Temperature dependence of spectroscopic properties of isolated polydiacetylene chains strained by their monomer single crystal matrix

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Abstract

The temperature dependence of exciton absorption and Raman frequencies of polydiacetylene (PDA) isolated chains is studied for 3BCMU and 4BCMU chains dispersed in their respective monomer crystal matrix. While isolated 3BCMU chains are practically unstrained, and behave as typical high quality bulk PDA, isolated 4BCMU chains are under a compression that increases as T decreases and show a very different behaviour. A simple model of chain deformation and its effect on the exciton energy is proposed, which qualitatively accounts for all the results.
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1. Introduction

The great sensitivity of optical properties to conformational changes is a pervading issue in the field of conjugated polymers. There is a need for model systems in which all chains in the sample have the same conformation, and in which the conformation can be modified in a controlled way. Polydiacetylenes (PDA) provide such a model system. Their general formula is $=(R–C–C\equiv C–C–R')_n=$ where R and R' are side groups, which may be different or identical, and may have very diverse chemical formulae. For several PDA, a polymer single crystal can be obtained by polymerization of a single crystal of the corresponding diacetylene (DA) monomer [1]. The initiation reaction is homogeneous and the transformation proceeds via a continuous series of monomer–polymer solid solutions with increasing polymer content.

In the present work, two DA known as 3BCMU and 4BCMU are studied. Their side-group formula is $R = R' = –(CH_2)_n–OCONH–CH_2–COOC_4H_9$ with $n = 3$ or 4 for 3BCMU and 4BCMU, respectively. These materials readily polymerize upon irradiation with UV, X or γ-ray photons, but show no significant thermal polymerization, so a small and constant chain concentration can be created and kept almost indefinitely. Polydiacetylenes show two different electronic structures, called "blue" and "red" [2]. In 4BCMU monomer all chains are blue, and in 3BCMU less than 10^{-3} of the chains are red. This work deals exclusively with blue chains. The first polymer chains formed at early stages of polymerization are individually dispersed in the monomer crystal matrix. They all have the same geometry and are embedded in the same periodic potential imposed by the matrix. In 3 and 4BCMU this is manifested by the small inhomogeneous broadening of absorption and emission lines, which are very narrow at low temperature [3,4]. These chains may be very long: an average length of 6 μm has been measured for monomer crystals of 4 and 3BCMU [5]. The ensemble of chains in a monomer single crystal thus provides a very well ordered

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state, which may even be better ordered than the corresponding pure polymer crystal.

Since the polymer chains show strong absorption in the visible range, with a maximum absorption coefficient for light polarized parallel to the chain direction $\alpha_{max} \sim 7 \times 10^5 \, cm^{-1}$ to $10^6 \, cm^{-1}$ at 300 K [6], whereas the monomer is transparent up to $v = 3.55 \times 10^4 \, cm^{-1}$ or 4.4 eV (Fig. 1), the chain spectroscopic properties can be studied down to very low polymer content, below 10^{-5} in weight. At such dilutions, the average distance between chains is larger than 100 nm, so there is essentially no electronic interaction between them. This system has been used as a good model for the study of electronic properties of conjugated polymers, since it is up to now the experimental system closest to theoretical models, and it has been shown that such isolated chains behave at low temperature as quasi perfect quantum wires [2–4,7–15].

It may also be a good model system for studying the effect of a controlled deformation of the chain on the electronic properties of a conjugated polymer. In fact, it will be shown below that in this system, chain geometries not otherwise accessible are present.

In the case of chains dispersed in their monomer crystal, the repeat distance along the chain is dependent of the surrounding matrix unit cell parameters, so it can be varied in a controlled way by varying the temperature, 3BCMU and 4BCMU are studied here in that way.

The temperature dependence of absorption and resonance Raman spectra of polymer chains diluted in the monomer crystal are studied to probe the effect of known strains. The wavelength of maximum absorption gives the T dependence of the exciton energy, thus information on the effect of conformation on electronic structure. The resonance Raman spectrum yields the frequencies of phonon modes most strongly coupled to the π electrons, thus information on the ground state geometry.

These two monomers were studied because they have quite different behaviour as far as their crystalline structure is concerned [16]. In 3BCMU monomer crystal, the parameter corresponding to the chain direction is always close to the relaxed polymer value, the difference being less than 0.5% at all temperatures. In 4BCMU, the chains are already under $\sim$1% compression at 300 K, and the strain increases steadily up to $\sim$3% at 15 K.

In all experiments the content of the polymer chains embedded in the monomer matrix is kept very low (less than 10^{-4} in weight). the polymerization process is studied elsewhere [17].

The paper is organized as follows: experimental methods are presented in Section 2, spectroscopic properties (absorption, Raman) and a comparison between isolated chain and bulk PDA in Section 3, while Section 4 is devoted to the discussion, and a model of chain geometry changes under compression is proposed to explain the red shift of the exciton energy.

2. Experimental

2.1. Absorption

A CARY 2300 double beam spectrometer equipped with polarizers is used, in the UV–visible range.

2.2. Raman

Excitation was produced by an Argon laser (Coherent Innova 90) pumping a dye laser (Coherent CR99) using Rhodamine 6G, Rhodamine 110 and DCM dyes. A continuous range of wavelengths from 560 to 680 nm is obtained. Below 560 nm the green lines of the Argon laser are used. The signal is dispersed in a double monochromator (Jobin Yvon Ramanor U1000) and detected by a cooled RCA C31034 photomultiplier. The obtained spectral resolution is 2 cm^{-1}.

2.3. Temperature variation

A circulating helium gas cryostat, stable to ± 1 K between 10 K and room temperature, can be adapted on both experiments.

3. Results and discussion

The exciton energy E_0 and the Raman frequencies vary with T quite differently in the two materials. These variations will be discussed in light of the structural changes described in [16].

3.1. Deformations of the chains with temperature

Characterizing the strain of the chain in the monomer matrix by the difference between the monomer and relaxed polymer repeat distances d_m and d_p in the chain direction
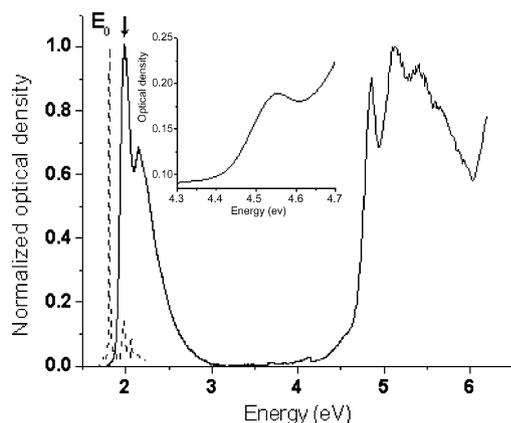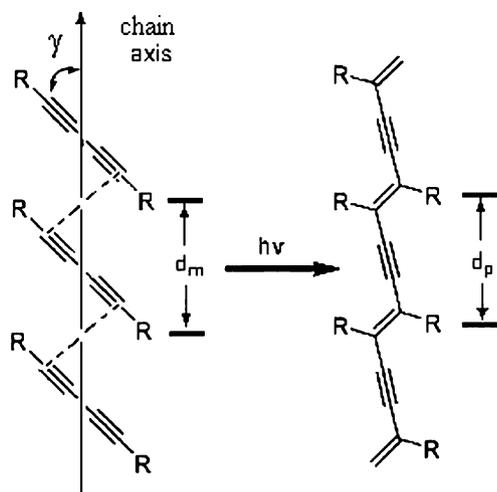

Fig. 1. Composite absorption spectrum of 4BCMU at room temperature: pure monomer spectrum for $E > 3.5$ eV, unpolarized light; The isolated chain absorption was recorded with light polarized parallel to the chains (solid line at 300 K, dashed line at 15 K), and that of the polymer on a 30 μm thick crystal with light polarized perpendicular to the chain direction. Spectra normalized separately.

Scheme 1. Topochemical polymerization.

(Scheme 1) may be intuitive, but it implicitly assumes that the isolated chain under stress in the monomer matrix keeps everywhere the monomer crystal periodicity. This is not obvious: the strain produced by an inclusion in a solid with different stiffness is shared between the inclusion and the matrix [18]. However, it has been shown in the case of another DA, pTS, that the periodicity of the isolated chain is that of the surrounding monomer matrix [19,20]. This may be related to the fact that the side-groups, which are the same for monomer and polymer, are much bulkier than the chains themselves [21]. The structural effect of polymer chains is to change continuously the lattice parameters of the monomer–polymer solid solution as the polymer content increases, the matrix and the chains sharing the same parameters.

Indirect evidence that this is also true in 3BCMU and 4BCMU is given by the absorption spectra of isolated chains. The experimental linewidths of the exciton absorption line near 10 K are 68 cm^{-1} (8.4 meV) in 3BCMU and 77 cm^{-1} (9.5 meV) in 4BCMU [9]. Since the exciton lifetime is very short, 135 fs in 3BCMU and 130 fs in 4BCMU [9], the homogeneous linewidth is at least 30 cm^{-1} (3.7 meV), so the inhomogeneous broadening is of the order of a few meV. Moreover, there is only a very small increase of these linewidths up to at least 5% polymer content [22]. This means that chains do not generate large stress in the monomer matrix. If the chains were not in register with the matrix, each chain end would generate a long range inhomogeneous strain field. Hence the chains have the same repeat unit length as the matrix. Both materials have comparable linewidths, and this is true at all temperature up to 150 K [9]. On the other hand their values of $d_m - d_p$ are very different (see below), and that of 4BCMU is temperature dependent. This further shows that the stress field due to the chains is not the cause of the inhomogeneous broadening.

The inhomogeneous broadening can be due to slightly different environment of the chains or in different part of

one chain. The weakness of the broadening shows that both effects are small. The chains are homogeneously deformed. Moreover, in both 3 and 4BCMU the spectroscopic properties variations are reversible after a complete temperature cycle. The studied deformations are elastics.

Above 200 K, the linewidth in 3BCMU keeps increasing slowly, but in 4BCMU it starts increasing rapidly, particularly above room temperature (see Fig. 3.12 of Ref. [2a]).

We conclude that in 3BCMU at all temperatures, and in 4BCMU up to 150 K at least, the chain is in register with the monomer lattice. In this discussion, a common value $d_p = 4.88$ Å is chosen as repeat distance, for both bulk polymers at 300 K. This value is measured in poly-4BCMU at room T [23], and is close to those found in all other PDA crystals [24,25]. Its temperature dependence is not known for the materials studied here, and there is indeed very little experimental information for any PDA.

The linear polymer thermal expansion coefficient is found to be very small, of the order of 10^{-6} K^{-1} [26–28]. This quasi constancy might result from two opposing trends: positive thermal expansion of the crystal as a whole and negative thermal expansion of the covalent chain [29]. Thus, for lack of better information, a temperature independent $d_p = 4.88$ Å will be assumed for both materials.

The situations in the two materials are contrasted. In 3BCMU, $d_m = b$ is never very different from d_p. At 270 K, $d_m - d_p = \Delta b = 0.003$ Å $\approx 6 \times 10^{-4}$ d_p; at 154 K $d_m \approx 4.87$ Å, $\Delta b \approx 0.01$ Å $\approx 2 \times 10^{-3}$ d_p; at 110 K, $\Delta b = 0.02 \pm 0.008$ Å $\approx 4 \times 10^{-3}$ d_p. In 4BCMU at 296 K, $d_m - d_p = \Delta c = 0.067$ Å $\approx 1.4\%$, and at 15 K $\Delta c = 0.16$ Å $\approx 3.3\%$ [16]. In summary, while the strain of 3BCMU chains remains small at all temperatures, it is always large in 4BCMU and increases, furthermore, with decreasing temperature. For comparison, the maximum elongation achieved by stretching a bulk PDA whisker crystal was 3%, beyond which plastic deformation and failure occurred [30].

We are thus dealing here with two quite different situations.

3.2. Absorption spectra

Typicals 4BCMU absorption spectra at 300 K and 15 K are shown in Fig. 1. 3BCMU absorption spectra are very similar [2–4].

The exciton optical transition energy E_0 of an isolated conjugated polymer linear chain in a crystalline matrix can be written [31]:

$$E_0 = E_b - W$$

E_b is the 'bare chain' exciton energy for a perfectly regular chain in vacuum having the same geometry as the chain in the crystalline matrix considered. W is the dispersion correction of the exciton state transition energy, due to van der Waals interactions between the chain and the surrounding medium. This term is different for monomer and polymer matrices as discussed in Section 3.4.1. If the unit

cell contains two or more units, that are not translationally equivalent but are related by another symmetry operation of the space group, a third term due to their interaction has to be added to the above equation, the so-called Davydov splitting D. It does not appear in the case of isolated chains, but might have to be considered for a bulk polymer crystal. The fact that the exciton states form a band and not a level [13] is not considered here, since we are only interested in the optically allowed transition at $k \approx 0$. Theoretical calculations usually concern E_b, while experiments give E_0.

There are two possible sources of variation of E_0 with T:

- the strain produces a change in the chain geometry, and this will affect E_b;
- the polarization correction W changes because the polarizabilities vary. The matrix contracts upon cooling, so the mean electron density and the dielectric constant increase, so W would increase and E_0 decrease as the matrix contracts [32]. On the other hand, if the chain geometry changes, the chain polarizability changes too.

3.2.1. 3BCMU

The variation of E_0 with T for isolated 3BCMU chains is shown on Fig. 2. It is small and continuous from 1.95 eV at 300 K to 1.90 eV at 2 K, with a narrow flat region at 160 K in the vicinity of a first order phase transition [16]. This cannot be compared to bulk 3BCMU polymer data, since the bulk monomer crystal does not polymerize completely by γ-irradiation [33]; however, thin (150–400 nm) single crystal polymer films have been prepared by epitaxial polymerization of the surface region of a monomer crystal [34]. In such films E_0 is about 1.96 eV at 300 K and 1.90 eV at 11 K. The 60 meV shift is typical of what is observed in the few PDA bulk crystals where it has been studied; for instance in poly-DCH E_0 decreases from 1.919 eV at 300 K [35] to 1.856 eV at 8 K [36]. The measured energy
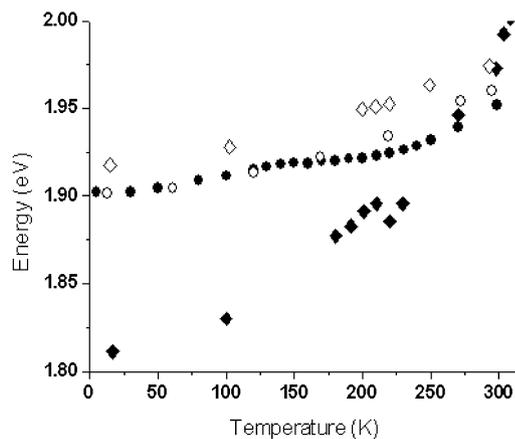

Fig. 2. Temperature dependence of the exciton energy E_0 of isolated polymer chains in the monomer crystal 4BCMU (solid diamonds) and 3BCMU (solid circles), of a thin 3BCMU polymer film (open circles) and of a bulk 4BCMU polymer crystal (open diamonds).

difference between isolated chain and bulk polymer exciton energies remains always $\leqslant 10$ meV.

The absence of any significant change of the chain repeat unit length suggests that the chain geometry does not depend on T, in which case neither E_b nor the chain polarizability should vary. The observed changes may then be ascribed to changes in the matrix dielectric constant, corresponding to a smooth 4% decrease in unit cell volume between 270 and 93 K. This is a consequence of an overall lateral contraction with a significant contribution of increased packing density of the side groups [16].

3.2.2. 4BCMU

The temperature dependences of the absorption peak energy E_0 of the bulk polymer crystal and of isolated polymer chains in the monomer crystal ($x_p \approx 10^{-4}$) are compared on Fig. 2 (see Ref. [3]).

For isolated chains, there is a very large continuous red shift of E_0 with decreasing temperature, from 2.07 eV ($v_0 = 16,700$ cm^{-1}) at 330 K to 1.98 eV (15,950 cm^{-1}) at room temperature and 1.80 eV (14,600 cm^{-1}) at 15 K. This shift is much larger than in any bulk PDA, including poly-3BCMU and poly-4BCMU where E_0 (T) decreases from about 1.98 eV at 300 K to 1.91 eV at 20 K as shown on Fig. 2.

On cooling, a discontinuous blue shift of about 12 meV is observed at 225 K, corresponding to the first order transition temperature of the monomer [16]. Another discontinuity is observed at the higher phase transition near 319 K, where v_0 shifts by ≈ 13 meV (105 cm^{-1}) to the red on cooling; the latter cannot be discussed further since there is no structural information on the high temperature phase of 4BCMU.

The blue shift at 225 K cannot be due to a change of W: the unit cell volume decreases by 4.7% at the transition [16], so one would expect a red shift. Therefore, the blue shift must be a consequence of an increase of E_b larger by 25 meV (200 cm^{-1}) than the expected increase of W. This must be associated to a geometrical change of the chain ground state. A discontinuity of the c parameter is indeed observed at the transition with $\Delta c = 0.035$ Å [16].

Apart from the step at 225 K, there is a continuous decrease of E_0 in both phases, more rapid than in 3BCMU. The red shift is 170 meV between 315 and 225 K in the room temperature phase, and 85 meV between 220 and 15 K in the low T one.

Temperature dependences of the excitonic peak absorption of several partially polymerized DA have been reported [37]. In a few cases, variations comparable to those found in 4BCMU are observed, but the monomer crystal structures and their temperature dependence are not known.

3.3. Resonance Raman scattering spectra

It is well known that the resonance enhancement in PDA is so large that the Raman scattering spectrum is

completely dominated by A_g symmetric vibrational modes involving the polymer chain C atoms, that are strongly coupled to the delocalized π electrons. This is true here also, so that a monomer with a very low polymer content ($<10^{-4}$ in weight) can be studied. We focussed our interest on two Raman lines which we shall call v_D and v_T since these normal modes mainly correspond to C=C and C≡C stretching vibrations, respectively (in several papers, they are called v_2 and v_1 [38]). They are known to be sensitive to polymer chain electronic structure [38]. Note first that in both materials, the Raman frequencies are independent of the excitation wavelength, as expected for a high quality single crystal.

Side groups however may play a role in two ways: atoms close to the chain are implied in the nuclear motions of a mode; and normal modes of some part of the side group may couple to chain modes. The former has been taken into account in modelling poly-pTS spectra, by replacing the whole side group by a dummy atom of adjustable mass at the position of the first C atom of the side group [38]. The latter has been invoked to explain the splitting of v_D in poly-pTS by a Fermi resonance [30], or in poly-DCH by coupling to several carbazole normal modes [39].

None of these couplings is present here, as v_D is a single line. However, both 3BCMU and 4BCMU isolated chains have a rich spectrum between 900 and 1350 cm^{-1} (Fig. 3), contrary to poly-pTS. In fact, it was found in modelling the Raman spectrum of another PDA having 4 CH$_2$ in the side group, that all 4 side groups C atoms had to be included in the calculation to account for the observed Raman lines [40].

In other words, the chain normal modes also imply motions of the side groups C atoms near to the conjugated chain.

So, Raman frequency changes may have two cause: a modification of the ground state chain geometry which will also causes a variation of the exciton energy E_0; and a change in the motion of the side group atoms participating to the normal mode under consideration, corresponding to a modification of the side group geometry, which is known to occur at least in 3BCMU [16]. This motion will not have a large effect on E_0. Qualitatively speaking, the latter effect may increase, or decrease, the importance of the dominant motion in the mode (that is the C=C or C≡C stretch in v_D and v_T, respectively).

3.3.1. 3BCMU

Fig. 4 shows the variation of v_D and v_T of isolated blue chains in 3BCMU. The excitation wavelength was kept constant at 620 nm at all temperatures.

When the temperature decreases from 300 K to 2 K, v_D increases from 1450 to 1458 cm^{-1} and v_T from 2077 to 2105 cm^{-1}. This is the generally observed behaviour in PDA [38]. There may be a small discontinuity at the phase transition for v_D, but for v_T the change is too small to conclude.

The weak T dependence of E_0 indicates that the chain ground state conformational changes are minimal. The observed large variations of Raman frequencies should then be related to changes of the internal structure of the modes.

3.3.2. 4BCMU

At room temperature, $v_D = 1450$ cm^{-1} and $v_T = 2085$ cm^{-1}. Fig. 5 shows the temperature dependence of v_D and v_T, respectively. Since in this case there are large variations of E_0, the excitation has been tuned to remain on resonance with the exciton zero phonon line v_0 at each temperature (Fig. 2).

The following features should be noted:

1. Discontinuities of 8 cm^{-1} at $T = 225$ K are clearly seen for both modes, reflecting an effect on the polymer chain, a signature of the first order transition of the monomer crystal.

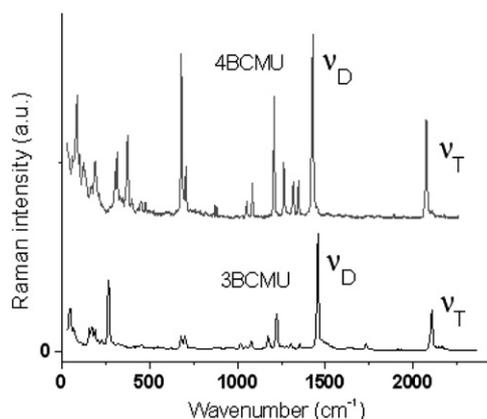Fig. 3. Raman spectra of isolated polymer chains in the monomer crystal at 2 K: below 3BCMU with $\lambda = 651.7$ nm excitation. On top 4BCMU with $\lambda = 685.6$ nm excitation at E_0.
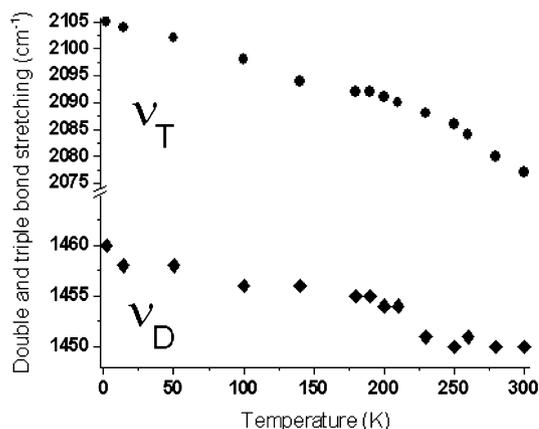

Fig. 4. 3BCMU: Temperature dependence of: (solid diamonds) the CC double bond (v_D), and (solid circles) triple bond (v_T) stretching vibrations of isolated polymer chains. The excitation wavelength was kept constant at 620 nm.
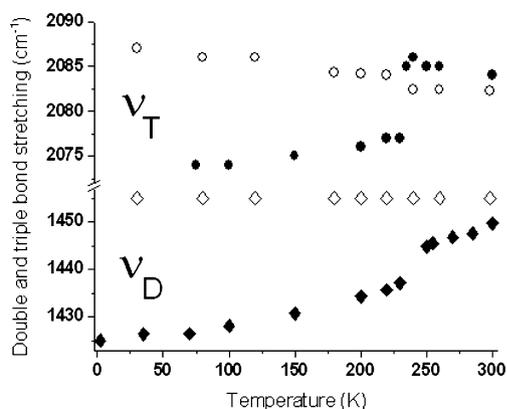
Fig. 5. 4BCMU: Temperature dependence of: the CC double bond stretching vibration ν_D of isolated polymer chains (solid diamonds) and of bulk polymer chains (open diamonds), the triple bond stretching vibration ν_T of isolated polymer chains (solid circles) and of bulk polymer chains (open circles). For isolated chains the excitation energy is tuned to be resonant with the exciton energy E_0 at each temperature (see Fig. 2); for bulk polymer chains the excitation wavelength is kept constant at 620 nm.

2. The overall temperature dependences of ν_D and ν_T are different; ν_D decreases with temperature whereas ν_T slightly increases in the high T phase and then decreases slightly with temperature below 225 K. Such a behaviour is not usually observed in PDA. On the same graph, the temperature dependences of ν_D and ν_T for bulk poly-4BCMU are also plotted; ν_D stays constant and ν_T decreases slightly.

The discontinuities at the transition correspond to a conformational change of the chain and possibly of the side groups as discussed for the exciton energy. The variation of ν_D requires further discussion. A simple model able to account for the variations of E_0 and ν_D with T, at least in the low temperature phase, is proposed in Section 4 below.

3.4. Comparison of isolated chain and bulk PDA spectroscopic properties

3.4.1. Exciton absorption temperature dependence

Since the absorption of a bulk PDA crystal is very high for light polarized parallel to the chain direction, the position of the excitonic absorption peak must be derived from the reflectance spectra by Kramers–Kronig transformation [36]. In a few cases, absorption for light polarized perpendicular to the chain direction can be recorded, as shown in Fig. 2 for poly-4BCMU, and the difference in peak positions is indeed very small. The variation ΔE_0 of the exciton transition energy between 300 K and low temperature has been determined in a few PDA [36,41–46], and it varies between 30 and 70 meV (250–550 cm^{-1}): for instance, in poly-DCH $\Delta E_0 = 35 \pm 5$ meV [36,42,43] and in poly-IPUDO, $\Delta E_0 \sim 70$ meV [44].

The values of ΔE_0 (Fig. 2) are 60 meV (500 cm^{-1}) both for poly-3BCMU and poly-4BCMU. The experimental value of ΔE_0 for isolated chains is 50 meV (400 cm^{-1}) in

3BCMU and 175 meV (1400 cm^{-1}) in 4BCMU. A specific process is at play in the latter, and a reasonable assumption is to relate it to the large and temperature dependent strain on isolated chains in 4BCMU monomer crystal.

Fig. 2 shows that $E_0(T)$ curves for isolated chains and bulk poly-4BCMU cross near 300 K. But this in fact corresponds to two quite different situations. The relevant monomer crystal parameter is 4.81 Å [16] while the polymer value is 4.88 Å [23]. So, different values of E_b are expected. The isolated BCMU polymer chain in its monomer matrix experiments a 1.4% compressive strain: if one can extrapolate the pTS tensile strain data [47], a 1.4% compressive strain corresponds to a 40 meV (300 cm^{-1}) energy shift.

The equality of the E_0's can be obtained if the W values differ by the same amount, with opposite sign. This is possible since the chain environments are different. The most obvious difference is that within a lamella, an isolated chain is surrounded by two rows of monomers, which in the polymer crystal are replaced by two polymer chains. The distance between chain axes is about 5.5 Å, large enough to make exchange interactions negligible, so only differences in van der Waals corrections are relevant.

The van der Waals interactions between two parallel conjugated chains might be anticipated to be large but all theoretical calculations [48–50] show that this interaction is anomalously small both in magnitude and in its variation with interchain distance R, decreasing as $R^{-\alpha}$ with $\alpha = 2.5$–3. These calculations usually consider straight chains, whereas actual polymers, and PDA in particular, have a zigzag chain geometry. It was shown by Silbey [51] that the magnitude, and even the sign, of the relevant matrix elements, strongly depend on the relative orientation of the two parallel zigzag chains.

Nevertheless, an experimental determination is possible. To do so, we are currently studying absorption spectra related to pairs of nearest neighbour poly-4BCMU chains diluted in the monomer crystal [52]. This situation is directly comparable to that of an isolated chain, since two neighbouring chains are related by a symmetry operation of the crystal: the environment of each chain in a pair is identical to that of the isolated chain, except that the other chain has replaced the stack of C4 monomer units from which it has been generated. The pair of chains experiences the same longitudinal strain as the isolated chain, since it is imposed by the surrounding matrix. The observed exciton absorption of a pair of chains is, at 10 K, lower by 25 meV than that of the isolated chains and this shift is only weakly temperature dependent.

In the poly-4BCMU crystal, each chain has 2 such nearest neighbours since the crystal is lamellar [16], the corresponding interchain distance being 3% smaller than in the monomer crystal. The reduced distance points to an increase of the van der Waals interaction W by about 60 meV, assuming negligible polarizability changes. This is close to the difference in E_b estimated above, and can account for the crossing of curves near 300 K.

The smaller energy difference of excitons in 3BCMU monomer and polymer is probably related to geometrical factors: a smaller interchain distance (see above) and sensitivity to relative orientations [51].

3.4.2. Raman frequencies

Their temperature dependence have been studied in poly-pTS [53,54] between 300 K and 4 K, and in poly-DCH [41] between 300 and 480 K. In both cases v_D and v_T increase with decreasing T. In poly-pTS the variations level off below 150 K; above 150 K it is in the range 1–3 cm^{-1} per 100 K. Bulk poly-4BCMU behaves similarly: v_D is almost independent of T and v_T increases by ≈ 5 cm^{-1} from 300 to 2 K (Fig. 5).

Contraction of the crystal lattice may be produced by hydrostatic pressure rather than by cooling. In two studies of poly-pTS under pressure, it was found that v_0 increases at a rate of 70 meV/GPa [54–56], and both v_D and v_T decrease with pressure at a rate of about 5–6 and 10–13 cm^{-1}/GPa, respectively [54]. Similar variations have been found in a disordered film of poly-4BCMU [57].

Summarizing, the above data correspond to situations in which the repeat unit length of the polymer is almost constant [26,58] and the lattice expands or contracts in the other directions. In this situation, the exciton energy E_0 decreases and the vibrational Raman frequencies increase as the lattice contracts.

The observed variations of isolated chains in 3BCMU follow this tendency, as well as the absolute values. Therefore, isolated poly-3BCMU chains are really typical of bulk PDA chains as far as the properties here discussed are concerned, and they can serve as a perfectly ordered reference state for blue bulk PDA. This is not the case of isolated poly-4BCMU chains, but in this case one is dealing with strained polymer chains, so one should rather refer to data on strained bulk PDA crystals.

3.4.3. The effect of strain

In some cases, PDA crystals can occur as long needles (whiskers) on which a tensile stress can be applied. The stress–strain curve is typically linear up to above 1% strain, corresponding to a stress of ca 0.5 GPa [41]. In the three cases studied [30,41,59], both vibrational frequencies decrease linearly under tensile stress, at a rate slightly dependent on the PDA: v_D decreases by about 10 cm^{-1}/ (% strain), and v_T by 20–30 cm^{-1}/%.

The effect of tensile strain on E_0 was also studied in poly-pTS [47]: v_0 increases by 27 meV/% strain or 54 meV/GPa.

These changes are very similar to those produced by hydrostatic pressure, even though the microscopic situations are different. It is assumed in the above studies that the chain is elongated by the same amount as the macroscopic strain, while under pressure the chain length is barely affected. This has been experimentally verified for poly-DCH [60], studied in [41] up to 0.5% strain at room temperature. To an axial elongation corresponds a lateral

contraction. A Poisson ratio ≈ 0.5 up to a 0.5% tensile strain, and larger at larger strain was determined for poly-DCH [61]. A value of 0.5 (resp 0.3) for the ratio would correspond to a 0.5 (resp. 0.3)% lateral compression per % strain. The linear compressibility of poly-pTS is almost isotropic in the directions perpendicular to the chain axis: $\kappa \approx 3\%$/GPa [31], so a 1% tensile strain is equivalent, as far as lateral changes are concerned, to a hydrostatic pressure of about 0.15–0.2 GPa. Thus, part of the effects of elongation may be due to changes in the packing of side-groups, and not to changes in the electronic structure of the chain itself.

This is not what is observed in isolated poly-4BCMU chains: the compressive strain increases as T decreases, yet v_D decreases. There is no report of uniaxial compression of a PDA crystal.

4. Model for the 2 eV electronic absorption for a chain under compressive strain (4BCMU)

### 4.1. Exciton energy variation with temperature

Any explanation of variations affecting the exciton energy E_0 thermal shift and discontinuity at the phase transition of the monomer single crystal (Fig. 2), has to be consistent with the evolution of the double bond stretching v_D with temperature (Fig. 5), which suggests a deformation of the chain in the ground state.

At the phase transition E_0 increases while v_D decreases, a torsion of the chain induces an increase of both E_0 and v_D so such a deformation can not explain the observations. We shall assume that the backbone carbons stay in a plane and deduce the chain deformations in agreement with the experimental data.

The simple model proposed here explains these deformations qualitatively, but is not meant to fit the results quantitatively. A fit of the Raman spectra would require a precise knowledge of the normal modes, which depend strongly of the side groups as described in Section 3.3.

Our model derives from [54] where an energy gap E_g is calculated using a tight binding approach in a formulation equivalent to the Hückel molecular orbital description. This model attributes the narrow peak in the optical spectrum (Fig. 1) to an interband transition but it is by now well known that the optical gap is excitonic in nature. Electroabsorption spectra [62] of 4BCMU isolated polymer chains show that the exciton binding energy is constant between 30 K and 300 K. The model therefore can be adapted to the shift of the exciton energy E_0. For simplicity the van der Waals interactions will be ignored. The exciton energy is then given by:

$$E_0 = 2\beta_{14}$$

$$\times \sqrt{\mu^2 + \frac{1}{2}(1 + \mu'^2) - \sqrt{\frac{1}{4}(\mu'^2 - 1)^2 + \mu^2(1 + \mu')^2}}$$

$$(1)$$
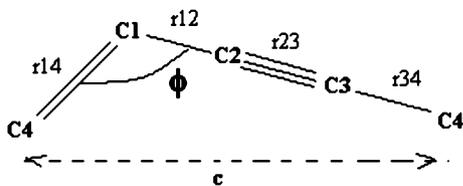
Scheme 2. Labelling of the carbon atoms, bond lengths and angles in the polymer chain skeleton.

where $\mu = \frac{\beta_{12}}{\beta_{14}}$ and $\mu' = \frac{\beta_{23}}{\beta_{14}}$. The β_{ij}'s are the resonance or hopping integrals between atoms i and j labelled as on Scheme 2.

To determine E_0 versus strain one needs to know the dependence of β_{ij}'s upon interatomic separation r_{ij} and angle ϕ (Scheme 2). The calculation will use two assumptions: (i) β_{ij} can be written $\beta_{ij} = f(\phi)g(r_{ij})$; (ii) the chain backbone remains planar at all temperatures. Indeed a deviation from planarity leads to a rapid increase of E_0 with torsion angle because the $2p_z$ orbitals are no more parallel and conjugation is decreased [63].

The first step is to determine the variation of β_{ij}'s with ϕ and r_{ij}. The function $f(\phi)$ is determined in appendix B. For the function $g(r_{ij})$ we assume the empirical form [64]: $g(r_{ij}) = \beta_0 e^{-r_{ij}/a}$ where β_0 and a are two parameters.

Finally the formulae deduced for μ and μ' used in Eq. (1) are

$$\mu = e^{(r_{14}-r_{12})/a} \frac{\sin \frac{\phi}{2}}{(1 - \cos \phi)\frac{4}{3} \sin^2 \frac{\phi}{2} + \cos \phi} \quad (2)$$

$$\mu' = e^{(r_{14}-r_{23})/a} \frac{1}{(1 - \cos \phi)\frac{4}{3} \sin^2 \frac{\phi}{2} + \cos \phi} \quad (3)$$

$$\beta_{14} = \beta_0 e^{-r_{14}/a} \left[(1 - \cos \phi)\frac{4}{3} \sin^2 \frac{\phi}{2} + \cos \phi \right] \quad (4)$$

where the parameters r_{14}, r_{23}, r_{12} and ϕ are related by the trigonometric formula

$$c^2 = (2r_{12} + r_{23})^2 + r_{14}^2 - 2r_{14}(2r_{12} + r_{23}) \cos \phi. \quad (5)$$

At room temperature, $E_0 = 1.976$ eV, the crystallographic c parameter is $c = 0.482$ nm and the triple bond length is taken as $r_{23} = 0.12$ nm the typical value of PDA [16]. For the double bond length r_{14} we use the typical value given in [24,25]: $r_{14} = 0.136$ nm, and we assume $\phi = 2\pi/3$.

Eqs. (1) and (5) used with this set of data give $\beta_0 = 64.6$ eV and $a = 0.0487$ nm. These values are close to those used in [54].

In [54] the E_0, v_D, v_T variations with temperature or pressure are explained by the variation of the bond length assuming a constant ϕ angle because the stress is assumed to act through the side groups.

The situation is different here where crystallographic data show that the strain is located along the carbon backbone. CC backbone is significantly stressed (compression), moreover, the step of E_0 at the phase transition has also to be explained. We assume the only bond that vary with

strain is the CC single bond (r_{12}) (the weakest bond), the double and triple bond keeping constant lengths with $r_{23} = 0.12$ nm and $r_{14} = 0.136$ nm. We are left with two adjustable parameters r_{12} and ϕ. These assumptions are consistent with experimental data on polyDCH [60], in which an applied tension of 0.26%, induced an extension of the CC single bond by 0.29% whereas the CC double and triple bonds did not vary. From the experimental values of energy E_0 (Fig. 2) and of the c parameter with T [16] and using Eqs. (1) and (2), we calculate the value of r_{12} and ϕ at each temperature. The results are shown on Fig. 6 for r_{12} and ϕ. Phases I and II of the monomer matrix are clearly distinct. In phase II, while the single bond length r_{12} shortens with the unit cell parameter c, ϕ stays almost constant around $2\pi/3$. At the phase transition, the value of r_{12} jump to its unstrained value while ϕ decreases slowly. It was pointed out in Section 3 that all van der Waals interactions lead to a red shift of the gap energy at the phase transition, whereas the decrease of the ϕ angle implies a decreasing delocalization and so a blue shift. The fact that the changes of the skeleton geometry are different in the two phases shows that they are not simply governed by the repeat unit length contraction (about 0.6% at the phase transition), but that the side group displacements within the monomer matrix play also an important role.

4.2. Variation of v_D with temperature

The model is too simple to make predictions on the triple bond stretching energy variation with temperature because we have assumed a constant orbital overlap and a constant interatomic separation length r_{23} (Scheme 2).

To qualitatively understand the unusual variation of the double bond stretching energy with temperature, we calculate a Taylor expansion of the transfer integral β_{14} Eq. (7) around $\phi = 2\pi/3$ in first order in ϕ, r_{14} being assumed constant: $\beta_{14} = \beta_0 e^{-r_{14}/a} \left(1 - \frac{\sqrt{3}}{2} \left(\frac{2\pi}{3} - \phi \right) \right)$. β_{14} is rewritten in the usual form for a transfer integral [64], $\beta_{14} = \beta_0 e^{-r'_{14}/a}$ where $r'_{14} = r_{14} + \frac{\sqrt{3}}{2} \left(\frac{2\pi}{3} - \phi \right) a$. The model shows that when ϕ decreases, r'_{14} increases while r_{14} stays constant, then β_{14}
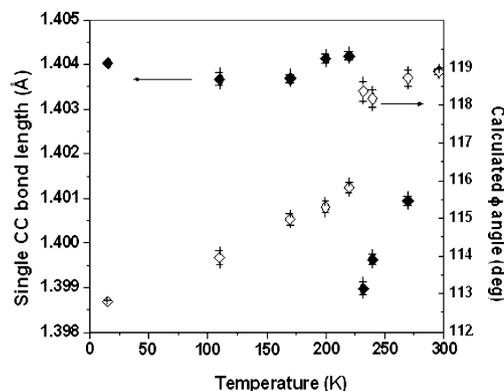

Fig. 6. Calculated temperature dependence of the single bond CC length r_{12} (see Scheme 5 for labelling) solid diamonds left scale, and of the ϕ angle (see Scheme 2 for labelling) open diamonds right scale.

decreases, so the frequency v_D of the double bond C=C decreases (Fig. 5).

Therefore fitting $E_0(T)$ with the above developed model leads to a decrease of ϕ as T decreases in the low T phase. To a decrease of ϕ corresponds an increase of r'_{14} hence a decrease of β_{14} without variation of the actual bond length r_{14}: so v_D also decreases. Indeed, as T decreases, the experimental value of v_D and the fitted value of ϕ both decrease. The anomalous T dependence of v_D is qualitatively explained by the same model as the variation of E_0.

We stress again that a variation of vibrational frequency is not necessarily due to bond length changes.

5. Conclusion

We had two reasons to study the 3 and 4BCMU structures [16]. The structure governs the topochemical reaction; it also governs the geometry of isolated polymer chains in the monomer matrix, the periodic potential in which they are embedded, and hence their spectroscopic properties, which have been studied in details.

The 3BCMU structure shows that unstrained isolated chains are in register with the monomer matrix at all temperatures, and so are representative of chains in bulk PDA. Indeed, the v_D and v_T frequencies indicate that the ground state geometry is very close to that of a typical blue PDA chain in a bulk polymer.

In the case of 4BCMU, the very small exciton absorption broadening shows that isolated polymer chains remain also in register with the monomer matrix, despite a longitudinal compression of 3% at low temperature. Such a geometry is not accessible by other methods. The decrease of E_0 shows that increasing compression does not shift the electronic structure towards the so called red one, in which both E_0 and the Raman frequencies are larger; this means that the chain remains planar, i.e., blue at all accessible compressions. A model of chain deformation at the monomer scale has been proposed. It shows the importance played by the side-groups packing since the first side-group C atom (C′) moves out of the chain plane.

Despite this compression, many properties of 3 and 4BCMU isolated chains, such as exciton size and binding energy [62], radiative [9] and non-radiative [7,8] relaxation mechanisms, are very similar: the chain electronic structure is robust relatively to non-negligible geometric changes, as long as the chain remains planar.

There is no hope to better determine the exact geometry of an isolated chain in its monomer matrix, with its side groups, by structural methods. However, the resonance Raman spectra (Fig. 3) contain much more information than has been used here; the many other normal modes imply more complicated motions than v_D and v_T. To fully use this information, a complete dynamical matrix for the chain with at least 4 carbon side group atoms should be optimized, using the measured frequencies, including out of plane vibrations. Its temperature dependence should be fitted as a function of geometrical variables (bond lengths and angles). This seems to remain a very difficult task.

Appendix. Determination of $f(\phi)$

To determine $f(\phi)$ given by $\beta_{ij} = f(\phi)g(r_{ij})$, we assume that

- The conjugated chain stays in a plane, whereas C′, the first carbon of the lateral group, can move out of this plane (Scheme 3a,b).
- Only angle ϕ is affected by the compression.

We shall show that a displacement of C′ out of the conjugated plane leads to a decrease of ϕ which produces an evolution of C_1 and C_4 atoms from sp^2 towards sp^3 geometry. Let θ be the angle between the $2p_z$ orbital axes of C_1 and the conjugated plane (Scheme 3a). In the absence of compressive strain, $\theta = \pi/2$ and $\phi = 2\pi/3$, corresponding to sp^2 geometry. Under compression C′ moves out of the plane so $\theta > \pi/2$ and $\phi < 2\pi/3$ (Scheme 3b). $\theta = 1.911$ rad (109.5°) and $\phi = 1.911$ rad (109.5°) would correspond to sp^3 geometry. To describe this variation, the method developed in [65] to treat rehybridisation in deformed conjugated molecules was used.

Let us define a reference frame with its x axis along the C_1–C_4 bond, y axis perpendicular to x and in the conjugated plane, z axis perpendicular to this plane, and decompose the atomic orbital overlap S along these axes (Scheme
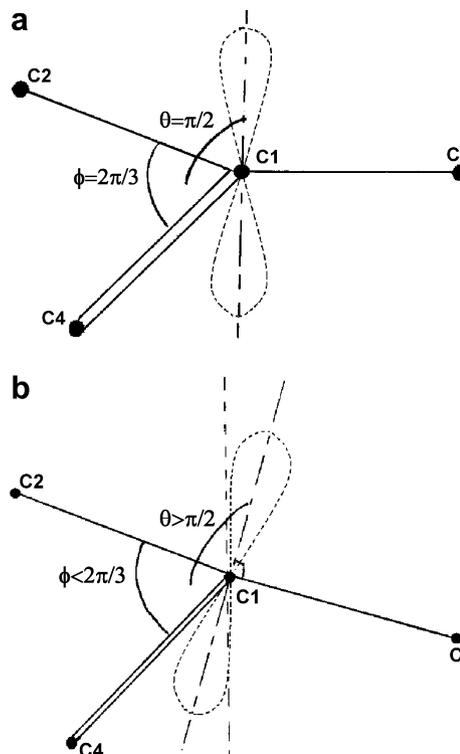
Scheme 3a,b. Orientation of the $2p_z$ orbital of atom C1; (a) in the unstrained state; (b) under strain.
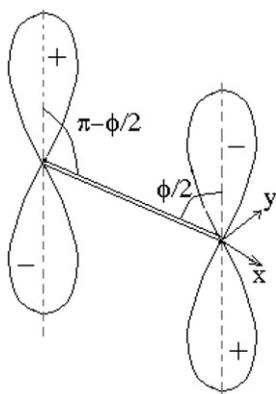
Scheme 4. Orientation of x, y, and z axes. Orientation and sign of the orbital lobes.

4). This gives for the z component $S_{zz} = S_{\pi\pi}\cos(\theta - \frac{\pi}{2})\cos(\theta - \frac{\pi}{2}) = S_{\pi\pi}\sin^2\theta$. But there appears a contribution in the $[x,y]$ plane given by $S_{\pi\pi}\sin(\theta - \frac{\pi}{2})\sin(\theta - \frac{\pi}{2}) = S_{\pi\pi}\cos^2\theta$, which must be subtracted because of the opposite signs of the two orbital lobes. In addition, a prefactor taking into account the contribution of the orbitals projection along x and y is to be calculated (Scheme 4). This is done using the method developed in [66], giving $S = S_{\pi\pi}\sin(\pi - \frac{\phi}{2})\sin\frac{\phi}{2} + S_{\sigma\sigma}\cos(\pi - \frac{\phi}{2})\cos\frac{\phi}{2}$. Taking into account that $S_{\pi\pi} \approx S_{\sigma\sigma} = S_0$ for $r \cong 0.136$ nm (see Figs. 1.10 and 1.11 of Ref. [66]), $S = -S_0\cos\phi$. Assuming that the resonance integral β and the atomic orbital overlap S are proportional [66], leads to

$$\beta_{14} = \beta_0(\sin^2\theta + \cos\phi\cos^2\theta). \tag{6}$$

The last step is to determine the relation between ϕ and θ. From Scheme 5 we can write $\sin\frac{\phi}{2} = \frac{O'C_4}{C_1C_4}$, $\sin(\pi - \theta) = \frac{OC_4}{C_1C_4}$, $\sin 60 = \frac{O'C_4}{OC_4}$ and conclude that

$$\sin\frac{\phi}{2} = \frac{\sqrt{3}}{2}\sin\theta \tag{7}$$

β_{23} for the triple bond is determined as follows: the $2p_z$ orbitals are supposed to stay perpendicular to the conjugated backbone plane, so the overlap in this plane is zero:
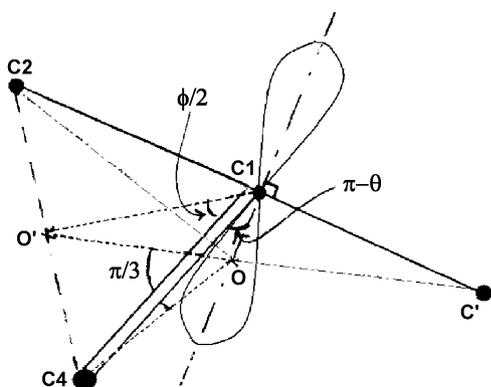
Scheme 5. ϕ and θ angles, and points O and O'.

$\beta_{23} = \beta_{23}^0$. For the single bond we take into account the angular deviation of the $2p_z$ orbitals of the atoms C1 and C4, so the β_{12} integrals vary as $\beta_{12} = \beta_{12}^0\cos(\theta - \frac{\pi}{2})$.

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