

A high energy exciton in polydiacetylene chains, involving electrons localized on the triple bond

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Abstract

UV spectra of polydiacetylene (PDA) chains in their monomer single crystal matrix show an absorption near 4 eV and above, predominantly polarized perpendicular to the chain direction. It is shown by combining absorption and electroabsorption studies that the spectrum corresponds to an excitonic transition. This exciton has polarizability and binding energy comparable to those of the well-known exciton near 1.9 eV in PDAs, but an oscillator strength smaller by more than two orders of magnitude. It is assigned to the excitation of a π electron localized on an acetylenic bond to the well delocalized π^* states. The transition gains intensity via resonant coupling to states of the continuum associated to the 1.9 eV exciton.

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1. Introduction

The electronic structure and properties of polydiacetylenes (PDA) have been the subject of a large amount of experimental and theoretical work, in particular because PDA are the only conjugated polymers that can be prepared as large good quality single crystals [1,2]. Such polymer crystals are prepared by topochemical polymerization of single crystals of the corresponding diacetylene monomer (DA). By stopping the reaction at a very early stage, one can obtain a dispersion of isolated PDA chains in the single crystal matrix of their corresponding DA monomer. Such chains are linear, straight, very regular, all in the same periodic potential (that of the surrounding DA crystal) and very long, and they are a good realization of a quasi-one dimensional organic quantum wire. Their low temperature absorption and emission spectra are well resolved (widths in the 1–10 meV range), thus allowing accurate and detailed spectroscopic studies [3–6].

It is now well established that the visible absorption spectrum of PDA is entirely dominated by a strong transition to a singlet exciton state of $1B_u$ symmetry lying at the bottom of a wide exciton band [7]. The corresponding continuum of ionized states can only be studied in electroabsorption where it shows up as a strong Franz–Keldysh signature; the binding energy of the exciton state is large, ≈ 0.5 eV [4,8]. Up to now, no other electronic state of the PDA chain has been experimentally detected in one-photon absorption. Other absorptions in PDA crystals are due to electronic transitions within the side-group substituents, unrelated to the conjugated chain itself (see for instance [9]).

The most studied electronic configuration of PDA chains, the so-called “blue state” [2], is only very weakly fluorescent [3], the very short exciton lifetime [10] being limited by non-radiative relaxation to singlet excited states of A_g symmetry within the optical gap [11].

A large part of the theoretical work on PDA has been concerned with the investigation of these A_g excited states, either below the $1B_u$ exciton (those that are responsible of the very low luminescence yield) or above it (these states playing an important part in the third-order

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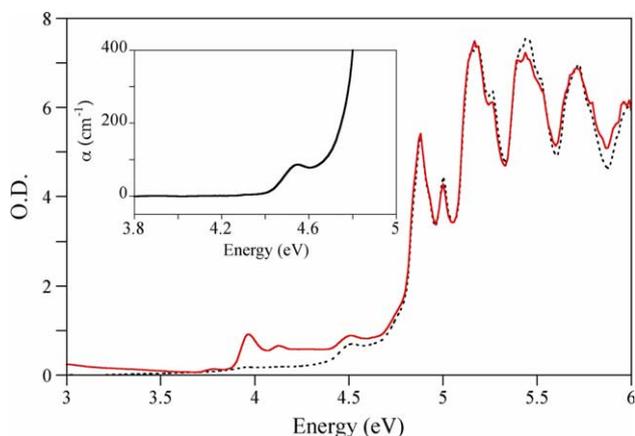


Fig. 1. Unpolarized absorption spectra at 10 K of two 3BCMU crystals containing respectively $x_p = 3.4 \times 10^{-2}$ (solid line) and $x_p = 1.5 \times 10^{-3}$ (dotted line) polymer in weight, showing the monomer absorption at high energy and the x_p -dependent absorption below 4.5 eV. Inset shows the absorption of a “pure monomer” containing 3×10^{-5} polymer.

non-linear spectroscopic properties of PDA [12,13]). In at least one calculation on DA oligomers, a higher lying B_u state was predicted [14]. We present in this report one-photon absorption spectra as experimental evidence for a high energy B_u state.

In many commonly studied DAs, the lowest energy transitions are those of the side-groups, lying in the near UV. For instance, in the DAs of the DCH [15] family, side-groups absorption starts at 3.6 eV [16]. In 3 and 4BCMU, the DA monomers used in all our previous work [3–7,10,11], the absorption spectrum of the side-groups starts with that of their central part $-\text{CO}-\text{NH}-\text{CH}_2-\text{COO}-$, which is almost identical to acetamidoacetic acid (also named *N*-acetylglycine): $\text{CH}_3-\text{CO}-\text{NH}-\text{CH}_2-\text{COOH}$. The crystal absorption of that molecule has been studied by Clark [17]; its lowest energy transition is a weak $n-\pi^*$ one, so-called “amide W band” at ≈ 5.65 eV (220 nm). Thus, in 3 and 4BCMU, the lowest energy transition is that of the DA $\text{C}\equiv\text{C}-\text{C}\equiv\text{C}$ unit itself, around 4.5 eV (see Fig. 1), offering the opportunity of a much wider energy window for such absorption investigation of high energy chain states.

2. Experimental

3BCMU and 4BCMU monomer single crystals were grown from saturated solutions in acetone or methylisobutylketone, in the dark at 4 °C. Typical crystal dimensions were: surface 0.5 cm², thickness 100 μm.

Controlled polymerizations were performed at room temperature by irradiation in a IBL 637 ¹³⁷Cs source, and occasionally by photopolymerization at 272 nm (see Section 3 below). Polymer contents in weight x_p were determined from the measured absorption in the visible

at room temperature, for light polarized perpendicular to the chain direction, using the previously determined calibration with α_{\perp} at the wavelength of maximum absorption of 1.6×10^3 cm⁻¹ for 3BCMU and 2×10^3 cm⁻¹ for 4BCMU [18].

Polymer contents were purposely kept below $x_p = 0.1$, since for such partially polymerized samples the high quality of pure monomer crystals is preserved, and stresses induced by polymerization are still low. Consequently, absorption spectra show narrower line-widths, and light scattering remains weak.

The samples were studied at low (10–15 K) temperature in a He gas circulation cryostat. Absorption spectra were taken in the visible and the UV up to 6 eV using a Cary 2300 double beam spectrophotometer. The incoming beams were polarized using 250 μm thick HN 32 sheet polarizers. Since such polarizers absorb above 4.1 eV, only unpolarized spectra could be taken at higher energies; in fact, these “unpolarized” beams are still slightly polarized due to the grating monochromator.

Electroabsorption measurements employed a sinusoidal field of 1 kHz frequency applied in transverse configuration across an electrode gap of 0.3 mm. Contacts were thin Cr films to improve the adherence to the crystal with a thick Mg overcoat blocking the light. The field induced change $\Delta\alpha$ of the absorption constant was derived from the ratio of field induced change ΔI of the transmitted light I and the thickness d of the sample:

$$\Delta\alpha = -\frac{1}{d} \frac{\Delta I}{I}. \quad (1)$$

The field was oriented parallel to the chains, and the sample mounted on a 0.5 mm thick quartz substrate for electrical insulation, was attached to the Cu heat sink of a He flow cryostat. Light of a tungsten halide lamp or a Xe arc was dispersed by a 1 m monochromator, polarized by a calcite polarizer and focused onto the electrode gap, to measure both the transmittance and its field induced change on the same spot. The field-induced change of the transmittance was measured at twice the frequency of the applied field. No signal was detected at the fundamental frequency, consistent with the inversion symmetry of the polymer chains. The 3BCMU and 4BCMU monomer structures are centrosymmetric [19a] and the 4BCMU polymer as well [20]. Although it is not possible to directly determine the structure of the PDA isolated chain, it seems indeed reasonable that the chain itself is centrosymmetric. The transmittance permitted in some samples polarized absorption spectra up to 5.2 eV but, due to the higher background of scattered light in this single monochromator system, no reliable absorption constants could be derived beyond 4.8 eV.

It was checked that the spectra before and after applying the contacts were identical, except for a larger background of scattered light.

3. Experimental results

3.1. Absorption spectra

Fig. 1 shows low temperature (10 K) unpolarized absorption spectra in the range 3–6 eV of two 3BCMU single crystals containing respectively $x_p = 1.5 \times 10^{-3}$ (dotted line) and $x_p = 3.4 \times 10^{-2}$ (solid line) polymer in weight. Inset shows the onset of the absorption spectrum of a “pure monomer” i.e. $x_p \approx 3 \times 10^{-5}$ in weight.

The spectrum of the sample with lower polymer content (dotted line) is dominated by the absorption of the diacetylene C_4 unit in the 3BCMU monomer. It starts with a weak band at 4.512 eV (274.8 nm) with a FWHM ≈ 60 meV. A similarly weak transition near 4.5 eV has been observed previously in crystals of 2,4-hexadiyne-1,6-diol at room temperature [21], and earlier in concentrated solutions of dimethyldiacetylene [22]. Much more intense DA absorption starts around 4.8 eV, corresponding to well documented transitions of diacetylene or dimethyldiacetylene [23].

The absorption coefficient measured at 275 nm from the inset data is $\alpha_{\max} \approx 50 \text{ cm}^{-1}$, thus, homogeneous photopolymerization can be carried out at that wavelength in a typical 100 μm thick crystal. At room temperature, this band is slightly red-shifted to 272 nm.

Samples with higher polymer content (full line) show no spectral changes above 4.8 eV, but a well defined absorption appears between 3.7 and 4.8 eV. It starts with a weak band at 3.78 eV, and shows a peak at 3.97 eV with a second maximum at 4.138 eV, ≈ 168 meV (i.e. 1355 cm^{-1}) above it, which is probably a vibronic replica. Below 3.7 eV the high energy tail of the polymer absorption in the visible range is observed. No other absorption appears in the whole studied range, that is, between the $1B_u$ exciton absorption near 1.9 eV and this new band. The new absorption is clearly associated to the polymerization process.

Fig. 2 shows the absorption spectrum of a crystal with a polymer concentration $x_p = 3.4 \times 10^{-2}$, in the range from 3 to 4.7 eV. Spectrum a corresponds to unpolarized light as in Fig. 1, spectrum b to light polarized parallel to the chains direction, and spectrum c perpendicular polarization. The high energy tail of the visible polymer absorption is as expected strongly polarized parallel to the chains direction. On the contrary, the new UV absorption is polarized primarily perpendicular to that direction: experimental dichroism $\alpha_{\perp}/\alpha_{\parallel}$ is 2.6 at 3.97 eV; this is in fact a lower limit of the true dichroic ratio, since the effect of light propagation in the biaxial crystal (3BCMU is monoclinic [19a]) is not taken into account. The maxima of this absorption are the same in both polarizations within 1 meV. The spectrum on the low energy side of the maximum is well fitted by a combination of two Lorentzians, both with FWHM = 78 meV, centered at 3.965 and 3.775 eV respectively.

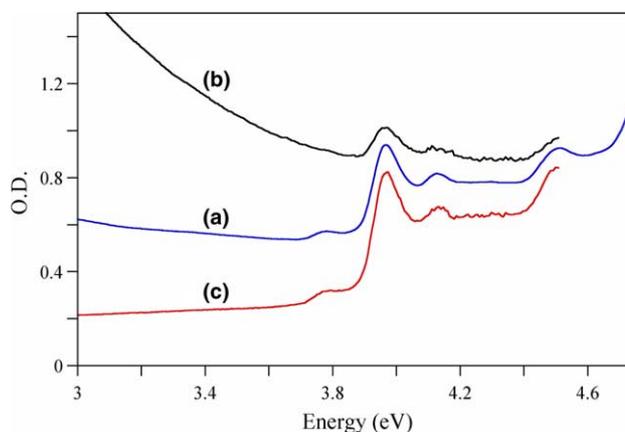


Fig. 2. Absorption spectra at 10 K of a 41 μm thick 3BCMU crystal with $x_p = 3.4 \times 10^{-2}$: (a) unpolarized light (same spectrum as on Fig. 1), (b) polarization parallel to the chains direction and (c) polarization perpendicular to the chains direction.

A similar absorption, also polarized primarily perpendicular to the chains direction, is observed in 4BCMU, though with some differences as shown on Fig. 3. The whole spectrum is less intense, and red shifted by 45 meV, now peaking at 3.93 eV (316 nm), with a second weaker maximum at 4.088 eV, again ≈ 168 meV above it. The main spectral difference is the absence in 4BCMU of the weak low energy absorption band at 3.78 eV seen in 3BCMU.

In 4BCMU, the low energy side of the most intense peak is well fitted by a Lorentzian shape with a FWHM of 53 meV at 10 K. This suggests that the line is homogeneously broadened. Indeed, the effect of crystal imperfections leads to an experimental inhomogeneous linewidth of only ≈ 8 meV for the $1B_u$ exciton [3,4], and there is no reason to believe that the UV exciton should

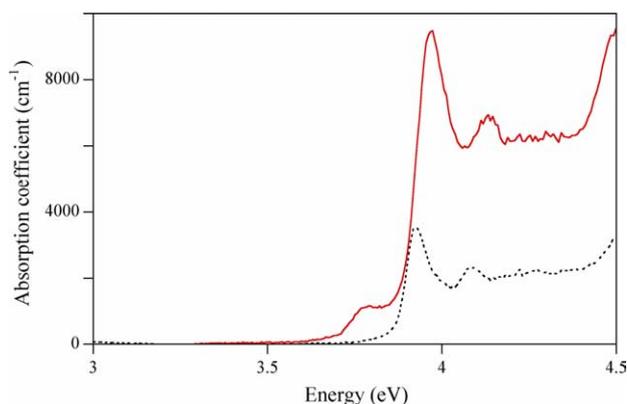


Fig. 3. Comparison of the absorption coefficients at 10 K in 3BCMU (solid line) and in 4BCMU (dotted line) versus energy in the region of the polymer absorption. The ordinate scale corresponds to the absorption coefficients in a hypothetical completely polymerized sample in which the chains would have the same absorption coefficients as when diluted in a monomer crystal.

be many times more sensitive to these imperfections. Thus, the linewidths at 10 K of 78 and 53 meV for 3BCMU and 4BCMU respectively can be taken as homogeneous. The lifetime of this state is then of the order of 5–10 fs.

The intensity of the new absorption is proportional to the polymer content x_p : Fig. 4 shows five spectra of 4BCMU for x_p between 6.5×10^{-3} and 7.4×10^{-2} . Shape and position are independent of x_p in the whole range studied, and as shown in the inset the integrated absorption is proportional to x_p . This proportionality shows that the absorption is due to the chains individually and not to interchain interactions. The same results are obtained on 3BCMU. From these data, it is possible to derive the maximum absorption coefficient α_{\max} corresponding to an hypothetical totally polymerized crystal ($x_p = 1$), in which the absorption would have the same spectral characteristics as in the partially polymerized crystals studied here. For perpendicular polarization, one obtains $\alpha_{\max} = 9500$ and 3600 cm^{-1} for 3BCMU and for 4BCMU, respectively. For such values of α_{\max} , a 100 μm thick bulk polymer single crystal would be totally absorbing. However, it was checked that this absorption is present with the expected magnitude in a 0.3 μm thick single crystal film. Integration of the absorption spectra yields for this exciton an oscillator strength $f \sim 4\text{--}5 \times 10^{-3}$, about 200 times less than that of the exciton near 1.9 eV for parallel polarization of light.

It is now clear that we are dealing with an absorption of the polydiacetylene chain itself, but polarized primarily perpendicular to the chain direction, whereas all previously known transitions are polarized parallel to it.

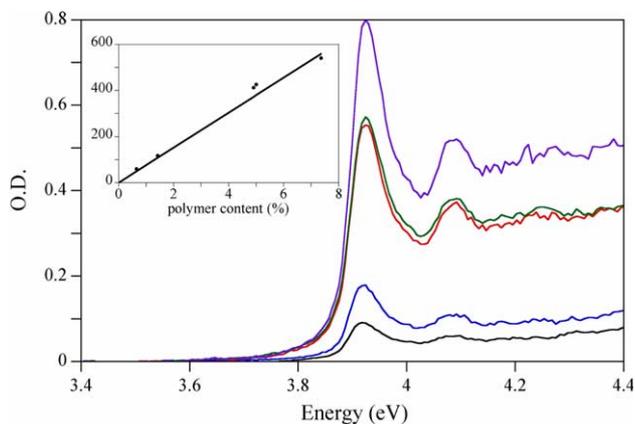


Fig. 4. Absorption spectra at 10 K of five 4BCMU crystals, with perpendicular polarization. The absorbances have been scaled to equal thicknesses for a meaningful comparison. The crystals contained (from bottom to top) 6.5×10^{-3} , 1.4×10^{-2} , 4.9×10^{-2} , 5×10^{-2} and 7.4×10^{-2} polymer in weight. Inset shows the variation of the integrated absorbance of the peak at 3.9 eV, fitted by a Lorentzian lineshape, as a function of polymer content.

3.2. Electroabsorption spectra

3.2.1. Visible range

Electroabsorption spectra have been studied in the visible range also, for a direct comparison to the response of the UV exciton. The visible electroabsorption spectra correspond to the transition to the $1B_u$ exciton and to the related electron–hole continuum, and had previously been studied only on isolated chains ($x_p < 10^{-3}$) [4], or by electroreflectance on bulk polymer samples [8], and only in parallel polarization.

Fig. 5 (upper panel) shows spectra of 4BCMU in the range of the fundamental gap of the $\pi\text{--}\pi^*$ visible transition, for light polarized perpendicular to the chains. In parallel polarization this 70 μm thick sample was opaque due to its high polymer content $x_p = 7.4 \times 10^{-2}$. The absorption shows the narrow peaks of an exciton at 1.832 eV and vibronic replica of double and triple bond stretch modes. At lower energy weaker transitions at 1.761 and 1.799 eV are observed. The origin of these transitions is not clear but they are also observed in samples of very low polymer content [3,4]. All these transitions respond to the electric field by a quadratic Stark shift to lower energy, obvious from the excellent agreement of the electroabsorption spectrum to the derivative of the absorption. We emphasize that despite a peak-to-peak width of only 12 meV, the $\Delta\alpha$ spectrum of the main exciton shows no significant deviation from the derivative lineshape. The quadratic Stark shift corre-

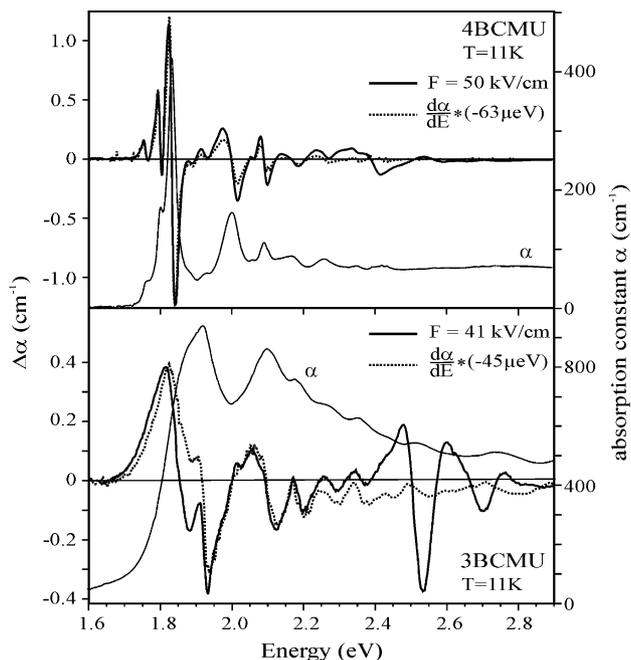


Fig. 5. Absorption α and electroabsorption spectra $\Delta\alpha$ in the visible, near the gap of $\pi\text{--}\pi^*$ transitions of 4BCMU and 3BCMU. The dotted line shows the derivative of the absorption spectrum scaled to a redshift by ΔE . Field F parallel and polarization of light perpendicular to the chain.

sponds to a polarizability $p = 7260 \text{ \AA}^3$. This value agrees well with that reported for the excitons in isolated chains and parallel polarization $p = 6480 \text{ \AA}^3$ [4].

The $\Delta\alpha$ spectrum shows a signal near 2.4 eV, which is not reproduced by the derivative of the absorption spectrum. This signal marks the band edge of free carrier states, and it depends very sensitively on long-range order, since it arises from the coherent acceleration of free carriers. Loss of long-range coherence on a scale much larger than the size of the exciton leads to rapid broadening, so that this signal, the Franz–Keldysh effect of the band continuum, is resolved only in high quality single crystals [24]. The weakness of this signal in the present spectrum thus points to a short coherent lifetime of free carriers states, possibly due to strain induced by the high polymer content. Indeed, neutron diffraction Bragg peaks in 4BCMU crystals start to broaden above $x_p \sim 7 \times 10^{-2}$ and evidence of strong disorder appears above $x_p \sim 0.1$ [19b].

The lower part of Fig. 5 shows the spectra of a 41 μm thick 3BCMU sample again in perpendicular polarization. Since, in this thinner sample, the polymer content $x_p = 3.3 \times 10^{-2}$ induced by γ -irradiation was too low for a study of the absorptions in the UV, the polymer content was increased by UV irradiation at 272 nm. The absorption spectrum shows the exciton at 1.917 eV with a low energy shoulder due to unresolved transitions at lower energy. The electroabsorption spectrum resolves a weak exciton at 1.878 eV and agrees in the range of the vibronic excitons with the derivative of the absorption spectrum. All derivative spectra were derived from the transmittance measured simultaneously with the electroabsorption spectra. The poorer agreement in the range of the peak absorption is attributed to the low transmittance together with a larger scattering background in the single monochromator setup. Spectra of samples with lower polymer content confirm the first derivative lineshape of the electroabsorption spectrum also in this spectral range. The Stark shift corresponds to a polarizability $p = 7710 \text{ \AA}^3$ and again agrees well with that of excitons on isolated chains $p = 7120 \text{ \AA}^3$ [4]. The signal above 2.5 eV is attributed to the band gap and a vibronic satellite. This signal increases sublinearly with the field and again its lineshape does not correspond to the derivative of the absorption. Note that this band gap signal is much more intense and better structured than the corresponding one in poly-4BCMU. This suggests that the 3BCMU monomer crystal is less perturbed by the polymerization process than 4BCMU, at least up to several percent polymer. This may be related to the fact that the mismatch between the polymer chain repeat unit length and the monomer lattice spacing is much smaller in 3BCMU [19].

The large polarizability of the excitons and the presence of the band gap signal confirm that the electronic states are not different from those of isolated chains,

although increasing inhomogeneity causes some broadening of the exciton and some reduction of the coherent lifetime of band states.

3.2.2. UV range

UV-spectra for perpendicular polarization are shown in Fig. 6. All spectral features below 4.4 eV appear only after polymerisation (see inset of Fig. 1). Poly-4BCMU shows a peak at 3.931 eV, with a satellite at 4.088 eV, most likely related to the double bond stretch mode (see also Fig. 4). Additional features at 4.177 and 4.252 eV are probably vibronic replicas of the triple bond and of the second harmonic of the double bond. A kink near 4.00 eV indicates another weak vibronic transition. The $\Delta\alpha$ spectrum again has a derivative lineshape, indicating a Stark shift of an exciton and its vibronic satellites.

The spectra of 3BCMU are very similar to those of 4BCMU. The absorption spectrum shows an exciton at 3.970 eV followed by a vibronic satellite at 4.138 eV and the weak transition near 3.78 eV, which is not observed for 4BCMU. The main features again have derivative lineshapes as in the 4BCMU spectrum. Weak signals are resolved at 4.217 eV, probably the triple bond replica, and near 4.35 eV, most likely the second harmonic of the double bond replica. Broader features with negative peaks appearing at 4.49 and 4.65 eV are not related to the onset of monomer absorption at 4.4 eV, but this onset probably explains why in that range the signal is very noisy. It is likely that this signal arises from the

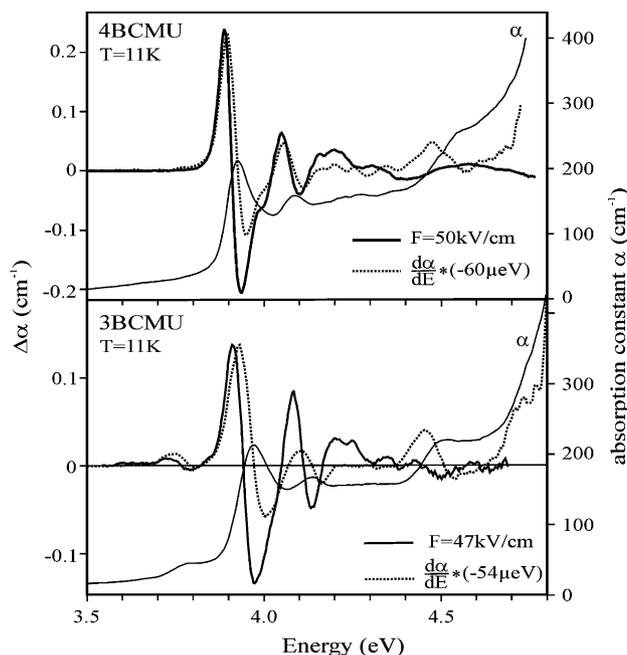


Fig. 6. Absorption α and electroabsorption spectra $\Delta\alpha$ of 4BCMU and 3BCMU in the UV region. The dotted line is the derivative of the absorption spectrum scaled by an energy shift to the height of the leading peak of $\Delta\alpha$. Field F parallel and polarization of light perpendicular to the chain.

continuum of the UV exciton. By comparing with the Franz–Keldysh effect of the exciton at 1.9 eV, a band gap near 4.46 eV is derived, hence an exciton binding energy of 0.5 eV, similar to that of the exciton at 1.9 eV.

All the stronger signals are also observed for parallel polarization with the same spectral shape and position. They are more difficult to measure due to the strong absorption tail extending from the visible region. The tail absorption decreases with increasing photon energy and is attributed to the exciton continuum which gives rise to the Franz–Keldysh effects near 2.5 eV. The strength of this absorption and the absence of an electroabsorption signal from the upper band edge, as expected from theory [25] and as seen in semiconductor superlattices [26], indicate that the upper edge of this π – π^* continuum has not yet been reached.

The peak-to-peak widths of the $\Delta\alpha$ spectrum of the UV exciton are 50 and 58 meV for 4BCMU and 3BCMU respectively, much broader than that of the excitons near 1.9 eV, indicating a much shorter lifetime of the order of 5–10 fs. Matching the leading positive peak of the $\Delta\alpha$ spectrum to the derivative of the absorption yields polarizabilities of 6910 and 7040 Å³ for 4BCMU and 3BCMU, respectively. The main uncertainty here is in the scaling of the derivative of the absorption to the electroabsorption spectra. Within that uncertainty, these polarizabilities are the same as those of the lower energy 1B_u excitons. These large polarizabilities show that the UV excitons also extend over several repeat units. It should be noticed that no clear signal is observed at the absorption edge of the monomer above 4.5 eV, consistent with the small size the corresponding states, localized on the diacetylene group which has a length of about 4 Å.

Although the $\Delta\alpha$ spectrum has a derivative lineshape, closer inspection reveals that the excitonic features of the electroabsorption spectra occur at lower energy than those of corresponding peaks in the derivative of the absorption. The energy shifts are 16 and 27 meV for 4BCMU and 3BCMU, respectively. The $\Delta\alpha$ spectra show in addition a stronger first negative peak than the derivative spectra. Such deviations are not observed for the much narrower spectra near 1.9 eV and indicate that the Stark shift is not the only response of the UV exciton to the electric field. Adding a component of second derivative lineshape improves the agreement to the $\Delta\alpha$

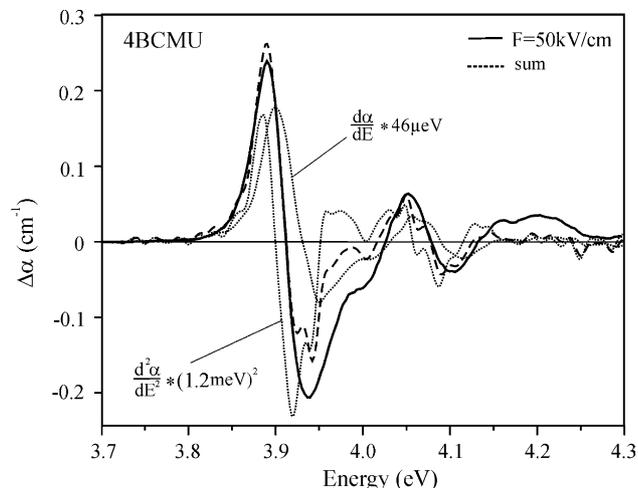


Fig. 7. Comparison of the electroabsorption spectrum (full line) of 4BCMU in the UV with the sum (dashed line) of properly scaled first and second derivative spectra (dotted lines). The dashed curve shows the sum of the derivative spectra. Fine structure of the second derivative of the absorption may be caused by interference fringes.

spectrum by shifting the modelled spectrum to the correct position and by enhancing the negative peak as shown for 4BCMU in Fig. 7. A similar improvement is obtained for 3BCMU.

The fit in Fig. 7 approximates the field induced change of the absorption by a sum of first and second derivatives of the absorption with scaling factors ΔE_1 and ΔE_2 :

$$\Delta\alpha = \frac{\partial\alpha}{\partial E} \Delta E_1 + \frac{\partial^2\alpha}{\partial E^2} \frac{(\Delta E_2)^2}{2}, \quad (2)$$

(the scaling factors were kept constant throughout the spectrum, but of course the ratio of the amplitudes of the two terms cannot be constant, since the lineshapes of first and second derivatives are different). A more detailed fit was not attempted, since the absolute values of the EA signal and its derivatives become less accurate at higher energies and the scattering background is no more negligible.

The scaling factor ΔE_1 is the Stark shift resulting from the exciton polarizability p along the chain. The derived value of p is smaller than above, since the Stark shift now only accounts for part of the signal (see Table 1).

The scaling factor ΔE_2 cannot be interpreted without understanding the underlying interaction with the field.

Table 1

Polarizability p and charge transfer dipole $\Delta E_2/F$ derived from scaling the electroabsorption spectra of the UV exciton to first and second derivatives of the absorption spectrum

	F (kV/cm)	Stark shift		CT dipole	
		ΔE_1 (μeV)	p (\AA^3)	ΔE_2 (meV)	$\Delta E_2/F$ ($\text{e}\text{\AA}$)
3BCMU	47	40 (55)	5220 (6910) \pm 10%	2.0	4.25 \pm 10%
4BCMU	50	46 (60)	5300 (7040) \pm 10%	1.7	3.4 \pm 10%

Values in parentheses are obtained if the signal is attributed to a Stark shift only.

Second derivative lineshapes may result from various effects. Recently it has been shown that coupling a strong transition dipole to the electric field yields such a second derivative lineshape [27]. This explanation can be excluded, since the oscillator strength of the UV exciton ($f \approx 4\text{--}5 \times 10^{-3}$) is far too small. We exclude also field-induced lifetime broadening, since it would result in a pronounced effect in the case of the much narrower exciton transition at 1.9 eV. Contributions of a second derivative lineshape may indeed arise from a linear Stark effect with exchange of oscillator strength between nearly degenerate states of different symmetry, if the field-induced splitting is comparable to the zero-field splitting, a situation encountered in weak charge-transfer transition [28]. The ratio of ΔE_2 and the field F then corresponds to the charge transfer dipole qr . The large value of qr , 3–4 eÅ, indicates that significant charge must be transferred over a distance of the order of the repeat unit.

4. Discussion

To summarize, the UV absorption studied here corresponds to an exciton, since one observes absorption lines, and since they respond to electric fields by a large quadratic Stark shift. Since this exciton is degenerate with the continuum associated to the lower lying $1B_u$ exciton, some coupling is expected, which may account for the deviation from a pure quadratic Stark shift in electroabsorption, modelled as a second derivative with a scaling factor ΔE_2 .

The new excited state of the polydiacetylene chain must involve delocalized π electrons to explain its large polarizability. However, it cannot involve delocalized π electrons only, since the transition is polarized primarily perpendicular to the chain direction. Therefore, the absorption does not correspond to high energy neutral states of u symmetry predicted in recent theoretical calculations dealing with delocalized π electrons only [29].

The most reasonable assignment is to a transition between a π level localized on the triple bonds (in the chain plane) and a delocalized π state of the double–triple bond system. Such an exciton is made of a heavy hole (in the very narrow valence band corresponding to the weakly coupled acetylenic π electrons) and a light electron in the very wide conduction band of the delocalized π electrons. Its polarizability is then expected to be similar to that of the exciton involving delocalized π electrons only. Such a transition should also have a substantial perpendicular component. The transition dipole should lie in the plane of the chain. If that plane has the same orientation as the plane of the DA groups, it makes in 3BCMU an angle of about 45° with the (a, b) plane [19], and the true dichroic ratio should be about 50% larger than estimated from the measured absorptions. The angle in 4BCMU is not known, but since the overall unit cell and molecular shape

are similar to that of 3BCMU, a similar angle should be expected in 4BCMU as well.

One would expect this transition to be forbidden or weakly allowed by symmetry. However, the electroabsorption data show that the spectrum is not built on a false origin, since the true origin would then become weakly allowed in the electric field, giving rise to a growing peak in the electroabsorption spectrum that is not observed. The UV exciton is resonant with the ionization continuum associated to the $1B_u$ exciton, which is observed in the same energy range as a continuous background absorption in the parallel polarization, slowly decreasing towards higher energies (see Fig. 2). The UV exciton lies approximately 2 eV above the $1B_u$ exciton absorption in the visible. An angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) study of a poly-4BCMU single crystal film has located the second valence band edge approximately 2.5 eV below the top of the uppermost valence band [30]. Moreover, the two bands overlap, so a strong mixing of these states is likely as required by the proposed assignment. The short exciton lifetime of 5–10 fs, derived from the absorption widths is then a natural consequence of the coupling.

Strong mixing of the triple bond state with the delocalized π band also explains the second derivative lineshape of the electroabsorption spectrum. Weak oscillator strength and a large charge transfer component is expected if an electron is excited from a localized triple bond to the delocalized states of the chain. The charge transfer dipole of 3–4 eÅ then corresponds to the mean displacement of an electron charge in that excitation process.

A transition of this type should be absent in polyenes. Indeed, Leising has measured the reflectivity of oriented *cis*- and *trans*-polyacetylene up to 4.1 eV and no such transition is observed in that energy range [31]. In theoretical calculations concerning PDA, the triple bond is usually taken into account only in that it determines the chain geometry, with two types of conjugated bonds of unequal lengths within a single π conjugated system [29]. That approximation is validated since we find here the electronic transitions involving the acetylenic π electrons around 4 eV, that is, far enough from the low lying excited states of the π electron system. Still, the localized acetylenic π electrons lying in the chain plane are also coupled to the main π electrons system, and must be included in any complete description of the PDA electronic structure. In other words, polydiacetylenes are not simply slightly distorted polyenes.

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