

Linear, non-linear and Raman spectroscopy of polydiacetylenes

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(Received 15 September 1988; revised 14 December 1988; accepted 18 January 1989)

Polydiacetylenes (PDA) exhibit a subpicosecond third-order non-linear response whose coefficient ($\chi^{(3)}$) in the transparent region is the largest of any material. With a view towards the design and synthesis of materials with further enhanced values of $\chi^{(3)}$, the crystal structure-linear spectroscopy relationship for PDA is developed. The significance of the local crystal packing environment of the conjugated chain to the linear spectrum is discussed, with particular reference to the thermochromic derivative, bis-ethyl urethane of 5,7-dodecadiyne-1,12-diol (poly-ETCD). The room-temperature resonance Raman (RR) spectrum of poly-ETCD is sensitive to both the wavelength of excitation and the presence of unreacted monomer. When excited with 488.0 or 514.6 nm light, the observed RR spectra of as-polymerized poly-ETCD crystals reveal the presence of two PDA electronic states. Extraction of residual monomer from such crystals leads to a marked diminution of the lines associated with the lower-energy spectral state. The electronic states of conjugated polymers in the solid state are better discussed in terms of different crystal environments rather than different effective conjugation lengths.

(Keywords: polydiacetylene; non-linear optics; linear spectroscopy; thermochromism; Raman spectra)

INTRODUCTION

The linear and third-order non-linear optical properties associated with the conjugated backbone of polydiacetylenes (PDA, **1**) have attracted the attention of numerous investigators over the past 15 years^{1,2}. This follows from the availability of PDA in the form of macroscopic single crystals, making them nearly ideal systems for the study of a one-dimensional electronic structure. Herein, the wavelength and temporal responses of the third-order non-linear optical processes in PDA are summarized. In the interest of enhancing these properties, especially involving the synthesis of new materials, a good understanding of a crystal structure-linear spectroscopy relationship is needed. Our recent studies³⁻⁶ of such a relationship in the thermochromic PDA derivative, poly-ETCD (**1a**), provide useful insights into this problem, and additional detail is revealed in resonance Raman (RR) studies of single crystals of this material.

THIRD-ORDER NON-LINEAR OPTICAL PROCESSES IN POLYDIACETYLENES

The following remarks are intended to summarize third-order non-linear optical phenomena as they are currently discussed in PDA^{7,8}. In bulk media, there is a non-linearity in the relationship between induced polarization (P_i) and the light field amplitude, which is expanded as a power series of electric-field components:

$$P_i = \chi_{ij}^{(1)} E_j + \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j E_k E_l + \dots \quad (1)$$

The linear optical properties are represented by $\chi^{(1)}$,

and the second- and third-order non-linear susceptibilities are represented by $\chi^{(2)}$ and $\chi^{(3)}$, respectively. $\chi^{(2)}$ occurs only in non-centrosymmetric media and is not discussed further here⁹.

In general, the third-order non-linear susceptibility describes the generation of a fourth frequency, ω_4 , due to input frequencies ω_1 , ω_2 and ω_3 . It is the quantity that describes the change in dielectric constant ϵ_1 with optical intensity. For an isotropic material, when expanded to the first non-linear term, ϵ is given by:

$$\epsilon = \epsilon_1 + 4\pi\chi^{(3)}|E|^2 \quad (2)$$

Since the non-linear contribution to ϵ is much smaller than the linear one, the index of refraction, n , may be written:

$$n = n_1 + n_2 I \quad (3)$$

where I is the optical intensity and n_2 , the non-linear index of refraction, is given by:

$$n_2 = 16\pi^2\chi^{(3)}/c\epsilon \quad (4)$$

where c is the velocity of light.

Experimentally, the first measurement of $\chi^{(3)}$ in a PDA was performed on bulk single crystals of poly-PTS (**1b**) by third-harmonic generation¹⁰. This process is described by $\chi^{(3)}(3\omega)$, where $\omega_4 = \omega + \omega + \omega = 3\omega$. This work indicated that parallel to the PDA chain, poly-PTS has the largest value of $\chi^{(3)}(3\omega)$, approximately 10^{-10} esu, of any material in its transparent region. Moreover, the temporal response was inferred to be in the subpicosecond regime.

For further study of PDA non-linear optical phenomena, samples in planar waveguide configuration are desirable. This was initially accomplished using

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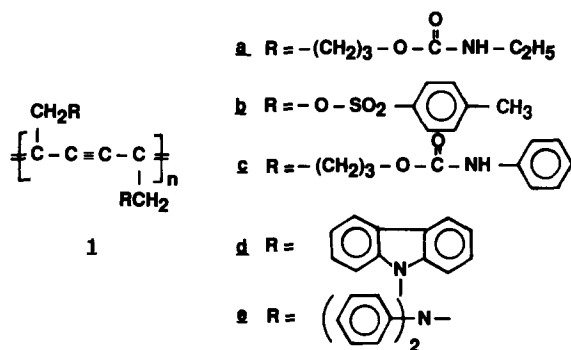
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Langmuir–Blodgett (LB) multilayers^{7,8}, and techniques for single-crystal PDA thin-film growth were developed^{7,11}.

Using optical-quality thin-film single crystals of poly-PTS, degenerate four-wave mixing experiments revealed that $\chi^{(3)}(\omega)$ was approximately 10^{-10} esu in the transparent region and that $\chi^{(3)}(\omega)$ was resonance enhanced to approximately 10^{-8} esu at 6515 \AA^{12} . Further experimentation, ultimately with 60 fs pulses, indicated that the excitonic state lifetime was 1.8 ps, and an initial excited-state process with a 100 fs lifetime was resolved^{13,14}.

A ground-state recovery time after resonant excitation of approximately 2 ps has been subsequently confirmed in both reflection¹⁵ and transmission¹⁶ studies on poly-PTS. The femtosecond time-resolved transient reflectivity measurements¹⁵ performed at the peak of the excitonic absorption find a value of n_2 three orders of magnitude larger than that found¹² in the absorption tail.

While PDA have the largest non-resonant $\chi^{(3)}$ of any material, it is desirable to find materials with still larger values. Towards this end, a better understanding of crystal structure–linear spectroscopy relationships is required for PDA, as discussed in the next section.



LINEAR SPECTROSCOPY AND THERMOCHROMISM OF POLYDIACETYLENES

The intense visible absorption associated with the conjugated PDA backbone has been studied in thick single crystals, primarily by polarized specular reflectance techniques^{17,18}. It is common practice to discuss the observed 300 K spectra of PDA as dividing into two classes, a 'red' spectrum with maximum absorption in the range 540–570 nm (e.g. bis-phenyl urethane of 5,7-dodecadiyne-1,12-diol (poly-TCDU) (1c) and lacking significant structure, and a 'blue' spectrum with absorption maximum in the range 600–660 nm (e.g. poly-PTS, poly-ETCD) with a band revealing significant structure. An understanding of the factors that give rise to 'red' and 'blue' PDA spectra would appear to be a central issue in the design and synthesis of new PDA with modified linear and non-linear spectral features.

At present, there is a broad consensus that the observed solid-state electronic spectra of conjugated polymers, including the fully crystalline PDA^{6,17,19–22} and the partially crystalline polyacetylene $(\text{CH})_x$ ^{6,23}, should be discussed in terms of the conventional approach²⁴, briefly summarized by:

$$E_k = E_0 + D + I(k) \quad (5)$$

where E_0 is the transition energy in the gas phase, D includes the energetics of the gas-to-solid shift, and $I(k)$

summarizes the exciton transfer interaction between equivalent and non-equivalent moieties.

It is convenient to regard the PDA chain as being embedded in a polarizable medium^{20,21}, i.e. the side-groups of the PDA act as a polarizable 'solvent' for the backbone. In this perspective, a major contributor to D in (5) would be a 'solvent shift' W :

$$W = \alpha_s n / 6R^6 (M^2 + E\alpha_c / 4) \quad (6)$$

where the polarizabilities of the conjugated chain and side-groups are α_c and α_s , respectively, the distance from the chain to the side-groups is R , and the number of side-groups is n . For poly-PTS, it has been estimated¹⁷ that W is about 15% of E_k .

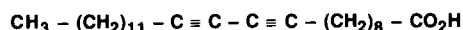
The PDA poly-ETCD exhibits thermochromism^{25,26}; near room temperature its absorption maximum is at 635 nm, while above 125°C the absorption maximum is observed at 540 nm. A knowledge of the factors underlying the poly-ETCD thermochromic phase transition will likely be generally useful in understanding the structure–spectra relationships in PDA.

In the initial specular reflection study²⁵ of thermochromism in poly-ETCD, it was suggested that the phase transition was due to an acetylene to butatriene transformation. Additionally, it was reported that the c axis dimension, and hence the crystallographic unit-cell volume, decreased as poly-ETCD was heated from 23 to 130°C. More recently, the possibility of an acetylene–butatriene transformation has been ruled out on theoretical grounds²⁷ and by the solid-state ¹³C cross-polarization/magic-angle spinning (CP-MAS) n.m.r. studies²⁸. Further, X-ray powder diffraction studies of poly-ETCD demonstrate that the unit cell expands 3.7% in volume on heating from 20 to 135°C⁵ rather than the contraction previously reported²⁵. Both Fourier-transform infra-red spectra³ and ¹³C CP-MAS n.m.r. spectra of poly-ETCD²⁸ reveal that the hydrogen-bonding network is not significantly disturbed by the thermochromic transition and that conformational changes occur in the methylene groups of the side-chain. In summary, thermochromism in poly-ETCD involves a first-order phase transition in which the unit-cell volume expands by 3.7%. The spectral shift to higher energy involves a conjugated backbone with more loosely packed surroundings at 135°C compared to 20°C.

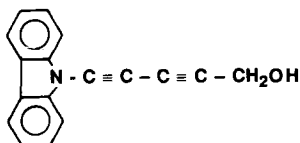
The similarity in the molecular structures of 1,6-(di-N-carbazolyl) 2,4-hexadiyne (poly-DCH) (1d) and 1,1,6,6-tetraphenyl-2,4-hexadiylenediamine (poly-THD) (1e) invites a comparison of their electronic spectra²⁹. It is convenient to regard these two PDA as a 'chromic pair' since the maximum reflectivity for poly-DCH is at 15250 cm^{-1} (refs. 19, 29), while that of poly-THD is at 17575 cm^{-1} (ref. 29). Since the poly-THD crystal structure exhibits a planar backbone, it follows that a PDA with a red spectrum need not have a non-planar backbone. For poly-THD, the unit-cell repeat volume is 2.4% greater than that of poly-DCH²⁹. The blue–red spectral changes in the poly-DCH/poly-THD pair and in poly-ETCD scale with unit-cell repeat volume. From these examples, following equation (6), the PDA with the more 'loosely packed' environment absorbs at higher energy.

Fatty-acid PDA prepared as LB films have long been known to exist in blue and red forms^{30,31}. Electron diffraction and small-angle X-ray techniques were used to study the conversion of the blue form of the PDA of the

Cd^{2+} salt of pentacos-10,12-diyonic acid (**2**) to the red form³¹. The orthorhombic blue form may be thermally converted to a slightly less dense triclinic form³¹. More recent high-resolution X-ray diffraction studies³² of five bilayer LB films of both blue and red forms of the Cd^{2+} salt of **2** revealed that long-range order was destroyed upon conversion of the blue to the red form. The electron density profiles in these studies indicated that the terminal CH_3 groups of **2** are well ordered in the blue form and 'disordered' in the red form. The results of these studies^{29,30} are consistent with the view that the blue-red spectral change is associated with a structural conversion to a more 'loosely packed' environment.



2



3

The synthesis of 1-(*N*-carbazolyl)penta-1,3-diyne-5-ol (**3**) and its conversion by ultra-violet or ^{60}Co gamma radiation to a material with an absorption maximum at 670 nm, a wavelength slightly longer than the poly-DCH maximum, has been recently reported^{33,34}. On the assumption that the material with the 670 nm absorption maximum has a PDA backbone structure, it was suggested that this material had a longer π -conjugation length than other known PDA. In view of the discussion herein on environmental effects on PDA absorption, the placement of the polarizable carbazolyl group directly on an acetylene carbon of a potential PDA backbone and possible local mechanical strains can qualitatively account for a 670 nm absorption maximum. In the initial spectral study of poly-DCH¹⁹, it was suggested that the effect of carbazolyl groups was to increase the polarizability of the chain environment. The potential role of conjugative effects between the backbone and carbazolyl group in **3** needs to be assessed.

EXPERIMENTAL

The synthesis, single-crystal growth and polymerization of ETCD were performed as previously reported^{5,35}. Extraction of poly-ETCD crystals with boiling methanol gave colourless extracts containing only ETCD monomer. Resonance Raman (RR) spectra were recorded as previously described^{36,37}. The wavelengths used for excitation are 488.0, 514.6, 570.2, 572.5, 591.6 and 632.8 nm.

RAMAN SPECTROSCOPY OF POLYDIACETYLENES

The utility of resonance Raman (RR) spectroscopy, also a third-order non-linear optical process, as a sensitive probe of PDA structure and electronic states was amply demonstrated in studies of poly-PTS, where complete excitation profiles were obtained for many normal modes, and other PDA by Batchelder and Bloor^{17,38}.

Additionally, RR techniques have been applied to the study of external mechanical strain in PDA³⁹, ion implantation in PDA⁴⁰, LB monolayer electronic structure³⁶ and the chemical modification of poly-DCH by bromine⁴¹.

The thermochromic phase transition of poly-ETCD was studied by RR spectroscopy using powdered samples²⁶. Motivated by the disordering of poly-ETCD crystal structure by the extraction of unreacted monomer^{4,5}, we have studied RR spectra of single crystals of poly-ETCD as a function of both wavelength of excitation and the presence of unreacted monomer⁴². The shift of the reflectance spectra of partially polymerized urethane-substituted PDA to higher energy upon solvent extraction of monomer was reported earlier⁴³. However, no X-ray diffraction data are reported in that work.

With excitation at 632.8 nm, RR spectra (20°C) of both as-polymerized (Unex) and methanol-extracted (Extr) poly-ETCD single crystals are in accord with the earlier data²⁶ for powdered samples with the exception that the shift reported²⁶ at 1254 cm^{-1} is at 1212 cm^{-1} in our spectra. The subsequent discussion herein will focus on the shifts associated³⁸ with the normal modes primarily involving triple-bond stretching and double-bond stretching. This information is summarized in Table 1 along with analogous information for two completely polymerized PDA with blue spectra (PTS, DCH) and one with a red spectrum (THD).

Markedly different RR spectra are observed for poly-ETCD crystals (Unex) when shorter excitation

Table 1 Resonance Raman spectra of PDA: shifts associated with triple (ν_1) and double (ν_2) bond stretching

PDA	λ_{exc} (nm)	ν_1 (cm^{-1})	ν_2 (cm^{-1})
PTS	632.8	2086	1485
DCH	632.8	2089	1494, 1472, 1456, 1426
THD	632.8	2111	1472
ETCD (Unex and Extr)	632.8	2082	1456
ETCD (Unex)	514.6	2115	1527
		2080	1456
ETCD (Extr)	514.6	2118	1525

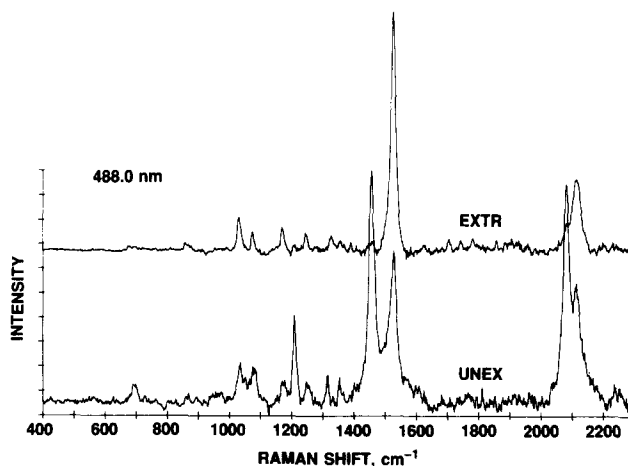


Figure 1 Resonance Raman spectrum of both as-polymerized (Unex) and methanol-extracted (Extr) single crystals of poly-ETCD recorded at 20°C

wavelengths are used; the data for 514.6 nm excitation are summarized in *Table 1*, and *Figure 1* exhibits the similar spectrum obtained with 488.0 nm excitation. In *Figure 1*, the triple-bond stretching region exhibits peaks at shifts of 2081 and 2113 cm^{-1} , while shifts of 1456 and 1531 cm^{-1} are observed in the double-bond stretching region. The RR spectra of poly-ETCD single crystals observed at room temperature with 488.0 and 514.6 nm excitation imply that both 'red' and 'blue' electronic states are present in the crystal. This observation is relevant to an earlier discussion by Batchelder and Bloor³⁸ concerning electronic states in poly-ETCD.

In the earlier RR study of poly-ETCD powders²⁶, visible absorption spectra of these powders dispersed in KBr exhibited three bands at 630, 540 and 460 nm. These bands were interpreted²⁶ to imply three different delocalization lengths on the PDA backbone, and room-temperature RR spectra of the powder were discussed from this perspective. In a review article³⁸, Batchelder and Bloor noted the similarity in room-temperature Raman shifts with 530.8 nm excitation and the shifts in the high-temperature ('red') phase and suggested that the lowest Raman and optical wavenumbers are due to polymer in the low-temperature ('blue') phase and that the Raman shifts noted with 530.8 nm excitation are due to polymer in the high-temperature phase which persists below the thermochromic phase transition. Restated, Batchelder and Bloor suggest that both 'blue' and 'red' phases of poly-ETCD coexist in the crystal at room temperature, a proposal in accord with our observations of poly-ETCD (Unex) at room temperature with 488.0 and 514.6 nm excitation.

Earlier, RR spectra (1.98 eV excitation) of thermally polymerized crystals of the PDA from the bisethylurethane of 2,4-hexadiyn-1,6-diol (EUHD) revealed two peaks in the triple-bond stretching region and three peaks in the double-bond stretching region⁴⁴. X-ray diffraction studies⁴⁵ of this modification of poly-EUHD indicate the presence of two phases in each of these crystals.

With both 488.0 and 514.6 nm excitation, the RR spectra observed after the crystals are extracted with boiling methanol reveal a marked diminution of the lines associated with the 'blue' phase. This information is summarized in *Table 1* and *Figure 1* (Extr). In *Figure 1*, the relevant shifts are found at 2113 and 1530 cm^{-1} . Hence, removal of unreacted monomeric ETCD by methanol extraction results in the loss of the 'blue' states with short-wavelength excitation.

The changes in the RR spectra of poly-ETCD single crystals with removal of monomer by methanol are viewed from the perspective of changes in the environment of the PDA chain, as discussed above for PDA linear spectroscopy. The presence of monomer and its attendant intermolecular interactions (including possible mechanical strains) in as-polymerized poly-ETCD crystals leads to a 'blue' RR spectrum with 632.8 nm excitation and both 'red' and 'blue' spectra with the higher-energy excitations. Monomer extraction leads to a slight disordering of the crystal structure^{4,5} along with loss of the intermolecular interactions of the monomer (including possible mechanical strains). Thus, in poly-ETCD (Extr), the local environment of the PDA backbone differs from that found in as-polymerized crystals, and the 'blue' spectrum is largely lost with shorter-wavelength excitation.

CONCLUSIONS

The broad general perspective that the local crystal packing environment around the chain of a conjugated polymer (e.g. PDA or $(\text{CH})_x$) is a key element of the crystal structure-linear spectroscopy relationship for these materials provides a useful starting point for the design of new materials with improved third-order non-linear optical properties. A more quantitative assessment of the various terms in equation (5) and other possible interactions is clearly in order. The role of substituents potentially providing direct conjugation between a side-chain and a PDA backbone is uncertain at present^{46,47}. It is probably more useful to discuss solid-state electronic spectra of conjugated polymers which lack chemical crosslinks in terms of different crystal environments rather than different 'effective conjugation lengths' or 'effective delocalization lengths'.

ACKNOWLEDGEMENTS

The authors thank S. Brown and C. S. Velazquez for their technical assistance.

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