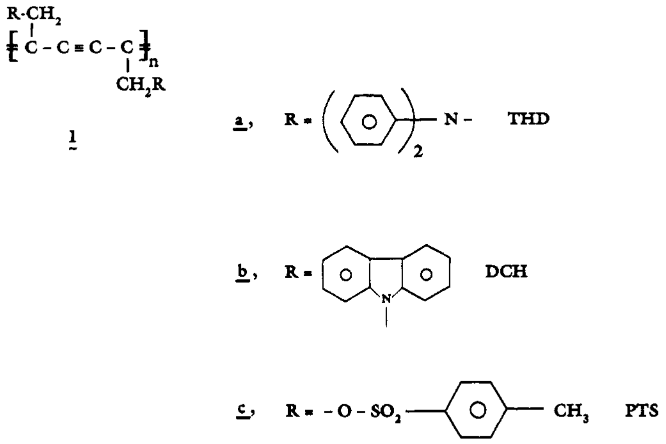
Communications to the Editor

Raman Spectroscopic Evidence for a Surface Phase on As-Polymerized Single Crystals of the Polydiacetylene from THD[1]

The polydiacetylenes (PDA; 1) are a class of polymers with conjugated backbones available in the form of macroscopic single crystals.[2] As such, they are the best defined class of polymers. While they are often described as "perfect" crystals, defect structures have been observed.[3] In this work, we present Raman spectroscopic evidence that the surface of the crystals of the PDA from 1,1,6,6-tetraphenylhexadiynediamine (THD; **1a**) has a structure distinct from the bulk crystal. The surfaces of crystals often have significant effects on the observed chemical and physical properties of the bulk solids.



In connection with comparative studies of the chemical reactivity[4-8] and spectroscopy[9] of single crystals of **1a** and the PDA from 1,6-di-*N*-carbazolyl-2,4-hexadiyne (DCH; **1b**), we have studied Raman spectra of single crystals of **1a** as a function of the wavelength of excitation, and we discuss the observations as providing evidence of a distinct PDA surface phase on crystals of **1a**. We conclude that the surface structure in **1a** arises because, in contrast to the bulk of the crystal, surface structure is not well controlled by the topochemical solid-state polymerization. Hence, surface structure in **1a** is distinct in origin from the photooxidized surface of the PDA from the bis(*p*-toluenesulfonate) of 2,4-hexadiyne-1,6-diol (PTS; **1c**).[10]

Electronic spectroscopy of **1a**[9] shows maximum absorption at 568 nm with a molar absorption coefficient greater than $5 \times 10^5\ \mathrm{cm^{-1}}$. Wavelengths of Raman excitation used in the present study are 1064, 632.8, 514.5, 488.0, and 457.9 nm. The blue and green argon laser lines probe regions of intense absorption in **1a**. Raman spectra obtained in this study were recorded as previously described.[7] The Raman spectrum obtained with 632.8 nm excitation polarized parallel to the backbone is displayed in Figure 1a. In this spectrum, the normal modes associated with triple-bond stretching and double-bond stretching are observed at shifts of 2115 and 1485 $\mathrm{cm^{-1}}$, respectively, in good agreement with the previous report,[9] as are the shifts of other Raman lines. These two modes will be the primary focus of discussion. The Raman spectrum of **1a** obtained from excitation at 1064 nm, a transparent wavelength, reveals the triple-bond and double-bond stretches at 2111 and 1485 $\mathrm{cm^{-1}}$, respectively. Additionally, the 1064-nm spectrum reveals a weak shoulder near 2099 $\mathrm{cm^{-1}}$. With 632.8-nm excitation, some crystals in the present study reveal a shoulder at approximately 2102 $\mathrm{cm^{-1}}$, and a weak shoulder at 2097 $\mathrm{cm^{-1}}$ was reported earlier.[9]

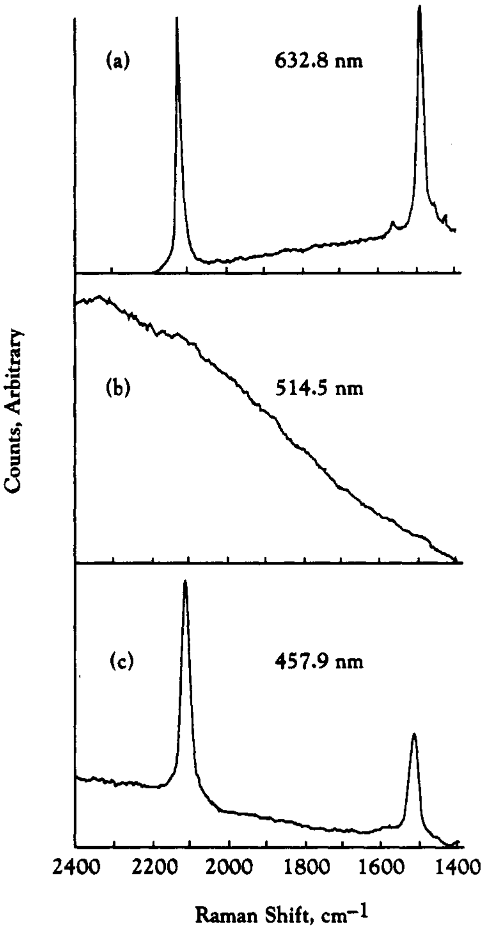


Figure 1. Raman spectra of **1a** recorded with light polarized parallel to the polymer chain axis with a band-pass of $\pm 5\ \mathrm{cm^{-1}}$ at 19 436 $\mathrm{cm^{-1}}$.

In marked contrast to the spectrum in Figure 1a is the spectrum obtained with 514.5-nm excitation. Displayed in Figure 1b, a broad, featureless, laser-induced emission peaking at a Stokes shift of about 2300 $\mathrm{cm^{-1}}$ completely obscures any hint of a Raman spectrum. This emission is noteworthy because it is found at an energy comparable to the maximum associated with excitonic absorption of **1a**. Moreover, emission from high-quality PDA crystals is negligible,[11] and observed emissions in solid PDA are attributed to disorder from mechanical damage or photooxidation.[11] If the usual "mirror image" relationship between absorption and fluorescence spectra may be assumed, it is estimated that an absorption maximum leading to the emission in Figure 1b would be in the 450–460-nm region. An absorption maximum in this wavelength region is characteristic of disordered PDA materials.[12] Other conceivable origins of the emission in Figure

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1b could be emission from a surface arylamine group or emission from a trace metal or other surface impurity. If data from a recent study[13] of emissions from arylamines are compared to our data, it is unlikely that the wavelengths of excitation used by us would excite such species. The spectrum in Figure 1b has much less structure than those reported.[13] At present, it is not possible to rigorously exclude the possibility of a surface impurity.

When 457.9-nm excitation is used, the spectrum in Figure 1c is observed on a weak, luminescent background. This spectrum is clearly different from that in Figure 1a and, hence, must have a different origin. The shifts associated with triple-bond and double-bond stretching are broader than those of Figure 1a and are observed at 2105 and 1504 cm^{-1}, respectively. Spectra observed using 488.0 nm as the wavelength of excitation reveal a Raman spectrum superimposed on an emission. The data in Figure 1 are found in crystals freshly polymerized in inert atmosphere, in crystals exposed to ambient conditions for extended periods of time, and in samples with freshly cleaved surfaces. Data in Figure 1 were recorded at 20 °C but do not differ significantly when recorded at −100 °C.[14] Further, crystals polymerized thermally and with ^{60}Co γ radiation gave similar data.

It is recognized that resonance Raman spectroscopy of PDA bulk single crystals is primarily a probe of the surface region of these crystals.[15] The most concise view of the spectra of parts b and c of Figure 1 is to associate them with a disordered PDA–THD surface structure, as well-ordered PDA do not emit light.[12] Additional shifts found in the 457.9-nm spectrum correspond well to those found in **1a** at longer wavelengths of excitation.[9] The shift at 2105 cm^{-1} in Figure 1c may correspond to the shoulders found near 2100 cm^{-1} in the 1064-nm spectrum and in some 632.8-nm spectra.[16]

A disordered surface phase of **1a** could arise by failure of the surface to control the topochemical and topotactic solid-state polymerization of the THD monomer, which is well controlled in the bulk of the crystal.[17] A corollary to this statement is that other PDA crystals might be expected to have disordered surface structures. Raman spectral indications of such surface structures are found in the spectrum of **1c** obtained with 406.8-nm excitation where "satellites" are found for both double-bond and triple-bond stretching modes[18] and in the spectrum of **1b** obtained with 457.9-nm excitation.[19] The latter spectrum appears on a weak fluorescent background, and the region associated with the double-bond stretching mode is considerably broadened compared to spectra of **1b** recorded with longer wavelengths of excitation.[6,8,9,15,19,20]

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References and Notes

(1) Preliminary accounts of portions of this work were presented at the 199th National Meeting of the American Chemical Society, Boston, MA, April 22–27, 1990, Abstracts of Papers, PHYS 211, and the Twelfth International Conference on Raman Spectroscopy, Columbia, SC, August 13–17, 1990; proceedings, p 738.

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(14) The data in Figure 1 are not the result of thermal decomposition induced by heating of the crystal by the incident laser beams. However, decomposition may be induced by irradiating the crystals with a higher laser power. Hankin, S.; Sandman, D. J., unpublished experiments.

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(16) We have considered the possibility that the shoulders near 2100 cm^{-1} in the 1064 and some 632.8-nm spectra could be associated with a second bulk phase in crystals of **1a**. Precession and Weissenberg photographs of crystals of **1a** are consistent with the reported[17] structure and provide no evidence for a second bulk phase. (Hamill, G. P., private communication.)

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