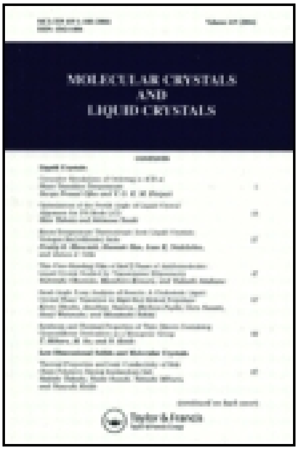

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Stress Induced Change of Electronic Structure in a Polydiacetylene Crystal†

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A stress induced change of phase in a single crystal of the polydiacetylene, TCDU, is observed wherein a change of electronic configuration of the polymer from a butatriene to an acetylenic electronic configuration is indicated. The stress induced phase is stable and is coexistent with the parent phase.

I INTRODUCTION

Interest in the electronic spectra and structure of polydiacetylenes has increased because their fully conjugated spine provides a model quasi-one-dimensional system which may be represented by the canonical structures shown in Figure 1. In the PTS polydiacetylene single crystal (R is $-CH_2SO_3C_6H_4CH_3$), x-ray crystallographic determination[1] has shown the acetylenic structure (I) to be characteristic. At temperatures below 200 K, the PTS unit cell doubles along the *c*-axis.[2] This results in two inequivalent sets of polymer chains in the unit cell which leads to an accompanying increase in complexity of the crystal spectra[3] since the number of bands will have doubled. Recently, the DCHD polydiacetylene crystal and molecular structure (R is a carbazolyl group) has been determined[4] wherein the acetylenic bonding pattern is also observed. In contrast to the PTS, however, no low temperature transition is observed in DCHD and the spectrum resulting from such a phase change is free of the congestion observed in the PTS. An important difference in the optical spectra of the two acetylenic systems is the energy at which the lowest reflection bands are observed at 300 K. In PTS this peak is found at 16,200 cm^{-1} (Ref. 3)

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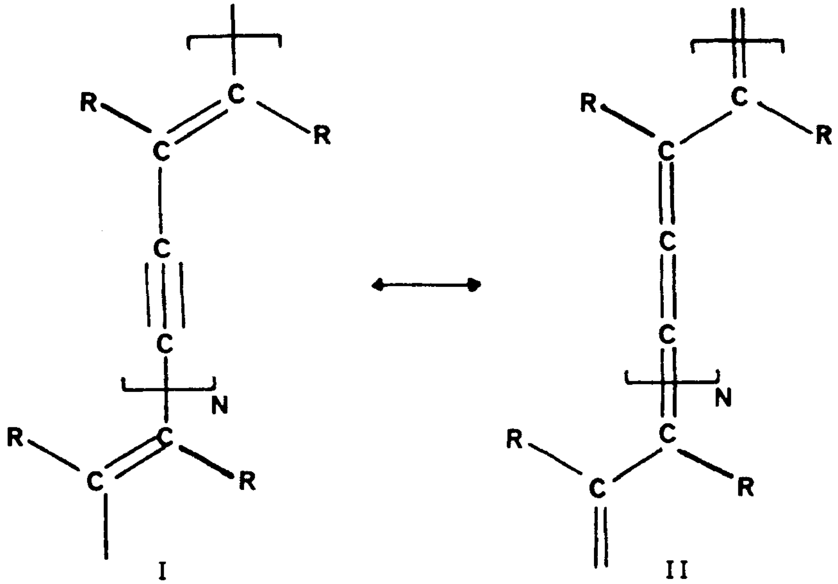

FIGURE 1

whilst in DCHD, the prototype acetylenic system, the lowest energy peak is observed at 15,300 cm^{-1} (Ref. 5). The x-ray structure of another polydiacetylene crystal, TCDU (R is $-(CH_2)_4OCONHC_6H_5$), has been determined[6] wherein the bonding pattern of the spine is that of the butatriene structure (II). Optical spectroscopic study of the TCDU crystal supports this structure.[7] Resonance Raman spectroscopy has further shown that the TCDU undergoes a reversible phase transition at temperatures less than 100 K or at pressures greater than 1.5 kbar.[8] This was conjectured to be different than the phase transition observed in PTS since it was suggested that the TCDU underwent a change from the butatriene to the acetylenic form.[8]

We report a stress induced phase transformation in TCDU which displays coexistent regions of both the butatriene and acetylenic forms of the polydiacetylene spine. The optical spectra observed for the two forms are akin to those reported for the two forms of the thermochromic polymer ETCD (R is $-(CH_2)_4-OCONHC_2H_5$),[10] but differ in that the induced phase is apparently stable.

By use of both modulated piezoreflectance and specular reflection spectroscopy, it has been shown that the acetylenic structure (I) may be associated with a characteristic golden metallic reflection which may be generally represented by the PTS or DCHD reflection spectra[3,5,9] (Figure 2). In

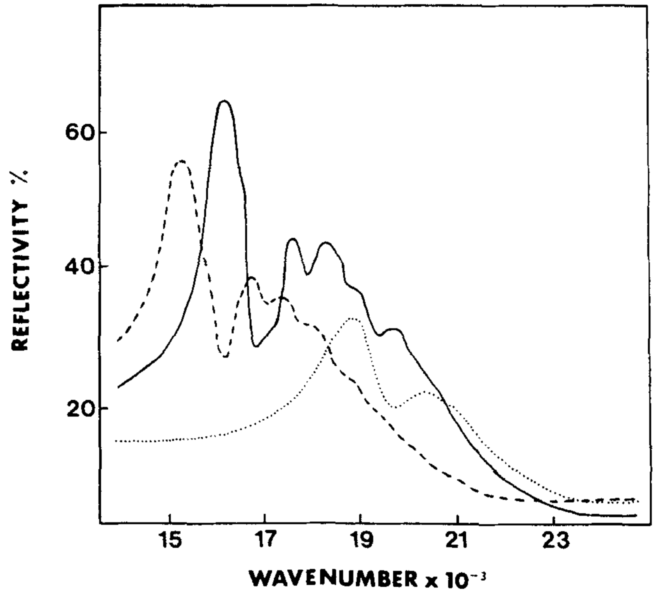

FIGURE 2 Specular reflection spectra of polydiacetylene crystals at 300 K with light polarized along the polymer chain direction: PTS (solid line); DCHD (dashed line); TCDU (dotted line).

contrast, the greenish metallic sheen of TCDU, which is associated with the butatriene structure (II), shows a spectrum which is blue shifted from that of DCHD by nearly 0.4 eV (Figure 2).[3]

The thermochromic ETCD polydiacetylene crystal shows a transition between the acetylenic and butatriene structures as the crystal is cycled between 300 K and 400 K.[10] Although a hysteresis is found, the golden metallic appearance of the crystals observed at 300 K cycles repeatedly to a green sheen at 400 K. The reflection peaks are at 18,500 cm^{-1} and 15,750 cm^{-1} respectively.

In an effort to further induce such transformations of the electronic structure of polydiacetylene crystals, the TCDU crystal was selected for further piezo-optic study. Because of the aforementioned resonance Raman studies at high pressure, this system was regarded as one most likely to display the desired effect.

II EXPERIMENTAL

Crystals of TCDU are monoclinic at 300 K with two monomeric units in the unit cell belonging to the $P2_1/c$ space group. The cell constants are: $a = 4.909$,

$b = 39.027$ and $c = 6.229$ Å with $\beta = 106.85°$. The chain direction is parallel to the a-axis.

A crystal of TCDU was mounted in epoxy on a lead-zirconate titanate ceramic disk and cooled to 77°K. This procedure subjects the crystal to great stress due to the contraction of the ceramic and epoxy. The strain induced on going from 300 K to 77 K has been determined by embedding a silicon strain gauge (BLH No. SR4) in the epoxy bonded to the ceramic and cooling to 77 K. A compressional strain of -1.5×10^{-3} at 77 K was imposed by the epoxy-ceramic mount on the expanding TCDU. The stress was essentially in the (010) plane of the crystal and may be taken to be isotropic in that plane.

The entire sample was contained in a cell with a quartz window. The cell can be fit into a microspectroreflectometer which allows direct observation of the sample either visually or photomicrographically. Polarized normal incidence reflection spectra are obtained through a dual beam arrangement wherein the light beam is divided with one part incident upon the sample and the other upon a reference mirror. The two parts are chopped at separate frequencies, recombined at the beamsplitter and then impinge upon a photo-multiplier. The resulting signal is sent to two lock-in amplifiers which demodulate the separate signals and furnish analog signals to a data acquisition system centered about a Hewlett–Packard 2112A computer. Ensemble averaging of the signals together with statistical testing of the data set samples provides that the data taken by a point-by-point scan can be assigned a 95% level of confidence.

III RESULTS AND DISCUSSION

The crystal of TCDU was observed to crumple upon cooling to 77 K. The product of this effect as observed under illumination of polarized white light is shown in Figure 3. Regions which show a golden luster as well as a green metallic sheen are observed to coexist in the same solid. Close examination reveals, however, that the regions are clearly divided from each other because of the crumpling of the crystal. The boundaries between the various golden and green regions are remarkably sharp. It is as if the conjugation between the various regions had been completely broken.

To quantify the obvious visual color change, polarized specular reflection spectra were obtained from golden and green regions (Figure 4). Comparison of the bandshape of the golden region spectrum to that of PTS and DCHD spectra shown in Figure 2 shows a great resemblance wherein the pressure induced TCDU band (golden) is somewhat less resolved. Most important, however, is the observation of the peak frequency of the lowest energy band

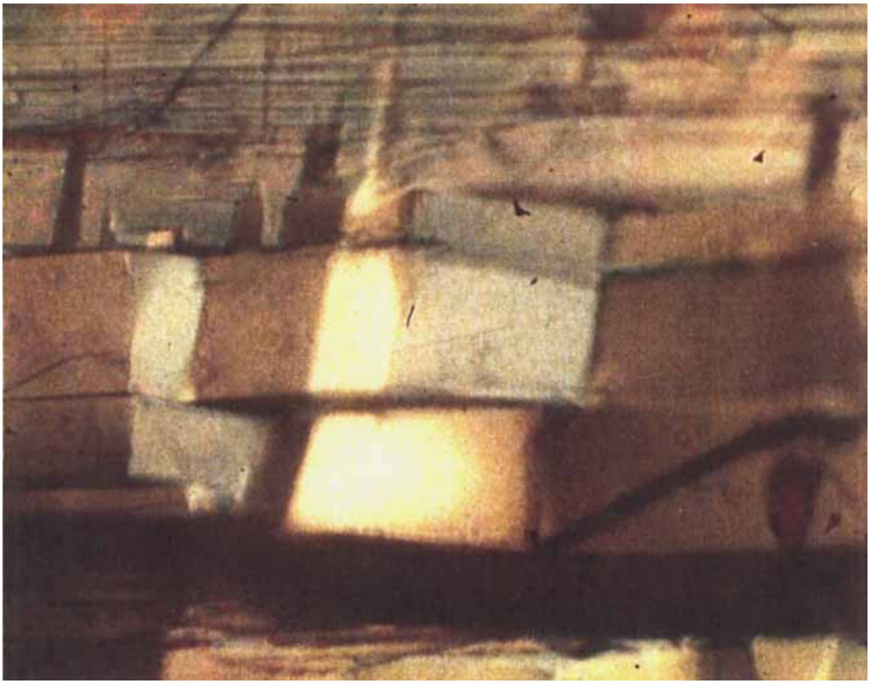

FIGURE 3 Photomicrograph of the stress transformed TCDU at 300 K and at a magnification of 200. Photograph was taken with white light polarized along the direction of the polymer chain.

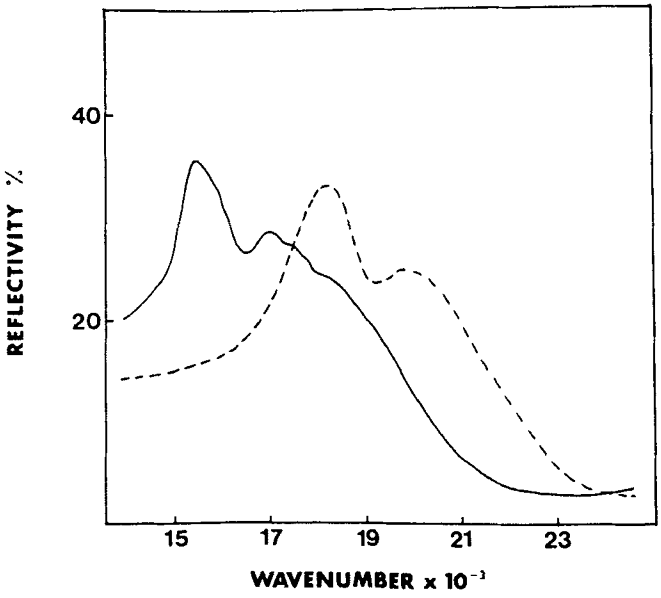

FIGURE 4 Specular reflection spectrum of the golden (solid line) and green (dashed line) regions of the stress transformed TCDU at 300 K with light polarized parallel to the polymer axis.

of the TCDU golden region at 15,500 cm^{-1} which, while it is to the red of the lowest energy band observed for PTS at 16,200 cm^{-1} at 300 K, differs from the lowest energy band of DCHD by only a 100 cm^{-1} blue shift. It should be noted, however, that the piezomodulated reflection spectrum of PTS at 300 K indicates that the lowest energy transition in PTS is near 15,800 cm^{-1}.[3] Because of the known phase transition in PTS and the apparent persistence of the structure at higher temperatures, complete agreement with the peak frequencies of PTS would be unexpected.

The green region's spectrum of Figure 4 is in reasonable agreement with the unstrained TCDU reflection spectrum. The peak reflectivity in stress-free TCDU is 18,800 cm^{-1} with a reflectivity of nearly 36%. In the strained sample the peak is observed at 18,300 cm^{-1} with a peak reflectivity somewhat less than 35%. Comparison of the TCDU spectra in Figure 3 and 4 of the stress-free and green region of the transformed TCDU crystal respectively, shows the close structural resemblance of the two spectra. Comparison of the golden region spectrum with that of the green region spectrum clearly shows that more structure is present in the golden region spectrum. Reflectivities in the golden region spectrum are less than those observed for both PTS and TCDU crystals because it was impossible to find an area which could be made near normal to the incident beam of light due to the extreme uneveness of the surfaces. Therefore, lower reflectivities should be expected.

Upon warming to 300 K, the two different regions of the TCDU sample remained stable and have been so for six months. Measurements of the strain on the strain gauge imbedded in the epoxy show that the epoxy-ceramic relaxes to essentially the same static stress at 300 K that it initially possessed at that temperature. Thus, the regions are not likely to be stabilized at 300 K by a strain on the order of that obtained at 77 K.

By comparison with the spectra for known acetylenic and butatriene polydiacetylene crystals, the spectra observed for the strained TCDU indicate that the TCDU can undergo a stress-induced change of electronic state from the butatriene structure (II) to the acetylenic structure (I). The phase regions have either a large range of stability, once formed, or else have an extremely long hysteresis.

This direct observation of the change of the electronic spectra is further supported by the resonance Raman work cited earlier.[8] It is evident that, at least in the case of TCDU, the transition from one electronic configuration to the other is independent of the nature of the R group substituent but it may, of course, be quite dependent upon the way in which those groups are packed about the polymer spine.

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