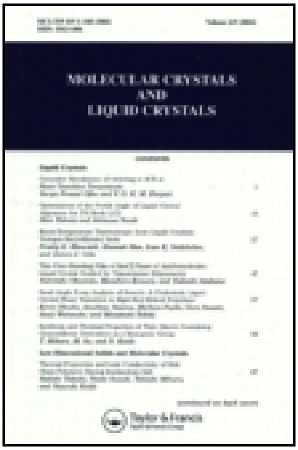

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Polyacetylene at High Pressures

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POLYACETYLENE AT HIGH PRESSURES

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Abstract The optical response of trans-polyacetylene, $(CH)_x$, has been studied at pressures up to 150 kbar. From the absorption edge position versus pressure, three main regions are identified: a stability region, 0–50 kbar, with a reversible red-shift of the absorption edge; a reactive region, 50–80 kbar, with the onset of irreversible behavior; and a transformation region, above 80 kbar, where a material transparent to visible light is formed. Raman spectra suggest that the identity of the polymer is maintained throughout the investigated pressure range. The drastic change in optical properties is attributed to the generation of crosslinks with consequent reduction of the average undisturbed chain length.

INTRODUCTION

We present an optical study of polyacetylene, $(CH)_x$, the prototype of (1D) conducting polymers[1], at high pressures. The motivation is twofold: (i) The optical gap of trans-$(CH)_x$ is only 1.4 eV at normal conditions with a large negative pressure coefficient (-17 meV/kbar).[2] Therefore, trans-$(CH)_x$ would appear as a promising candidate to achieve, by increasing pressure, valence-conduction band overlap and thus metallization. (ii) On the other hand, several organic materials are known to undergo chemical transformations even at pressures well below 100 kbar. A determination of the stability range of trans-$(CH)_x$ provides some guidance for the safe investigation of doped samples under pressure.

EXPERIMENTAL PROCEDURE

Pressures were generated in a gasketed diamond anvil cell and measured by the ruby fluorescence method.[3] Samples with initial thickness of 30 - 40 µm were studied in H_2O and methanol-ethanol pressure medium and also without pressure medium. Absorption, reflection, and Raman measurements were performed by using a microoptical system described elsewhere.[4] Samples for absorption measurements had a low content of long chain segments, so that the optical absorption edge could be observed at the given thickness.

RESULTS AND DISCUSSION

Fig. 1 shows the pressure dependence of the absorption threshold measured up to 130 kbar under nearly isotropic (in H_2O) and non-isotropic (sample only) conditions. In the first range of pressure from normal to about 50 kbar (region I), the red-shift is appreciable (-0.5 eV) and consistent for hydrostatic and nonhydrostatic pressures. The initial slope (-15 meV/kbar) compares well with previous experiments to 13 kbar.[2] The lowering of the π-π^* excitation threshold may primarily be attributed to an increase in interchain coupling.[2] A decrease in compressibility would account for the nonlinear behavior above 20 kbar. It is important to remark that the behavior in region I is reversible, as verified by releasing samples, kept at 50 kbar, back to normal pressure.

Above 50 kbar (region II), the red-shift saturates at a minimum energy of about 0.85 eV. In this pressure range bleaching of the sample by visible laser irradiation is very critical, leading to luminescence spanning all the visible. In region II, the pressure dependence of the absorption edge starts to become irreversible.

A characteristic behavior at pressures above 80 kbar (region III) is the sudden disappearance of the well-defined absorption

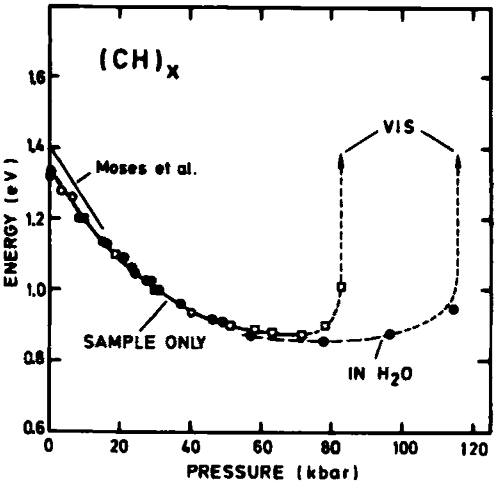


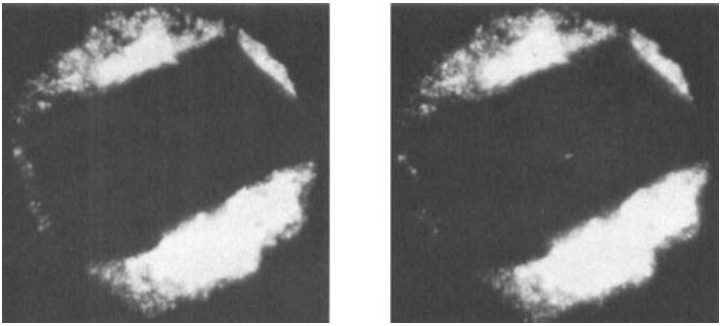
FIGURE 1 Optical absorption edge of $(CH)_x$ versus pressure.

edge in the IR with the sample turning transparent in the red and orange spectral range. The "transformation" pressure varies from 80 to 130 kbar depending on sample and pressure medium. The transition is irreversible. This striking feature is pictured in Fig. 2, where a $(CH)_x$ sample kept in H_2O has been photographed at 150 kbar and after being released back to almost normal pressure. Fig. 2 also demonstrates the very weak pressure dependence of the spectral transmission in the transformed material.

Optical reflection spectra (to be presented elsewhere) first exhibit an overall (reversible) red-shift, in accordance with absorption measurements. Above 50 kbar, the strength of optical transitions starts to decrease and at 100 kbar the stronger optical transitions below 3 eV are completely bleached out in reflection.

The "identity" of the polymer is tested by measuring the dominant Raman lines of trans-$(CH)_x$. As shown in Fig. 3, the frequencies of both ν_1 and ν_3 modes increase linearly with pressure at a rate of 0.5 cm^{-1}/kbar (441.6 nm excitation). The frequencies given correspond to that part of the Raman profile which is resonantly enhanced by π-π^* transitions on short chain segments.[5] Despite of the strong luminescence in transformed $(CH)_x$, traces of both modes are still detectable up to 150 kbar <u>and</u> after returning to normal pressure. The persistence of these lines in the transformed material suggests that the basic molecular unit is maintained over the entire pressure range investigated here.

The qualitative interpretation of the transformation in $(CH)_x$ is straightforward: Above the reversible regime (region I), pressure reduces interchain distances to a critical value (region II) for the onset of chemical reactivity. At higher pressures (region III), the formation of crosslinks going along with the generation



(a) (b)

FIGURE 2 (a) A $(CH)_x$ sample photographed in transmitted light at 150 kbar and (b) after releasing to normal pressure. For a color print see separate page in this volume.

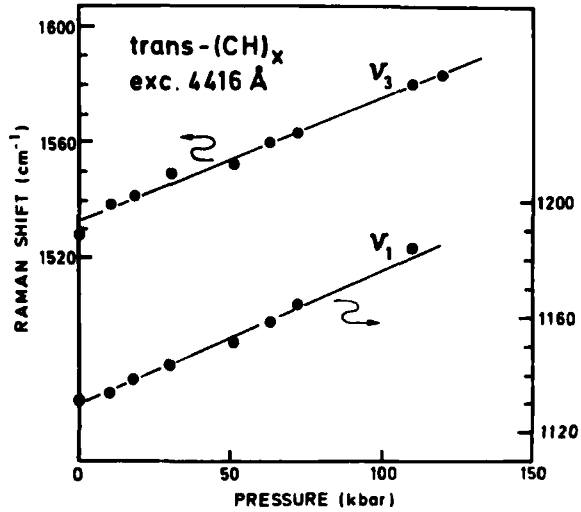


FIGURE 3 Raman frequencies of trans-$(CH)_x$ versus pressure.

of defects (free radicals) becomes very efficient resulting in a reduction of the conjugation length of polyene chains. Shorter chains absorb at higher energies, as reflected by the irreversible blue-shift of the absorption edge and the bleaching of stronger optical transitions below 3 eV. The remaining weak visible and near-IR absorption in transformed $(CH)_x$ is attributed to defects, which also give rise to the broad luminescence. At present it is not known if the transformation can be considered as a "chain" reaction in the sense that the two free radicals formed for each crosslink trigger the formation of further crosslinks. The crosslinking reaction fits into a general picture, according to which high pressure favours sp^3 hybridization with respect to having unsaturated C-C bonds. A related example is the formation of hexagonal diamond from graphite at pressures near 150 kbar.

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