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Publisher: Taylor & Francis

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Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.tandfonline.com/loi/gmcl16>

Photoinduced Spectroscopy and Resonant Raman Study of Poly(1,6-Heptadiyne)

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Version of record first published: 17 Oct 2011.

To cite this article: R. Zemach, Z. Vardeny, O. Brafman, E. Ehrenfreund, A. J. Epstein, R. J. Weagley & H. W. Gibson (1985): Photoinduced Spectroscopy and Resonant Raman Study of Poly(1,6-Heptadiyne), *Molecular Crystals and Liquid Crystals*, 118:1, 423-426

To link to this article: <http://dx.doi.org/10.1080/00268948508076250>

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PHOTOINDUCED SPECTROSCOPY AND RESONANT RAMAN STUDY OF POLY(1,6-HEPTADIYNE)

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Abstract Photoexcited e-h pairs in poly(1,6 heptadiyne) are studied by photoinduced absorption and photoluminescence spectroscopy. Most of the pairs quickly recombine; some form metastable neutral states. Resonant Raman scattering spectra reveal coexistence of two polymer structures with two different gaps, each has a set of three strongly coupled phonons.

INTRODUCTION

The structural, optical, electrical and magnetic properties of doped and undoped poly-(1,6 heptadiyne) - PHD, were recently studied[1] and compared to those of polyacetylene (PAC). Although the backbone structures of PHD and PAC are similar (see insert of Fig. 1 for PHD), their morphology and magnetic properties (upon doping) are different. PAC is very porous, being comprised of (80-90% crystallinity) fibrils of ~ 200 Å diameter[2]. In contrast, PHD has very little void space and displays no crystallinity to X-ray diffraction[1]. With these differences in structure, morphology and crystallinity between PHD and PAC, we undertook a study of photoinduced spectroscopy and resonant Raman scattering (RRS).

PHOTOINDUCED-ABSORPTION

The signal in photoinduced absorption (PA) arises from the changes $\Delta\alpha$ in the optical absorption constant α due to the presence of excited carriers[3]. The excess carriers are produced by absorption of an excitation beam ("pump") usually a laser with photon energy larger than the optical gap, while $\Delta\alpha$ spectrum is measured by scanning the photon energy of a second light beam ("probe") with a broad spectral range. The detailed experimental set-up is described elsewhere[3]. For excitation ("pump") we used a cw Ar⁺ laser at $\hbar\omega_L = 2.7$ eV; $\hbar\omega_L$ larger than the PHD energy gap (~ 2 eV). The variable wavelength probe beam was an incandescent light source which was dispersed by a monochromator. The thin films ($d \sim 1000$ Å) of PHD were polymerized onto sapphire substrate[1] to help eliminate heating during exposure to the laser light[3].

In Fig. 1 the induced absorption ($-\Delta T/T = d\Delta\alpha$) at 80K obtained with a laser intensity I_L of 20 mWcm^{-2} is plotted versus the probe photon energy

between 0.2 and 2.5 eV. The spectrum consists of an asymmetric PA band ($\Delta\alpha > 0$) peaked around 1 eV, and a shoulder at 0.5 eV. These bands are much broader than the PA bands observed in PAC[4]. At about 1.8 eV (isosbestic point) the PA changes into induced bleaching ($\Delta\alpha < 0$). This shows that the two PA bands are intrinsic to the polymer chains and derive their strength from the bleaching of the interband optical transitions. The PA life-time is extremely long (longer than 0.1 sec) and it is characteristic of amorphous semiconductors[5]. The laser chopping frequency f used for the PA measurements was 150 Hz and therefore the small magnitude of $\Delta T/T$ ($\sim 10^{-4}$) compared to PAC[4] ($\sim 10^{-3}$) is misleading; the PA magnitude increases when f is reduced.

Both PA bands (0.5 and 1 eV) share a common origin. $\Delta\alpha$ for the two bands increases linearly with I_L over 3 orders of magnitude in I_L , indicating monomolecular recombination kinetics[3]. We also measured the PA strength as a function of temperature. Both bands decrease in a similar way when the temperature increases; the decrease is more pronounced for $T > 200\text{K}$.

PHOTOLUMINESCENCE

The PA signals are accompanied with two photoluminescence (PL) bands at 1.95 eV and at 1.4 eV. Although the PL bands are quite broad (FWHM of 0.5 eV) they have Gaussian lineshapes. Both PL bands could follow the laser chopping frequency and they change very little when the temperature increases. Except for their width, the PL bands in PHD have similar properties as the PL band (~ 1.9 eV), in *cis* PAC[6]. We therefore identify the 1.95 eV as band-edge PL. The lower PL band is caused by e-h pairs which undergo a strong 1-D localization or is due to the coexistence of a second PHD polymer structure, in addition to the main structure (Fig. 1). The later interpretation is based on the following RRS results.

RESONANT RAMAN SCATTERING

The RRS spectra measured with 3 different laser frequencies are given in Fig. 2. The spectra are composed of 3 resonantly enhanced doublets at 1150 cm^{-1} ,

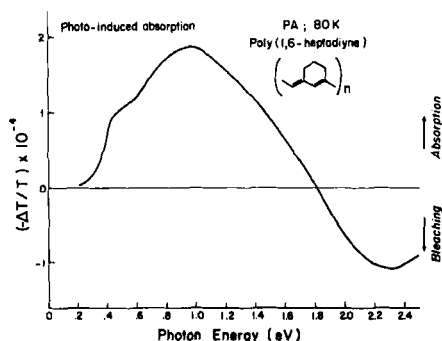


Fig. 1: PA spectrum of poly(1,6-heptadiyne) at 80K, excited with $\hbar\omega_L = 2.7$ eV. The insert shows the structure of PHD.

1210 cm^{-1} and 1510 cm^{-1} , and several lines in between. The intensity of the higher frequency component of each doublet increases for shorter laser wavelength. This behavior is accentuated for the doublet at 1510 cm^{-1} , (Fig. 2). The Raman lines are broader than the RRS lines in *cis*-PAC[7] but narrower than those in *trans*-PAC[7,8]. The lower components of the 3 doublets probably belong to PHD polymer chains which have low energy-gap and thus are resonantly enhanced at lower ω_L . The higher components of the 3 doublets belong to PHD chains which have high energy-gap and therefore they are resonantly enhanced for higher $\hbar\omega_L$. The two kinds of PHD chains may even have different molecular structures. A possible candidate for the higher energy gap polymer was identified in Ref. 1.

The RRS spectra of PHD are different from the RRS spectra of *trans*-PAC[7,8]. Although three resonantly enhanced vibrations were identified in *trans*-PAC[7,8] each of them develops a high frequency satellite line whose frequency changes with ω_L . Therefore a distribution of energy-gaps was needed to explain the *trans* PAC RRS results[7,8]. For the PHD case, only two kinds of chains (with two different gaps) is sufficient to explain the RRS data. We note that similarly as in *trans*-PAC[8], only three ir-active vibrations are formed in PHD upon doping[1]. This supports our assignment of 3 main phonon lines (doublets) in PHD; the lines between 1300 and 1450 cm^{-1} (Fig. 2) are not strongly coupled to the electronic system.

DISCUSSION

In this work we have found ample evidence which indicates that PHD is indeed amorphous. The broad spectral lines in both PA and PL measurements, the long PA life-time and the PL fatigue are commonly found in amorphous semiconductors[5]. Yet the RRS spectrum and its dependence on ω_L shows the coexistence of two kinds of polymer structures; one with low E_g , the other with higher E_g . This may indicate that each component of the two PA and PL bands observed in PHD may be correspondingly associated with the two polymer structures: the low energy bands and high energy bands may belong to the low and the high E_g polymer structure respectively.

However we cannot exclude that the two PL and PA bands belong to the main PHD polymer structure; the second PHD structure may not contribute

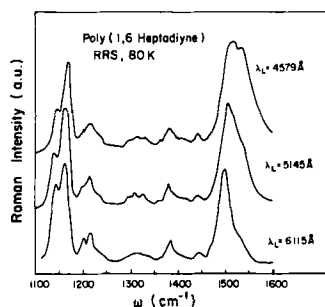


Fig. 2: RRS spectra of poly(1,6-heptadiyne) at 80K, excited with different laser frequencies.

to the spectra at all probably since the photoexcited carriers will quickly recombine in these skewed polymer chains. In this case the 1.95 eV PL results from band edge, while the 1.4 eV band is due to e-h pairs which undergo strong 1-D localization. Then the two PA bands belong to the same metastable excitation, which may be a neutral bipolaron[9]. In this case the lower energy PA band is due to optical transition from the valence band to lower energy level of the bipolaron (or from the higher bipolaron level to the conduction band), while the high energy PA band is due to the optical transition from the lower to the higher level of the bipolaron[9]. In this case (in the absence of Coulomb correlation) the sum of the PA energies adds to the value of E_g [9]. Indeed $0.5 + 1.0 + 0.5 = 2$ eV which coincides with the PHD energy gap[1].

CONCLUSIONS

From the studies of PA, PL and RRS in poly(1,6-heptadiyne), the following conclusions were reached.

- (1) Coexistence of two structures in the PHD film, each has different energy gap and different set of 3 strongly coupled phonons.
- (2) The PHD film is amorphous and consequently influences all spectral lines.
- (3) Most of the photoexcited e-h pairs quickly recombine. Some form metastable overall neutral states from which may be interchain excitons[10] or self trapped neutral bipolarons[9].

This work was supported in part by the Israeli Academy for Basic Research, Jerusalem, Israel.

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