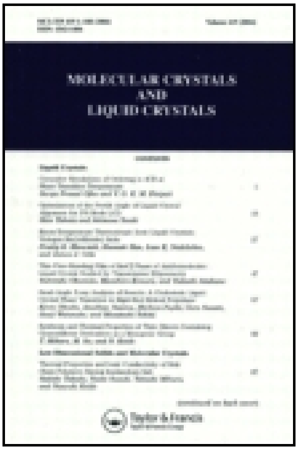

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Temperature and Crystal Size Dependence of Excitonic Absorption for Polydiacetylene Microcrystals

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The excitonic absorption of well defined polydiacetylene microcrystals was measured as a function of temperature and crystal size. Poly-DCHD microcrystals were prepared by a recently reported reprecipitation method, and crystal size was controlled by changing the concentration of diacetylene monomer solution injected into water. The excitonic absorption peak position was blue-shifted from 650 nm to 635 nm with decreasing crystal size from 120 nm to 30 nm. On the other hand, the peak position was red-shifted by 15 nm (300 cm^{-1}) upon decreasing the temperature from 273 K to 4 K. Narrowing of the half peak width was also observed to accompany this red-shift. These phenomena are considered to be related to the coupling interaction between the excitonic state and phonons depending on crystal size and temperature.

Keywords: polydiacetylene; microcrystal; exciton; absorption spectrum; crystal size; phonon

INTRODUCTION

Polydiacetylene, which is prepared by solid-state polymerization in the diacetylene single crystal, is a π-conjugated crystalline polymer, and has been extensively studied not only for its unique solid-state polymerization behavior but also due to its interesting, nonlinear optical properties[1]. Polydiacetylene has shown high third order nonlinear optical susceptibility ($\chi^{(3)}$) along the π-conjugated backbone[2]. However, the polycrystalline sample form generally available presents some problems from a practical standpoint including optical loss and low processability among others. To overcome these disadvantages, microcrystallization is considered to be an alternative effective approach. Further, microcrystals are expected to exhibit interesting optical properties depending on crystal size, which isolated macromolecules and bulk crystals may not possess. So-called size effect has already been confirmed experimentally in the optical properties of semi-conductor microcrystals[3]. In organic systems these effects could not be studied because there was no fabrication method available for the preparation of organic microcrystals. Recently, a novel technique for the preparation of organic microcrystals, a reprecipitation method[4], has been proposed for the first time, and it has been possible to fabricate different kinds of organic microcrystals. This provides an opportunity to investigate the fundamental optical properties of organic microcrystals, and establish their dependence on crystal size if such is the case. In the present paper, we have investigated the dependence of the excitonic absorption spectra of polydiacetylene microcrystals on crystal size and temperature, and will discuss a coupling interaction between the excitonic state and phonons in a microcrystal lattice.

EXPERIMENTAL

Diacetylene monomer used was 1,6-di(*N*-carbazolyl)-2,4-hexadiyne (DCHD), whose conversion to polymer by solid-state polymerization is 100%[5]. Microcrystals were fabricated with the reprecipitation method as described elsewhere[4]. The crystal size of DCHD microcrystal was controlled by changing the concentration of DCHD solution injected into water[6]. As shown in Figure 1, 50 nm and 100 nm size microcrystals were obtained from 2.5 mM and 10 mM solutions, respectively. These DCHD microcrystals were solid-state polymerized by UV(254 nm)-irradiation for 20 minutes. In consequence the color of the water-dispersion liquid was observed to change from white turbid to blue, which means poly-DCHD microcrystals were formed successfully. Absorption spectra were measured in the state of water dispersion at room temperature. For measurement of absorption spectra at low temperature microcrystals were dispersed in a gelatin thin film fabricated by spin coating method. It should be noted that the spin coated sample and the water dispersion sample had similar absorption spectra. This spin coated sample was mounted in a cryostat, which was connected with the absorption spectrometer (V-570, JASCO). Liq. He was flowed into the cryostat for obtaining a stable given temperature.

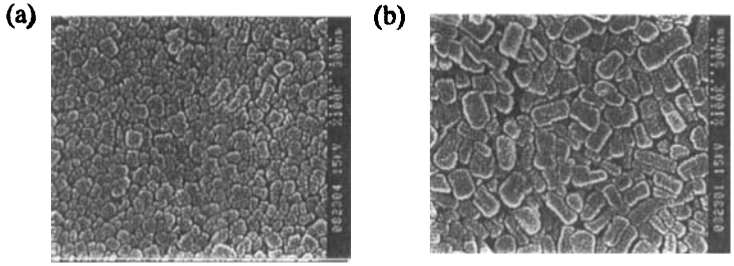

FIGURE 1. SEM micrographs of poly-DCHD microcrystals. Average crystal sizes are (a) 50 nm and (b) 100 nm.

RESULTS and DISCUSSION

Crystal Size Dependence We have investigated the dependence of excitonic absorption peak position (λ_{max}) of poly-DCHD microcrystals dispersed in water on crystal size at room temperature. As shown in Figure 2, the values of λ_{max} were changed with crystal size. The plots of λ_{max} vs. crystal size are indicated in Figure 3. The blue-shift with decreasing crystal size can be clearly seen.

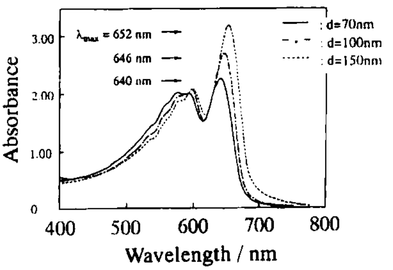

FIGURE 2. Absorption spectra of poly-DCHD microcrystals dispersed in water with various crystal size.

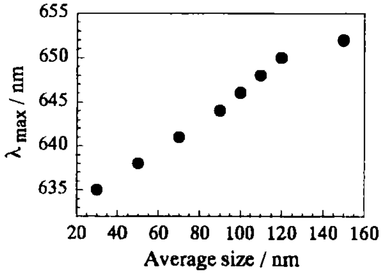

FIGURE 3. The plots of excitonic absorption peak position vs. crystal size.

Similar size dependent shift has been recently confirmed in both absorption and luminescence spectra for perylene microcrystals[7] as well. It is interesting to note and somewhat difficult to explain these observations as quantum size effect described for inorganic nanocrystals[3]. Such effects for inorganic nanocrystals appear in the crystal size range one-order of magnitude smaller compared with poly-DCHD and perylene microcrystals. The possibility of scattering effects influencing the shift of λ_{max} has been eliminated by the following experiment. The absorption spectrum was measured while shielding the center spot of the transmitted light in the optical alignment of absorption spectrometer. Figure 4 indicates the re-measured absorption spectra of 100 nm poly-DCHD microcrystals. Though scattered light spectrum was of low optical quality, there was no difference in peak position between center-shielded and non-shielded spectra. If the scattered light contributes to the shift of λ_{max}, λ_{max} were apparently shifted by center-shielding. The same results were confirmed in the case of 50 nm size microcrystals. Scattering effects are not responsible for the shift of λ_{max}.

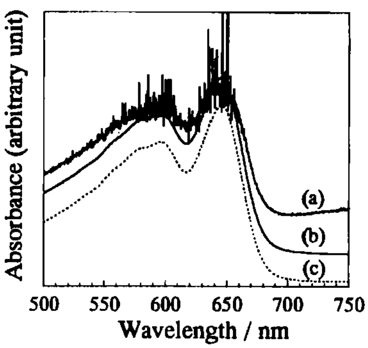

FIGURE 4. Spectra of poly-DCHD microcrystals dispersed in water. Transmitted light is partially shielded in the optical alignment. Shielded spot is (a) center, (b) off-center, and (c) none.

Temperature Dependence To discuss the origin of the shift of λ_{max} further, we have measured the absorption spectra at various temperatures. The spectral changes of the excitonic absorption feature with temperature for 50 nm and 100 nm poly-DCHD microcrystals are indicated in Figures 5(a) and (b), respectively. The plots of excitonic absorption peak position (ν_{max} / cm^{-1}) vs. temperature in each crystal size are shown in Figure 6. About 300 cm^{-1} of red-shift was observed in the ν_{max} with decreasing temperature from 273 K to 4 K. In addition, the slope of ν_{max} vs. temperature was changed at around 130 K and became gentler below this temperature.

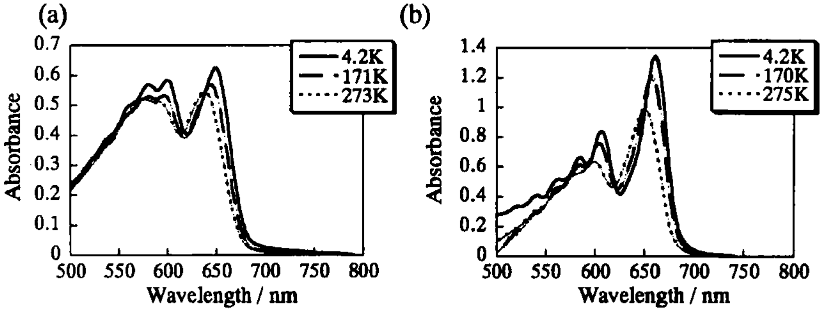

FIGURE 5. Variations of absorption spectra of poly-DCHD microcrystals with temperature. Average sizes are (a) 50 nm and (b) 100 nm.

The value of ν_{max} at 4 K can be regarded to be approximately an intrinsic excitonic band gap, depending on crystal size alone and not being influenced by the effect of phonons in the microcrystal lattice. Clearly the ν_{max} at 4 K decreases with increasing crystal size. On the other hand, as shown in Figure 6, the slopes were roughly parallel for different size microcrystals which implies that thermal effects from phonon further shifting the ν_{max} are independent of crystal size. The above discussion can be further advanced by studying the change of the half width of excitonic absorption with temperature as shown in Figures 7(a) (50 nm) and 7(b) (100 nm). The absolute half width for 50 nm microcrystals was always wider than that of 100 nm microcrystals.

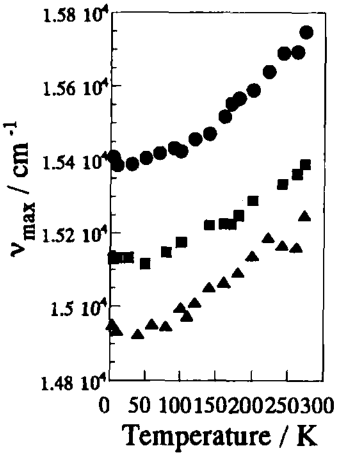

FIGURE 6. Temperature dependence of excitonic absorption peak position (ν_{max} / cm^{-1}) of poly-DCHD microcrystals. Average crystal sizes are 50 nm (●), 100 nm (■), and 1 μm (▲).

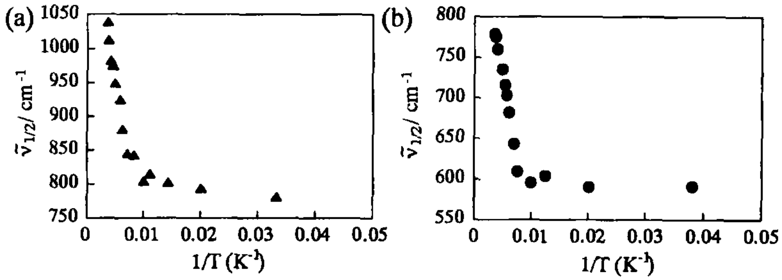

FIGURE 7. The plots of half width of excitonic absorption vs. the reciplocal of temperature for poly-DCHD microcrystals. Average crystal sizes are (a) 50 nm and (b) 100 nm.

However, the pattern of dependence of half width on temperature for the two microcrystal sizes was the same as seen in Figures 7(a) and 7(b). Drastic increases in half width were observed from 130 K with increasing temperature in both crystal size samples. This temperature is roughly the same where the slope in the plot of ν_{max} vs. T as shown in Figure 6 was changed. The phonon is influenced not only by temperature but also crystal size. The influence of phonon becomes stronger with decreasing crystal size as the lattice of microcrystal is softened. The coupling between the phonons and the excitonic state is remarkable and may lead to instability. As a result, the exciton band gap may become larger, which leads to the blue-shift of λ_{max}. Alternatively, the exciton formed may be further excited to high exciton band due to remarkable phonon. The shift of λ_{max} as shown in Figure 2 was also observed by the variations with pH and dielectric constant of dispersion liquid, which suggest that some kind of effect on the microcrystal surface were going on. However, the main cause of the shift of λ_{max} is considered to be strong coupling with phonon, which may be effective relatively in organic microcrystals compared with inorganic and/or semi-conductor microcrystals because of molecular crystalline material.

CONCLUSION

We have investigated the absorption spectra of poly-DCHD microcrystals and confirmed the crystal size and temperature dependence of the excitonic absorption and their half width. As a result, absorption maximum position was blue-shifted and half width was increased with increasing temperature and decreasing crystal size, which related to the strong coupling between exciton and phonon in a microcrystal.

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