

Temperature and size effects on photopolymerization dynamics of diacetylene nanocrystals dispersed in water

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Diacetylene derivatives are well known to show solid state polymerization induced by γ - (or UV) irradiation or thermally. The reaction is promoted by the spatial arrangement of the monomer molecules in the crystal matrix, and the mechanism were investigated for bulk crystals, thin polycrystalline films, and nanocrystalline colloids. In the present work, we investigated temperature and size effects on the photo-polymerization dynamics of diacetylene nanocrystals dispersed in water, and demonstrated that the photopolymerization of the nanocrystals changed drastically in the temperature region from 20°C to 70°C. We prepared water dispersions of nanocrystals of 1,6-di(N-carbazolyl)- 2,4-hexadiyne (DCHD) and 10,12-heptacosadiynoic acid (14,8-ADA), and examined the polymer conversion by UV (300 nm) irradiation by measuring the characteristic absorption of π -conjugated backbone chain of polydiacetylene.

As a representative example, the results of DCHD nanocrystals (100-nm particle size) are shown in Figure 2. The kinetics of polymer formation shows some interesting properties. In the beginning, there is a slow increase of the conversion, the induction period, followed by the autocatalytic region where the reaction rate strongly increases. The behavior is quite similar to a bulk crystal. The unconventional reaction kinetics is considered to be due to the crystal strain caused by the mismatch of the polymer (or oligomer) molecules in the monomer crystal matrix. There is energy barrier of translation and rotational motion of monomer molecules in addition reaction, and the activation energy will decrease with polymer i.e. the amount of polymer molecules in the monomer crystal matrix. It is worth to note that the polymer formation kinetics changed drastically around 50°C. The polymer formation time above 50°C shortened 100 times in comparison to 30°C, while the induction period decreased gradually with temperature. This suggests that lattice properties of DCHD nanocrystals will change after 50°C, leading to decrease of the activation energy of addition reaction.

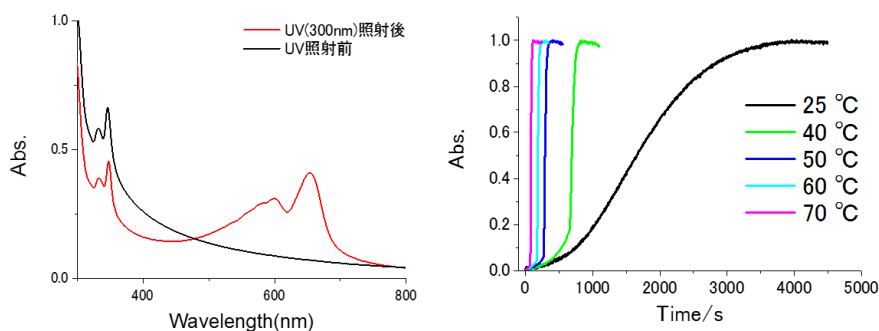


Figure 1. Absorption spectra of DCHD nanocrystals before and after UV irradiation (left) and Fraction of polymer conversion (absorbance at 640 nm) as a function of irradiation time at different temperatures

In the case of 14,8-ADA, the similar temperature effect on the polymer formation dynamics was observed. Figure 2 shows the absorption spectra of 14,8-ADA nanocrystals (50 nm size) after UV irradiation. The absorption peaks at 610 nm and 650 nm similar to that of polyDCHD was assigned to the absorption of the polymer having a long-range structural order in the p-conjugated backbone chain (blue phase) and the peaks at 520 nm and 550 nm are of the polymer with a short-range one (red phase). For increasing of the temperature from 10 to 45°C, the conversion of blue phase polymer decreased and red phase one was almost constant. For further temperature increasing, the polymer conversion decreased and above 60°C the polymer did not form. Since polymerization of 14,8-ADA occurs exclusively in crystalline phase, the nanocrystals having 50 nm size became to amorphous nanoparticles above 60°C. On the other hand, the nanocrystals of 200 nm size showed photopolymerization at 60°C but did not above 70°C. Because the melting point of the bulk crystal was 68°C, it is suggested strongly that the melting point of 14,8-ADA nanocrystal having 50 nm particle size decreased than that of bulk crystal. This result will be an experimental demonstration on depression of melting point of nanoparticles for organic compounds.

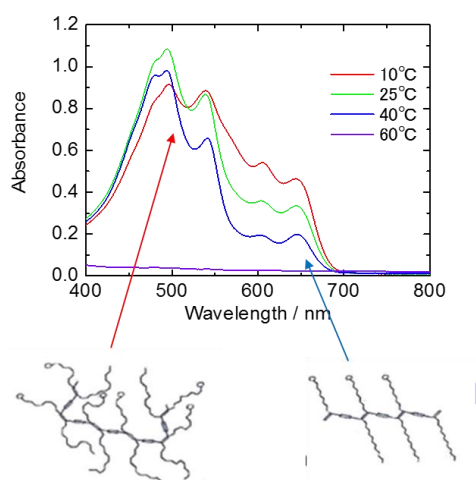


Figure 2. Absorption spectra of 14,8-ADA nanocrystals (50 nm size) dispersed in water after UV (300 nm) irradiation at different temperatures for 10 to 60°C.

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