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Single-Crystal-to-Single-Crystal Transformation of Diolefin Derivatives in Nanocrystals

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Topochemical polymerization is useful to obtain stereoregular polymers in crystalline form. For example, several diacetylene[1] and (*Z*,*Z*)-muconic acid[2] derivatives are known to show single-crystal-to-single-crystal transformation even in bulk crystals via chain polymerization to give the corresponding polymer single crystals. Especially in polydiacetylene, its molecular weight control was qualitatively demonstrated in its size-controlled nanocrystals.[3] Molecular weight difference was also found in ethyl (*Z*,*Z*)-muconate crystals prepared in different sizes.[4] On the other hand, topochemical polymerization behavior of diolefin derivatives[5] in nanocrystals has not been reported. Different features of diolefin compared with the former two series of monomers are that diolefin derivatives polymerize successively by [2 + 2] cycloaddition and their bulk crystals become polycrystals from a single crystal because of the accumulation of strains.[6] In this Communication, the polymerization behavior of two diolefin derivatives was investigated in both bulk crystals and nanocrystals and characteristics of diolefin nanocrystals were explored.

Two diolefin monomers, i.e., methyl *p*-phenylenediacrylate (PDA-Me)[7] and 2,5-distyrylpyrazine (DSP)[8] as shown in Figure 1, were prepared according to the literature procedures. Photopolymerization of bulk crystals was carried out by irradiating UV light from a 500-W ultrahigh-pressure mercury lamp for 2 h. The appearance of bulk crystals during polymerization was observed under a polarizing microscope. The nanocrystals of PDA-Me and DSP were prepared by the reprecipitaiton method[9] as follows: 200 μL of a diolefin tetrahydrofuran (THF) solution (5.0 mmol/L) was injected using a microsyringe into pure water (10 mL) stirred vigorously. Immediately their nanocrystals were produced in an aqueous media. The size and shape of nanocrystals were verified using a scanning electron microscope (SEM). For observation, the nanocrystals were collected on a Millipore filter by filtration, dried, and platinum-coated. Nanocrystals dispersed in water were polymerized by irradiating UV light at 302 nm from a 6-W UV lamp for 5 min. UV−visible spectra were measured in water dispersion, while IR spectra were obtained for filtered powder dispersed in potassium bromide.

At first, crystal shapes of PDA-Me and DSP were observed before and after UV irradiation. As reported previously, a PDA-Me bulk crystal (Figure 2a) was broken into fragments during polymerization (Figure 2b). Figure 2c shows the SEM image of the fragmented poly(PDA-Me) crystals, whose minimum size is around 1 μm. Their shapes are not uniform and the size distribution is wide. For a DSP bulk crystal (Figure 2d), cracks were generated in the course of polymerization[10] (Figure 2e). Even in a small crystal about 10-μm thick, similar cracks were observed in a SEM image (Figure 2f). Although these diolefins are polymerized in a topochemical manner, lattice parameter differences between monomers and the corresponding polymers are relatively large.[11] Accordingly, the existence of the polymer structure in a monomer crystalline lattice during polymerization accumulates strain in single crystals. Finally, the monomer single-crystalline form cannot be maintained and the strain is relieved by breaking the crystals. Fragmentation of bulk crystals by UV irradiation was also observed in the water dispersion state.

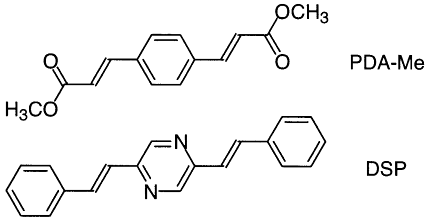

Figure 1. Structures of diolefin derivatives studied.

The monomer nanocrystals were successfully prepared when THF was used as the solvent. The shape of PDA-Me nanocrystals was platelike and the size was about 500 nm a side (Figure 3a). DSP nanocrystals were rod shaped and the length varied from 150 nm to about 400 nm (Figure 3c). Solid-state photopolymerization of these nanocrystals in water was confirmed by UV−visible and IR spectra. In the UV−visible spectra, the absorption band at 381 nm for PDA-Me and that at 377 nm for DSP, which are originated from a π-conjugated system extending whole molecules, disappeared after UV irradiation. In the IR spectra of PDA-Me, a peak at 1628 cm^{-1} for $\nu_{\text{C=C}}$ vanished and a peak at 1707 cm^{-1} for $\nu_{\text{C=O}}$ corresponding to the conjugated ester carbonyl group shifted to 1732 cm^{-1} for $\nu_{\text{C=O}}$ corresponding to the isolated ester carbonyl group upon UV irradiation. DSP nanocrystals also showed peak extinction at 1630 cm^{-1} for $\nu_{\text{C=C}}$. All these data support quantitative conversion of monomers to the corresponding polymers. The crystal structures of PDA-Me and DSP nanocrystals in both monomer and polymer were evaluated by the powder X-ray diffraction method. Diffraction patterns of nanocrystals agreed well with the corresponding bulk crystals, indicating that photopolymerization in nanocrystals proceeded in the same manner as in bulk crystals. The same crystal structure of polymers between the nanocrystals and bulk crystals was also confirmed by electron diffraction experiments.

Morphology of polymer nanocrystals was observed using the SEM, and images for PDA-Me and DSP are displayed in Figures 3b and 3d, respectively. Interestingly, in contrast to the polymer bulk crystals, the shape and size of polymer nanocrystals are almost the same as those of the corresponding monomers and no cracks were recognized. Even in the isolated dried state, these nanocrystals

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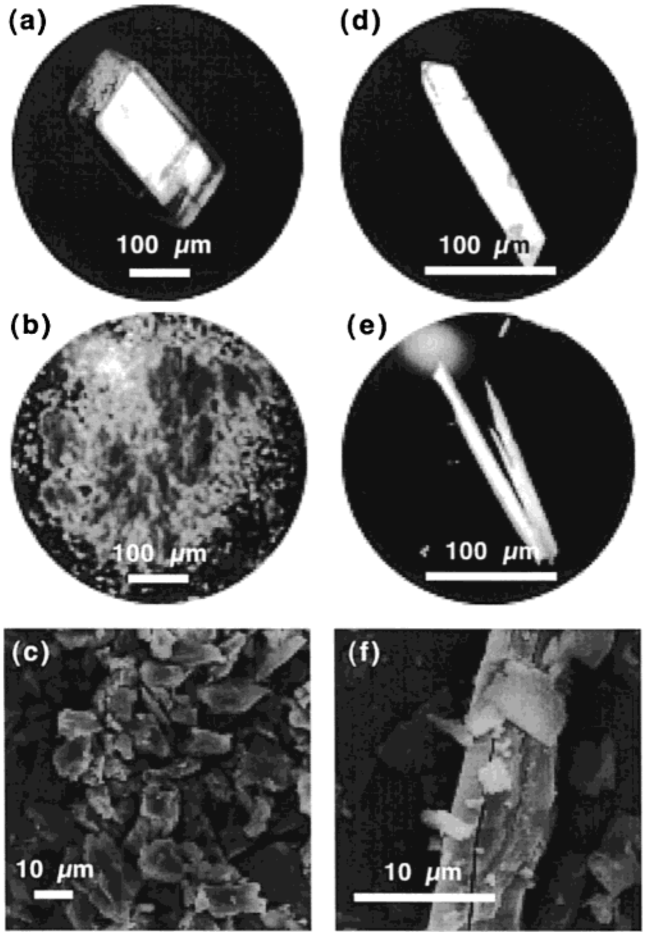

Figure 2. Morphology of diolefin bulk crystals before and after UV irradiation: (a) a PDA-Me monomer crystal, (b) and (c) poly(PDA-Me) crystals, (d) a DSP monomer crystal, and (e) and (f) polyDSP crystals. Figures (c) and (f) were taken using a SEM, while others were taken using a polarizing microscope. Crystals in (b) and (e) were obtained from the crystals in (a) and (d) after UV irradiation, respectively.

maintained their single-crystalline phase in the course of polymerization. These results suggest that single-crystal-to-single-crystal transition becomes possible in nanocrystals even in the case of the corresponding bulk crystals giving polycrystals from a single crystal during topochemical polymerization. The strain accumulated in nanocrystals seems to be easily released by deforming the crystal shape. Actually, the larger interior angle of developed parallelogram surfaces of PDA-Me monomer nanocrystals seems to become smaller in the polymer nanocrystals (see Figures 3a and 3b). This change must be directly related to the lattice parameter variation. Advantages of miniaturizing crystals into micrometer sizes in a topochemical reaction were also discussed by Kusto et al.[12]

In conclusion, nanocrystals of two diolefin derivatives were successfully prepared, and these nanocrystals were found to transform from a monomer single crystal to a polymer single crystal. Thus, single-crystal-to-single-crystal transformation may be possible by nanocrystallization even for compounds whose bulk crystals do not show single-crystal-to-single-crystal transformation. Accordingly, topochemical polymerization along one direction from one end to the other end in nanocrystals may be shown to produce single crystalline polymers with definite molecular weight controlled by crystal size. Details will be published elsewhere.

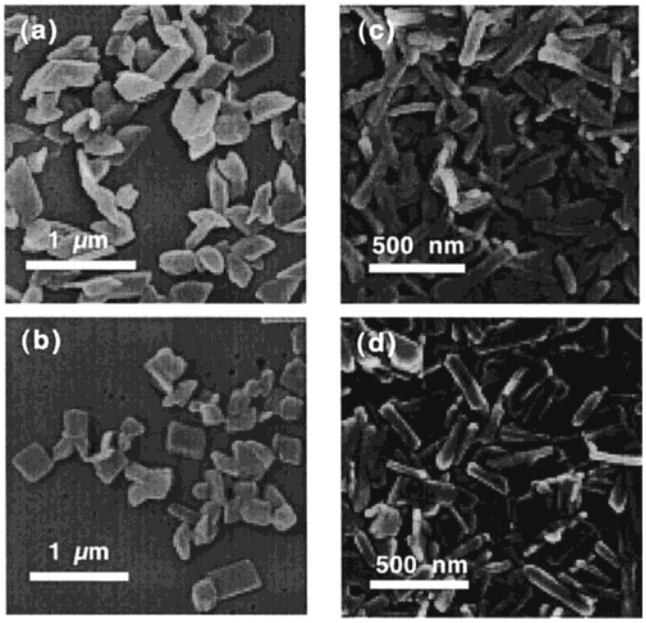

Figure 3. Morphology of diolefin nanocrystals before and after UV irradiation observed by a SEM: (a) PDA-Me monomer, (b) poly(PDA-Me), (c) DSP monomer, and (d) polyDSP.

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