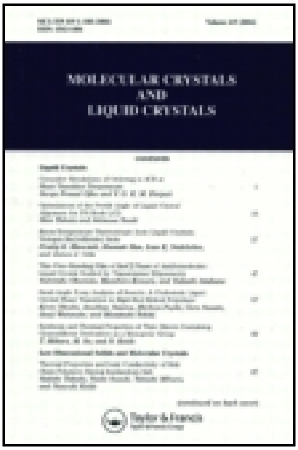

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Nanocrystal Fabrication of Acrylic Acid Derivatives with a Long-Alkyl Group and Their Solid-State Polymerization

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*Nanocrystals of octadecyl acrylate **1**, octadecyl methacrylate **2** and N-octadecylacrylamide **3** were prepared by the reprecipitation method as water dispersion for the first time. Their sizes were from 120 nm to 350 nm depending on the preparation conditions. Although polymerization of **1** through **3** in nanocrystals was essentially the same as that in bulk crystals, it is interesting that **1** showed smaller average molecular weight and dispersity index in nanocrystals compared with in the bulk crystals.*

Keywords: acrylamide; acrylate; methacrylate; nanocrystal; solid-state polymerization

INTRODUCTION

Fabrication of organic nanocrystals is considered to be one of the important subjects because the resulting nanocrystals may be useful

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components for microelectronics and photonics. They may also show interesting size-dependent physical and chemical properties different from those in the bulk states. From the point of view of polymer synthesis, solid-state polymerization in size-controlled nanocrystals without defects is an ideal condition to prepare stereo-regular polymers with monodispersed molecular weight. Their properties are expected to be sharp compared with conventional polymers having less stereoregularity and broader molecular-weight distribution. In our previous studies, we have investigated solid-state polymerization of diacetylene and diolefin monomers [1,2], whose polymerization is known to proceed in topochemical manners. In the case of the diolefin monomers, single-crystal-to-single-crystal transformation was observed in nanocrystals although the bulk single crystals were broken into fragments due to strain accumulated during polymerization. Similarly, if solid-state polymerization is performed in a nanometer scale, the obtained polymers may persist the structure succeeded from the monomer nanocrystals. In this connection, monomers, whose solid-state polymerization was not recognized as topochemical one in bulk crystals, were investigated in this study. Monomers selected were octadecyl acrylate **1**, octadecyl methacrylate **2** and *N*-octadecylacrylamide **3** [3–5]. Although their polymerization behaviors have been studied for Langmuir-Blodgett films [6,7] and physical vapor deposited films [8,9] other than bulk crystals, fabrication and polymerization of their nanocrystals have not been reported so far.

EXPERIMENTAL

Monomers **1** through **3** were synthesized by the conventional route (Fig. 1). The structures were confirmed by IR, ^{1}H- and ^{13}C-NMR and elemental analysis. The reprecipitation method [10] was used to prepare nanocrystals as dispersions. As shown in Table 1, acetone or THF solution (200 μl) of the monomers was injected into 10 ml of stirred pure water. Soon stirring was stopped and the mixture was kept for 30 min. The nanocrystal dispersions were obtained as slightly

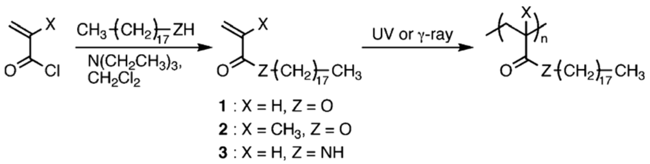

FIGURE 1 Synthesis and polymerization of octadecyl-substituted acrylic-acid derivatives **1** through **3** used in this study.

TABLE 1 Nanocrystal Preparation Conditions and Some Data on the Resulting Nanocrystals

Compound	Solvent for injected solution	Solution concentration/mmol l^{-1}	Average size of monomer nanocrystals/nm	Zeta potential of monomer nanocrystals/mV	Average size of polymer nanocrystals/nm	Remark[a]
1	Acetone	5.0	220	−35.7	210	*
	THF	5.0	260			
2	Acetone	2.5	130			
	Acetone	5.0	180	−47.6	230	*
	Acetone	10.0	210			
	THF	5.0	120			
3	THF	5.0	350	−30.8	–[b]	*

[a] Asterisks indicate typical conditions to prepare each nanocrystal sample.
[b] The size was not able to be determined by DLS.

turbid liquid. Since measured melting points of **1**, **2** and **3** were 33°C, 28°C and 80°C, respectively, the experiments were performed at ambient temperature less than 28°C. Average crystal sizes in dispersion were evaluated by dynamic light scattering (DLS) using an Otsuka DLS-6000 photometer. Zeta potentials were evaluated using a Malvern Zetasizer Nano ZS apparatus. For polymerization (Fig. 1), UV at 254 nm was irradiated to the monomer nanocrystal dispersions or the bulk crystals using a 4-W UV lamp (UVP UVG-254). IR spectra were obtained by using a Horiba FT-210 spectrometer. Since monomers and polymers of **1** through **3** can be dissolved in chloroform, the nanocrystal dispersions were extracted with chloroform and the extracted solution was cast onto CaF_2 plates to measure IR spectra for polymerization studies. IR spectra of the bulk crystals were recorded for their KBr-pelletized samples. Monomer conversions to the corresponding polymers were obtained from the decreasing ratio of the relative intensity of the peak assigned to $\nu_{C=C}$ after UV irradiation. Nanocrystals before and after UV irradiation were collected by suction filtration using Millipore Teflon filters with a pore size of 0.2 μm. Filtered nanocrystal samples were used for SEM observation and X-ray diffraction measurements. Scanning electron microscope (SEM) images were taken using a JEOL JSM-6330F microscope for the samples coated by Pt-Pd. Powder X-ray diffraction patterns were measured by using a Rigaku Ultima-XG/YP diffractometer with a Cu $K\alpha$ source. Nanocrystals in 500-ml water dispersion and bulk crystals of **1** were also polymerized by γ-ray irradiation with 1 kGy dose using a ^{60}Co source. Gel permeation chromatography (GPC) was performed for chloroform extracts of both filtered nanocrystals and bulk crystals using Toso TGKgel 4000H columns. Polystyrene was used as a standard for average molecular weights.

RESULTS AND DISCUSSION

Average monomer nanocrystal sizes evaluated by DLS were 120–350 nm as shown in Table 1. When solution concentration of **2** was varied from 2.5 to 10 mmol l^{-1}, crystal size increased with increasing the concentration. This tendency was similar to a diacetylene monomer studied previously [11]. The monomer nanocrystals prepared in the typical preparation conditions showed large negative zeta potential values (Table 1) indicating stable dispersion states. When UV was irradiated to nanocrystal dispersions, crystal size of **1** was not so changed while crystal size of **2** became slightly larger suggesting partial coagulation of nanocrystals (Table 1). In the case of **3**, precipitation was observed after UV irradiation. From IR spectral study, conversions to the polymers in nanocrystals by UV were estimated to be 77%, 87% and 47% for **1**, **2** and **3**, respectively. Conversions of the corresponding bulk crystals in the same experimental conditions were 63%, 64% and 36%, respectively, and slightly lower than those of the nanocrystals. However, efficient UV irradiation was expected for the nanocrystals compared with the bulk crystals in our experimental conditions, these differences seemed to be not essential. Although clear SEM images could not be obtained for monomer nanocrystals owing to electron-beam damages, those of polymerized nanocrystals could be taken as shown in Figure 2. Nanocrystal size of **1** was observed to be about 200 nm or less, and that of **2** was larger. Nanocrystals of **3** were found to be integrated. These results almost agreed with the crystal sizes observed in dispersion states mentioned above.

Figure 3 shows X-ray diffraction patters of **1** as a typical example. The diffraction patterns of monomer nanocrystals were essentially the same as those of the corresponding bulk crystals, which are assigned to be β-form [3,4]. Although the β-form crystals were reported to be less polymerizable, we observed their polymerization initiated by UV or γ-ray. After UV irradiation, X-ray diffraction patterns of bulk crystals were deteriorated and only the broad peaks assigned to be periodicity of packed alkyl chain remained. Nanocrystals also showed similar diffraction patterns, indicating that crystallinity was not preserved even in nanocrystals in this series of compounds.

Compound **1** in nanocrystalline and bulk-crystalline forms was also polymerized by γ-ray irradiation. Quantitative conversion of these samples was confirmed by IR spectra. GPC was performed for chloroform extracts of both samples, and number-average molecular weights ($\overline{\mathrm{Mn}}$) of the nanocrystals and the bulk crystals were obtained to be 3100 and 15600, respectively. Number-average

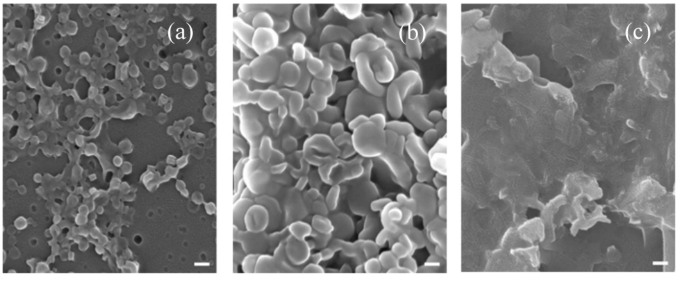

FIGURE 2 SEM images of nanocrystals after UV irradiation: (a) **1**, (b) **2** and (c) **3**. Length of bars at the lower right corners indicates 200 nm.

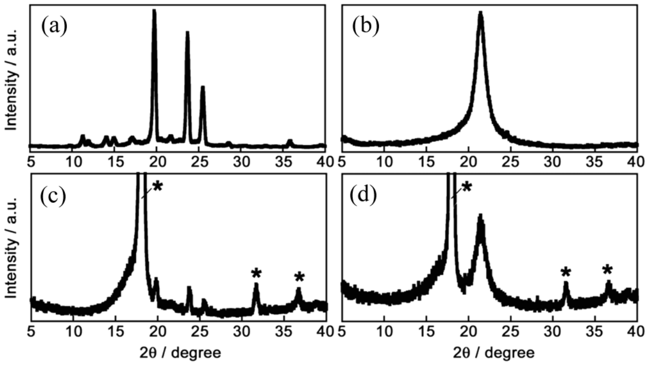

FIGURE 3 Powder X-ray diffraction patterns of **1**: (a) Monomer bulk crystals, (b) polymer bulk crystals, (c) monomer nanocrystals and (d) polymer nanocrystals. Asterisks in Figures (c) and (d) indicate diffraction peaks from Teflon filters used for nanocrystal collection.

degrees of polymerization were calculated to be about 10 and 48, respectively. Polydispersity index ($\overline{\mathrm{Mw}}/\overline{\mathrm{Mn}}$) for the nanocrystals was 1.1 while that for the bulk crystals was quite large up to 8.1. This result indicates that polymerization in nanocrystals of **1** proceeds within a limited length in each nanocrystal. Since covalent-bond length between two atoms is shorter than van-der-Waals contact length of the two atoms, polymer length should be shorter than the total length of the corresponding monomer array. Thus, if polymerization in nanocrystals proceeded in a unique direction, further polymerization may not proceed when the distance between the end of the polymer with a shrunk length and the adjacent monomer in the crystalline lattice becomes too long to form covalent bond.

In conclusion, nanocrystals of **1** through **3** were successfully fabricated by use of the reprecipitation method. From the IR and X-ray diffraction studies, polymerization behaviors in nanocrystals were found to be quite similar to those in the corresponding bulk crystals. However, it is interesting that $\overline{\mathrm{Mn}}$ and $\overline{\mathrm{Mw}}/\overline{\mathrm{Mn}}$ of **1** in nanocrystals were found to be smaller than those in bulk crystals.

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