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PREPARATION AND CHARACTERIZATION OF POLY-DIACETYLENE MICROCRYSTALS

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ABSTRACT

The microcrystals formation process of diacetylene (DCHD) in the reprecipitation method has been investigated by SEM and light scattering. Amorphous DCHD particles were confirmed to be formed first, and then to crystallize. The size control of DCHD monomer microcrystals could be achieved by controlling the size of such amorphous DCHD particles, which depended on the concentration of the injected solution. The solid-state polymerization of DCHD monomer microcrystals was carried out by UV-irradiation, and the size of resulting poly-DCHD microcrystals were 50 nm to 150 nm. The size was unchanged during the solid-state polymerization. By adding SDS in the reprecipitation process, poly-DCHD microcrystal size was further reduced to ca. 15 nm, whose dispersion showed extremely low scattering loss, and expected to be the promising nonlinear optical material.

INTRODUCTION

Recently, microcrystals have raised much interest due to their unique optical properties in the photonics field, which appear neither in a molecule nor in bulk

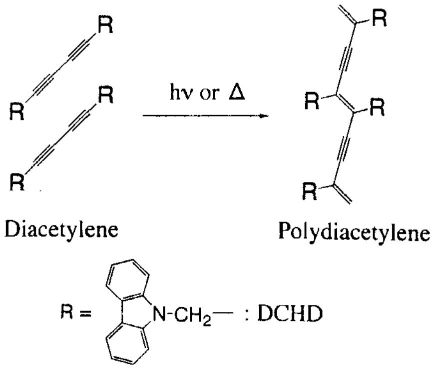


Figure 1. Scheme of solid-state polymerization in a diacetylene crystal.

crystals. A quantum confinement effect [1] in microcrystals is one of the most attractive and important phenomenon in nonlinear optics (NLO). This could lead to an enhancement of third-order NLO susceptibility ($\chi^{(3)}$), and has already been confirmed in inorganic microcrystals (or microparticles) such as metals [2] and semi-conductor [3] microcrystals. So far, however, there are few reports regarding organic microcrystals.

For the first time, we have proposed a reprecipitation method [4] to fabricate organic microcrystals of low molecular weight aromatic compounds such as perylene [5], some kinds of dyes [6], and diacetylene compounds [7]. In diacetylene microcrystals, the behavior of solid-state polymerization shown in Figure 1, e.g., polymerization rate and conversion, was found to be different from that in a bulk diacetylene crystal [7]. The physical properties of polydiacetylene microcrystals have been evaluated, and were expected to be a new type of material in third-order NLO.

However, it is difficult to control crystal size and monodispersity in the reprecipitation method. In this article, a crystallization process in the reprecipitation method was investigated, and the trial of reducing of a crystal size was carried out.

EXPERIMENTAL

A diacetylene compound used in the present study was 1,6-di(*N*-carbazolyl)-2,4-hexadiyne (DCHD). Solid-state polymerization was known to occur through phase transition in the state of bulk DCHD crystal, and the conversion was approximately 100% [8, 9].

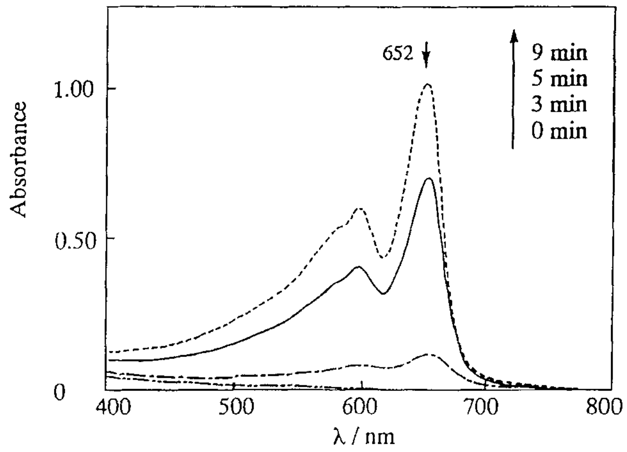


Figure 2. Absorption spectral changes of DCHD microcrystals dispersed in water with UV-irradiation time: 0 minutes, 3 minutes, 5 minutes, and 9 minutes. UV-irradiation was carried out after t_r = 30 minutes. The physical meaning of t_r is the time between injection of solution and starting of UV-irradiation.

Under the typical reprecipitation conditions, 100 μl to 200 ml of DCHD monomer acetone solution was injected into distilled water (10 μl) stirred vigorously, and after a given retention time (t_r), UV-irradiation (254 nm) was carried out in order to prepare poly-DCHD microcrystals: i.e., t_r means time interval from the solution injection to the starting of UV-irradiation. The t_r values were varied from 0-20 minutes. The resulting UV-irradiated DCHD microcrystals were dispersed in water. The size and shape of UV-irradiated DCHD microcrystals were evaluated with a scanning electron microscope (SEM; Hitachi, S-900). On the other hand, the intensity of scattered light was measured in order to monitor a crystallization process of microcrystals (DLS; Otsuka electronics, DLS-7000), and a UV-VIS spectrometer (Shimadzu, UV-240) was used . The ξ-potential of poly-DCHD microcrystals was measured in the water dispersion state (Otsuka Electronics, ELS-800). All experiments were carried out at room temperature.

RESULTS AND DISCUSSION

Immediately after injection of the DCHD acetone solution into water, the dispersion liquid was white turbid, and the stability was very good. In other words, no aggregates formed in air at room temperature, even for one year. The solid-state

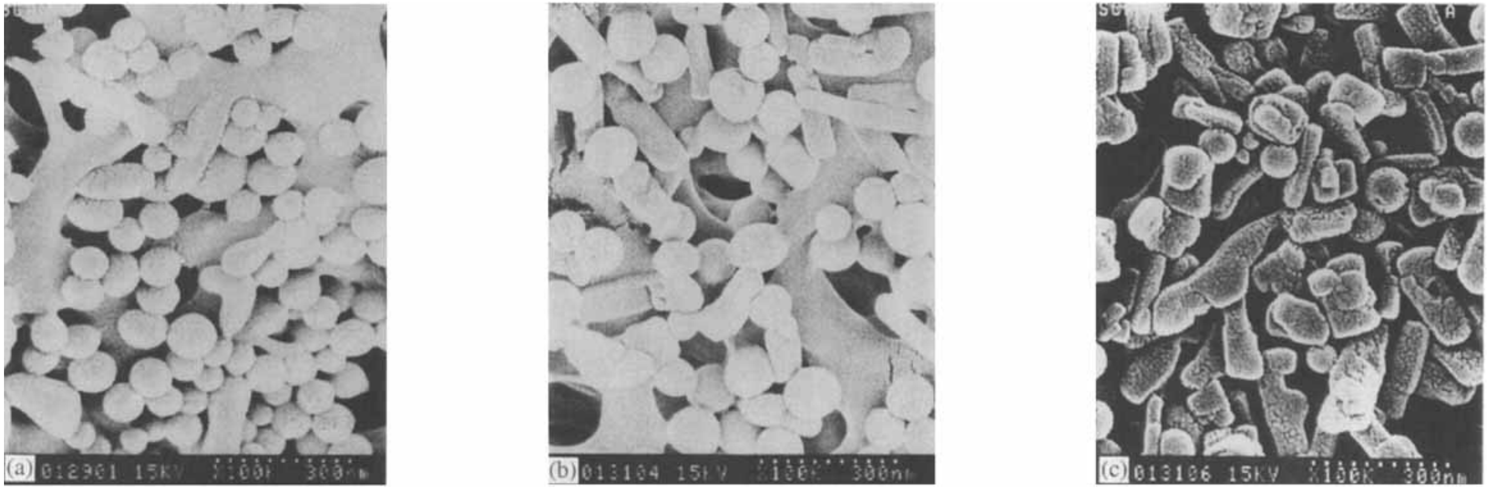


Figure 3. SEM photographs of UV-irradiated DCHD microcrystals at various t_r: (a) $t_r = 0$ minutes; (b) $t_r = 5$ minutes; (c) $t_r = 10$ minutes. The colors of dispersion liquid were (a) yellow, (b) pale blue, and (c) blue, respectively.

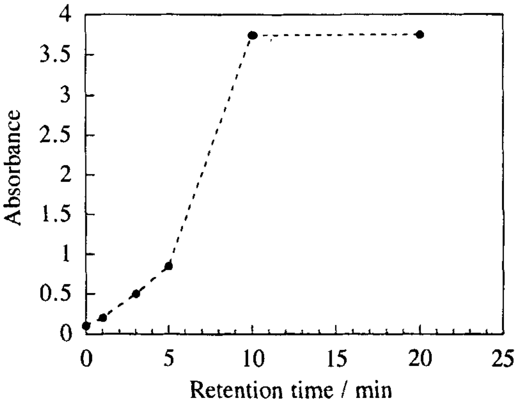
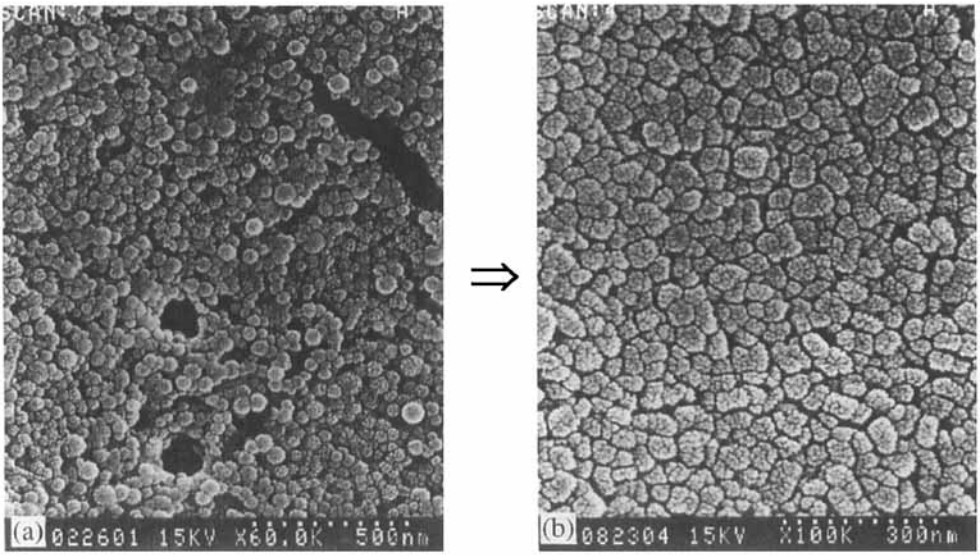


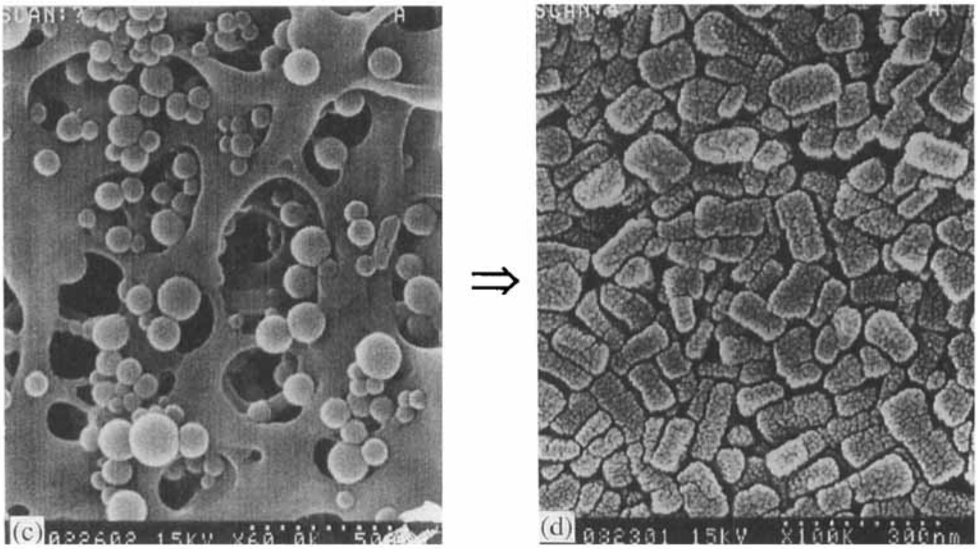
Figure 4. Dependence of excitonic absorbance at λ_{max} = 650 nm on t_r UV-irradiation was carried out for 20 minutes in any t_r.

polymerization of DCHD [8, 9] microcrystals was achieved by UV-irradiation at t_r = 30 minutes. The UV-irradiation time dependence of absorption spectra of the poly-DCHD dispersion liquid is shown in Figure 2. The absorption peak (around 650 nm) gradually increased with irradiation time, but not shifted, and the color of the dispersion liquid turned to blue. This absorption peak attributes to the formation of exciton along one-dimensional π-conjugated poly-DCHD chain in microcrystals. The absorbance was saturated and reached to ca. 3.0 after 20 minutes of UV-irradiation time (Figure 6).

Figure 3 shows SEM photographs of UV-irradiated (20 minutes) DCHD particles at various t_r. The shape at t_r = 0 minute was spherical, and varied to cubic at t_r = 10 minutes. The color of the dispersion liquid at t_r = 0 minutes turned to yellow, not blue by UV-irradiation. Figure 4 exhibited the excitonic absorbance dependence at λ_{max} = 650 nm on t_r. Although UV-irradiated time was 20 minutes in any t_r samples, the absorbance was scarcely detected at t_r = 0 minutes, gradually increased until t_r = 10 minutes, and then saturated. This fact suggests that spherical DCHD particles at t_r = 0 minutes as shown in Figure 3(a), not polymerizable, may be amorphous, and crystallization proceeds gradually for t_r = 10 minutes. Thus, amorphous DCHD particles become solid-state polymerizable DCHD monomer microcrystals. Actually, powder X-ray diffraction patterns have supported the above discussion: the diffraction peaks at t_r = 0 minutes were not observed, but appeared clearly on the sample of t_r = 10 minutes



(I) 2.5 mM



(II) 10 mM

Figure 5. SEM photographs of amorphous DCHD particles and DCHD monomer microcrystals. The concentration of injected DCHD acetone solution were, respectively, 2.5 mM and 10 mM. In any concentration, the photographs at the left column, (a) and (c), are the ones (amorphous DCHD particles) at $t_r = 0$ minutes, and the photographs at the right column, (b) and (d), are the ones (DCHD monomer microcrystals) at $t_r = 20$ minutes.

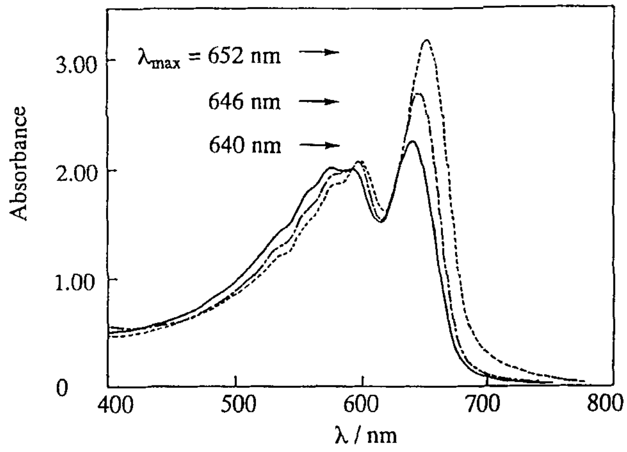


Figure 6. Relationship between excitonic absorption peak position (λ_{max}) and the size of poly-DCHD microcrystals: ———, 70 nm; — · —,100 nm, and --------, 150 nm.

In Figure 3, besides the change of shape, the average size at $t_r = 0$ minutes was roughly similar to that at $t_r = 10$ minutes. To control the DCHD microcrystals size, it is necessary to control the size of amorphous particles at $t_r = 0$ minutes Figure 5 displays SEM photographs of size-controlled DCHD amorphous particles and the corresponding DCHD monomer microcrystals by changing the concentration of the injected solution. The size of amorphous particles clearly decreased with reducing the concentration. In addition, the resulting microcrystals size also became smaller than that of the high concentration. By employing this procedure, we succeeded in size control of DCHD microcrystals in the range of 50-150 nm. We investigated the characteristics of these different sizes of poly-DCHD microcrystals by means of a UV-VIS spectrometer. Figure 6 shows the dependence of the size of poly-DCHD microcrystals on the excitonic absorption peak (λ_{max}). The excitonic absorption peaks were blue-shifted with decreasing crystal size and this behavior is the same as that which appeared in the perylene microcrystals [5]. Unfortunately, this is not explainable by the concept of quantum size effect discussed in the field of inorganic microcrystals, which is argued usually in less than 10 nm of crystal size. However, the unique size effect of organic microcrystals, appeared here. To further confirm the crystallization process in the reprecipitation method, we monitored the scattered light intensity (Is/Io) for the dispersion liquid.

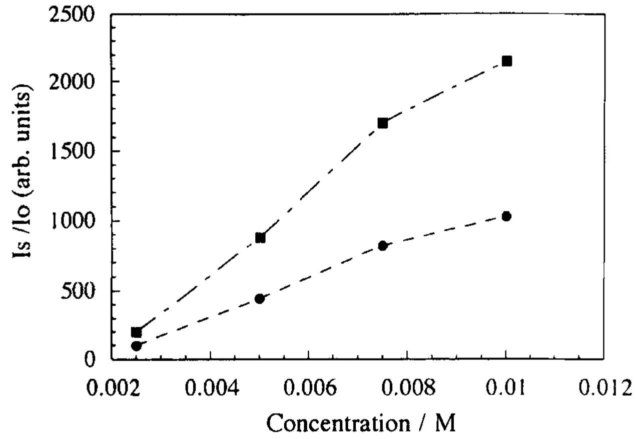


Figure 7. The plots of scattered light intensity Is/Io vs. concentration of the injected solution at t_r = 0 min. The injected amounts were 100 μl (●) and 200 μl (■), respectively.

Figure 7 shows the relationship between scattered light intensity, Is/Io, immediately after the injection of solution, concentration, and amount of the injected solution. In accordance with the Rayleigh theory [10], Is/Io is expressed by,

$$\mathrm{Is}/\mathrm{Io} = \mathrm{FNv}^2 \tag{1}$$

where, v is the volume, N are the number of scattering bodies, and F is the prefactor depending on dielectric constant, etc. As shown in Figure 7, Is/Io was proportional to the injection amount of the solution at any concentration. Assuming that F is constant, the fact can be considered that when the injected amount was changed, and the concentration was constant, the value of N would change. On the other hand, the reduction of Is/Io with decreasing the concentration seems to correspond to the decrease in the size of amorphous particles.

Due to our experimental results, we propose the following reprecipitation method as a model for the formation of DCHD microcrystals. As shown in Figure 8 (schematically), after the injection, fine droplets disperse in stirred water at the first state. Next, the acetone, removes and dissolves smoothly and rapidly from the droplets into water at the second state, and amorphous DCHD particles are formed. However, in this state, solid-state polymerization still cannot occur by UV-irradiation. During the retention time, molecules in amorphous particles reorientate

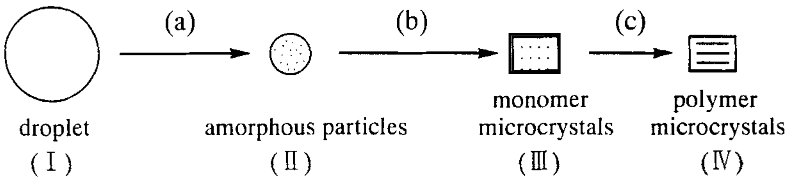


Figure 8. Schematic model for crystallization process of DCHD microcrystals in the reprecipitation method: (a) removing of acetone from droplet and dissolution into surrounding water; (b) reorientation of DCHD molecules in amorphous particles and crystallization; (c) solid-state polymarization by UV-irradiation.

and crystallize at the third state, where microcrystals formed are solid-state polymerizable by UV-irradiation. They are then converted to poly-DCHD microcrystals at the final state. As suggested in the SEM photographs in Figure 3, the average size of amorphous DCHD particles, DCHD monomer microcrystals, and poly-DCHD microcrystals were almost constant during both the crystallization and solid-state polymerization processes, respectively. In our model, the average droplet size is determined by mechanical factors, such as stirring conditions in the reprecipitation method. In other words, if the amount of the injected solution doubles, the number of the droplet would also double. On the other hand, if the concentration of the injected solution is higher, the droplet becomes highly concentrated without changing droplet size, which would lead to larger amorphous particles and microcrystals. The above prediction was in qualitative agreement with the facts shown in Figure 5.

Finally, we have tried to prepare smaller sized poly-DCHD microcrystals, which are less than 50 nm. A small amount of surfactant was added to a DCHD acetone solution (2.5 mM), and the reprecipitation treatment was carried out in the same manner. Three kinds of surfactant were used: HGDE (hexaethyleneglycoldodecylether) as a neutral surfactant; SDS (sodium dodecylsulfate) as an anionic surfactant; and, DTMAC (*n*-dodecyltrimethylammonium chloride) as a cationic surfactant. Figure 9 shows the SEM photographs of poly-DCHD microcrystals prepared in the presence of surfactant. As shown in Figure 9(a), when HGDE was used, the resulting poly-DCHD microcrystals were rod-like, and their size was huge, while their shape and size were roughly the same as those without the surfactant in the case of DTMAC. In other words, HGDE and DTMAC did not work to decrease the crystal size. Moreover, the aggregation of poly-DCHD

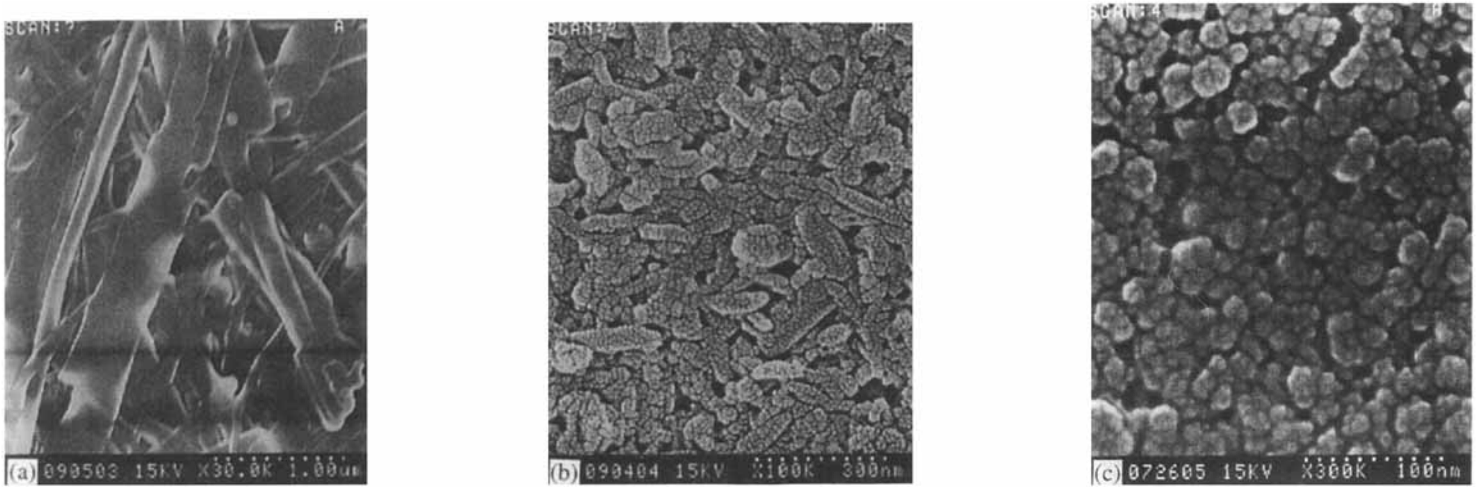


Figure 9. SEM photographs of poly-DCHD microcrystals, which were prepared in the presence of the surfactants: (a) HGDE, (b) DTMAC, (c) SDS. The concentration of DCHD acetone solution used was 2.5 mM.

microcrystals was observed in the sample containing DTMAC. On the contrary, the size of poly-DCHD microcrystals clearly decreased to ca. 15 nm when SDS was used. In our research of organic microcrystals, this size is the smallest. In addition, the values of Is/Io became approximately one twentieth, compared with the same physical quantity of poly-DCHD microcrystals fabricated in the absence of SDS. The ξ-potential of poly-DCHD microcrystals prepared without surfactant was about -40 mV. This implies that the surface potential at electrical double layer and poly-DCHD microcrystals dispersed in water are negative, and positive, respectively. The interfacial potential may generate in water just after the solution injection. When an anionic surfactant such as SDS exists, hydrophobic hydrocarbon chains could be easily absorbed in the amorphous DCHD particles, and the anionic part would face the direction of the water. As a result, it is possible to produce smaller and stable amorphous particles in the water. In the case of DTMAC, however, the cationic part might make an attractive interaction with the surface of negatively-charged electrical double layer and this may be the reason for the aggregation. Regrettably, the interactions of HGDE and amorphous DCHD particles are unknown. In any case, it was found that only SDS was effective in reducing the crystal size in the present experimental framework.

CONCLUSION

The crystallization process of DCHD in the reprecipitation method was investigated. As a result, soon after the solution injection, amorphous DCHD particles were produced, and these gradually crystallized. The resulting DCHD microcrystals dispersed in water were confirmed to be solid-state polymerizable. It has become apparent that the size of poly-DCHD microcrystals are dependent on the size of amorphous DCHD particles in the initial step, which could be controlled by changing the concentrations of injected DCHD acetone solution or by adding some kinds of surfactant. Poly-DCHD microcrystals size were successfully reduced to 15 nm by using anionic surfactant SDS. The dispersion liquid system of poly-DCHD microcrystals of such small size would be a promising and new type NLO material.

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