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Size-controlled production of quinacridone nanocrystals using hot compressed water recrystallization method

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Abstract

Continuous production of quinacridone nanocrystals via a hot compressed water (HCW) recrystallization method was studied using a flow-through experimental apparatus at 24 MPa at temperatures from 523 K to 573 K. Quinacridone crystals were dissolved in HCW and precipitation was initiated by mixing with room temperature water (RTW), which gave the nanocrystalline product. Polyoxyethylene lauryl ether and sodium dodecyl sulfate were found to be useful for reducing aggregation of the nanocrystals. The effects of temperature and flow rate on the size of the crystals were examined; increasing the degree of supersaturation caused crystals to decrease in size. Nanocrystals that had an average diameter of ca. 36 nm could be obtained at 573.8 K and 24 MPa at a flow rate of 10 g/min for HCW and 100 g/min for RTW.

Keywords: Quinacridone; Nanocrystal; Recrystallization; Hot compressed water; Continuous production; Red pigment

1. Introduction

Nanoscale organic crystals are attracting attention in both industry and academia because of specific properties such as colour and electroluminescence. Several synthetic methods have been proposed, such as laser ablation [1], sol–gel [2], and reprecipitation [3,4]. We previously reported a hot compressed water (HCW) recrystallization method as a possible technique for preparing organic nanocrystals [5–7]. In this work, HCW, which has a low dielectric constant (ε) of between 5 and 50, is used to form a saturated or supersaturated solution that is mixed with water at room temperature to initiate solute precipitation [8]. Many organic compounds that are sparingly soluble in room temperature water can dissolve easily in HCW [8,9]. From the viewpoint of green chemistry, HCW has the potential to reduce the use of organic solvents and to control solubility. In the recrystallization method, organic crystals are dissolved in HCW within a saturation cell; nanocrystals are formed by mixing the saturated or supersaturated high-temperature aqueous solution with a cooling solvent in a mixing tee. The cooling solvent can be a pure solvent or an appropriate mixture of water, acetone, ethanol, or methanol. The size of the nanocrystals can be controlled by changing the saturation temperature and composition of the cooling solvent. Although some studies have been performed on the HCW recrystallization method [5–7,10], the precipitation mechanism is unclear. To translate the method to an industrial scale, it would be useful to understand the relationship between particle size and the experimental factors associated with nucleation, crystal growth and solubility.

This paper concerns the production of quinacridone nanocrystals by HCW recrystallization method and their analysis on the basis of the degree of supersaturation. Quinacridone

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is a well-known pigment used in inkjet and laser printers, for which, the control of particle size within the nano-range is important for industrial applications [11]. Quinacridone has high thermal stability and its solubility in HCW is known [9].

2. Experimental

β-Quinacridone crystals were purchased from Tokyo Kasei Kogyo with a purity of 94% and an average diameter of 1.8 μm, as measured by TEM. Ultrapure water (resistivity > 0.18 MΩ m) was used for dissolution of the crystals in both the saturation and cooling solvents. Sodium dodecyl sulfate (SDS, purity $> 98\%$) and 30% polyoxyethylene(23) lauryl ether (POE) solution (Brij 35) were used as dispersants and were supplied by Kishida Chemical and Alfa Aesar, respectively. Both POE and SDS were used at a concentration of 0.4%, 0.8% or 1.6% in the cooling solvent.

Fig. 1 shows the flow-through experimental apparatus for production of the quinacridone nanocrystals. Ultrapure water was fed by a high-pressure pump 1 at a constant flow rate of 10 g/min and it was heated to the desired temperature with a preheater. The preheated water was allowed to flow into the saturator cell that contained 25 g of crystals. The cell was fitted with a 0.5 μm sintered stainless steel filter to retain any free quinacridone crystals. After the solution became saturated with quinacridone crystal [9], the solution was mixed with cooling solvent that contained POE or SDS surfactant at the mixing point. The cooling solvent was fed by pump 2 at flow rates of 10−100 g/min. The effluent was quenched to room temperature after the mixing point with an external water jacket.

The temperature in the cell was maintained within ±0.1 K using a sheathed heater located along the inner wall. The saturation temperature is referred to as T and the solution temperature after mixing as T_0. The system pressure was maintained at 24 ± 0.1 MPa with a back pressure regulator that was placed subsequent to the cooler.

The tubing (o.d. 1.58 mm, i.d. 0.59 mm) used in the main part of the apparatus was made of 316 stainless steel; a 1/16″ tee (i.d. 0.3 mm) made of 316 stainless steel was used for the mixing point. The microheater and 316 stainless steel tubing (o.d. 1.58 mm, i.d. 0.13 mm) were used to reduce precipitation and plugging in the tube between the saturation cell and the mixing tee that occurred as a result of decreasing temperature and flow velocity. The details of the saturation cell have been described previously [9]. To ensure that the solutions became saturated, the rotation speed of the electromagnetic stirrer was set to 1000 rpm [9].

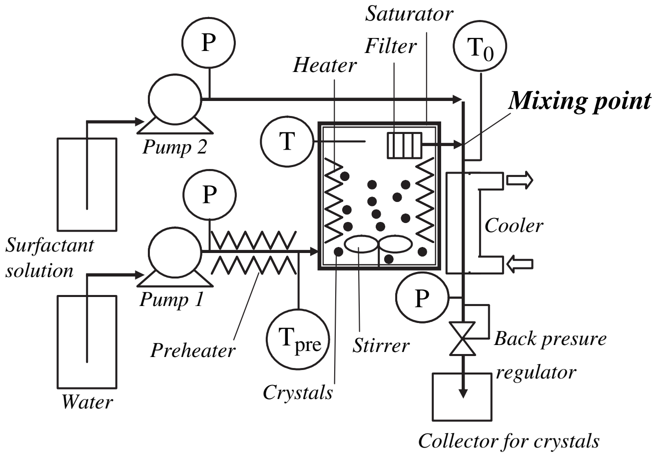

Fig. 1. Schematic diagram of experimental set-up for quinacridone fabrication.

After cooling and depressurization, the precipitated crystals were collected in a glass flask as slurry. The solids in the effluent solution were filtered by a membrane filter, washed with pure water and dried at 333 K in an oven for 24 h. The products were observed using transmission electron microscopy (TEM, Tecnai20, Tecnai). The average particle size was determined by dynamic light scattering (DLS, DLS-6000AL, Otsuka Electronics) and the crystal structure was analyzed by UV/Vis spectrophotometry (V-570, JASCO).

3. Results and discussion

Experimental results are summarized in Table 1 from which it is apparent that the flow after mixing was turbulent. From the result, it can be considered that the saturated solution and cooling solvent were rapidly mixed, which caused abrupt crystallization. The rapid cooling probably led to the small particle sizes shown in Table 1. The Reynolds number obtained just after the mixing tee was calculated using flow velocities and properties of pure water. Typical results (run 13) for TEM measurements are shown in Fig. 2. The crystal sizes determined using TEM and DLS measurements for run 13 were 50 nm and 91 nm, respectively. It is apparent that crystal size depends on the analytical method used. Typical results of absorption spectra of the quinacridone crystals dispersed in liquid are shown in Fig. 3. The absorption spectrum in the case of POE can be assigned to the single phase β-form (stable phase) of the quinacridone crystal [12]. No significant differences in absorption spectra were observed at other conditions with POE. In contrast, the absorption spectrum with SDS can be assigned to the single phase α-form (metastable phase) of the quinacridone crystal [12]; no significant differences were found in the absorption spectra for the other SDS concentrations used.

In previous work, in the absence of dispersant [10], large crystals of average size 1691 nm were obtained due to strong aggregation; in contrast, the present work has shown that the addition of dispersants reduced aggregation of the precipitated nanocrystals and allowed the formation of small crystals with an average size of 85−241 nm. An increase in dispersant concentration lowered crystal size, as shown in Table 1. In previous work [10], the form of the crystals obtained changed from the α-form to the β-form as the cooling water flow rate decreased. Generally, the transition from the metastable to the stable phases proceeds at high temperatures. Precipitation at high cooling water flow rates promoted formation of the metastable α-form of the crystals. In contrast, precipitation at low

Table 1
Experimental conditions and results

Run no.	F_{RTW} [g/min]	T [K]	T_0 [K]	Surfactant[a] [wt%]	Re [−]	D_m [nm]	S^* [−]
1	10	523.0	411.8	0.8	6890	241	4.9
2	20	523.1	377.7	0.8	7280	140	6.0
3	50	523.5	335.6	0.8	8960	72	7.6
4	100	523.2	318.0	0.8	12 230	90	8.4
5	10	548.5	411.5	0.8	7650	102	6.5
6	20	548.0	367.6	0.8	8000	87	7.8
7	50	548.3	331.2	0.8	95 90	53	9.3
8	100	547.7	316.0	0.8	12 810	60	10.1
9	10	562.4	427.4	0.8	8080	116	7.1
10	20	573.7	377.8	0.8	8800	104	9.1
11	50	573.2	336.6	0.8	10 270	64	10.7
12	100	573.8	320.9	0.8	13 460	36	11.5
13	20	574.6	386.5	0.4	8840	91	9.1
14	20	573.1	375.6	1.6	8790	85	9.5
15	20	574.6	386.5	0.4	8820	223	9.3
16	20	573.2	375.1	1.6	8790	167	9.7
17[b]	20	574.6	386.5	0.0	8840	1691	9.1

[a] All runs used POE except for runs 15 and 16 that used SDS.

[b] Data from our previous work [10].

cooling water flow rates gave the stable β-form, probably due to the crystals having been kept at a relatively high temperature that allowed phase transition from the α-form to the β-form. The crystal form of the products seemed to strongly depend on the cooling rate during precipitation. The surfactants, SDS and POE, provided stabilization of the dispersion by electrostatic repulsive forces and steric hindrance. Generally, the thermal diffusivity of water is higher than that of organic molecules such as hydrocarbons [2]. Since POE has a longer aliphatic chain than SDS, its greater hydrophobic nature prevents some water molecules from having close interactions. Thus, it seems possible that in the case of POE, β-crystals are produced by a slow cooling rate and phase transition occurs during the prolonged duration at high temperature. In contrast, the α-form is secured using SDS as a result of rapid quenching rates most likely because of the greater quantity of water that would be attracted to the surfactant/particle precipitants.

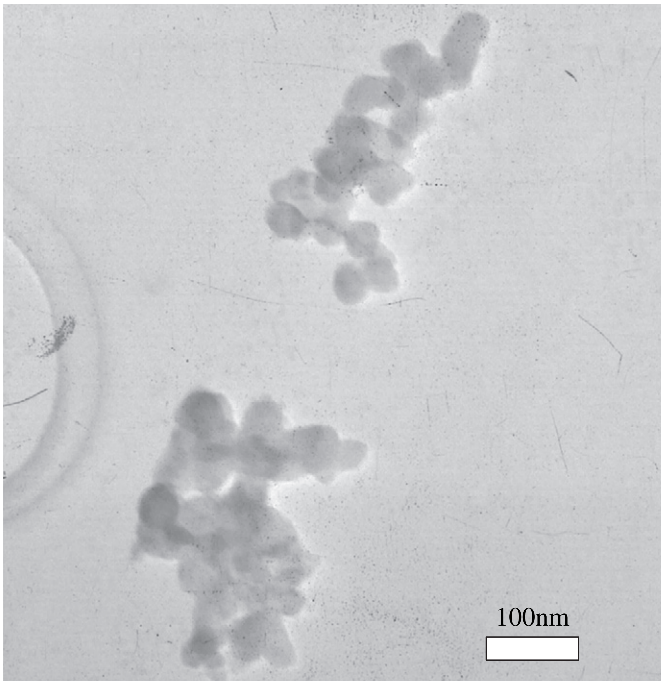

Fig. 2. TEM observation of fabricated nanocrystals at saturation temperature of 574.6 K (run 13).

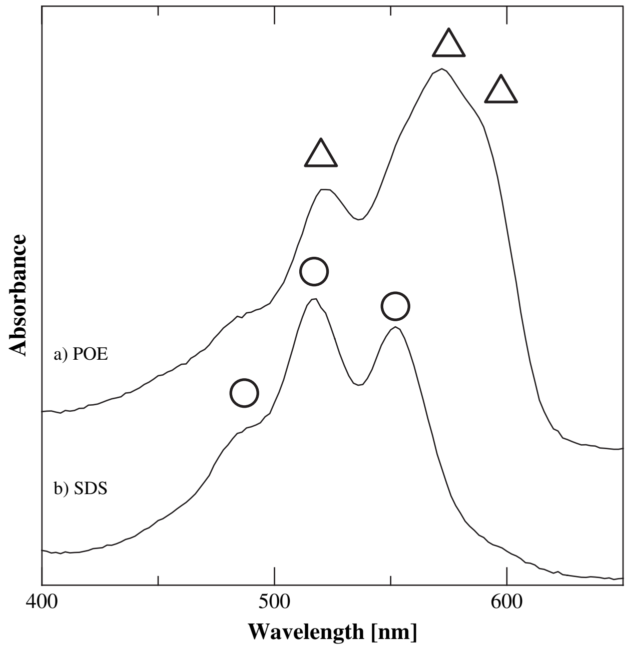

Fig. 3. Absorption spectra of quinacridone nanocrystal dispersion liquid at 574.6 K with (a) 0.4 wt% POE (run 13) and (b) 0.4 wt% SDS (run 15). Circle and triangle denote the α and β crystal forms, respectively.

Supersaturation S^* is the driving force for precipitation and it is defined by the following relationship [13]:

$$S^* = \ln \frac{S}{S_0} \tag{1}$$

where S and S_0 denote solubility at saturation temperature T and that at temperature after cooling T_0, respectively. On the basis of nucleation theory [13], the diameter of a critical nucleus D^* can be expressed as

$$D^* = \frac{4\sigma v_s}{kTS^*} \tag{2}$$

where σ, v_s, and k are the interfacial tension of the solute [N/m], the solute molecular volume in the solid phase [m^3], and the Boltzmann's constant [1.38×10^{-23} Nm/K], respectively. On the basis of Eq. (2), increasing supersaturation should give smaller particles. For example, increasing the cooling water flow rate from 10 g/min to 100 g/min at a given temperature decreases particle size (runs 1–12) and smaller nanocrystals are produced of with an average particle diameter of 36 nm at a saturation temperature of 573.8 K and cooling water flow rate of 100 g/min (run 12). Quinacridone solubilities in high-temperature water without dispersants were taken from literature [9]. Fig. 4 shows the relationship between

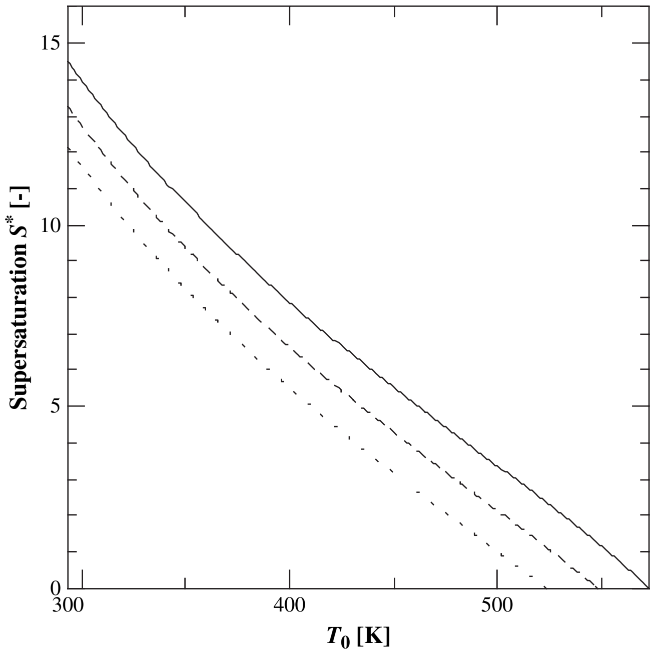

Fig. 4. Estimated supersaturation as a function of saturation temperature and temperature after cooling. Solid, dashed, and dotted lines represent the saturation temperatures of 573 K, 548 K and 523 K, respectively.

temperature after cooling T_0 and supersaturation at temperature T determined from Eq. (1). As shown in Fig. 4, supersaturation increased linearly with decreasing temperature after cooling, which shows the importance of rapid cooling for the production of nanocrystals. Fig. 5 shows the relationship between supersaturation $1/S^*$ and mean particle size; as the degree of supersaturation increased, the mean particle size decreased in accordance with Eq. (2).

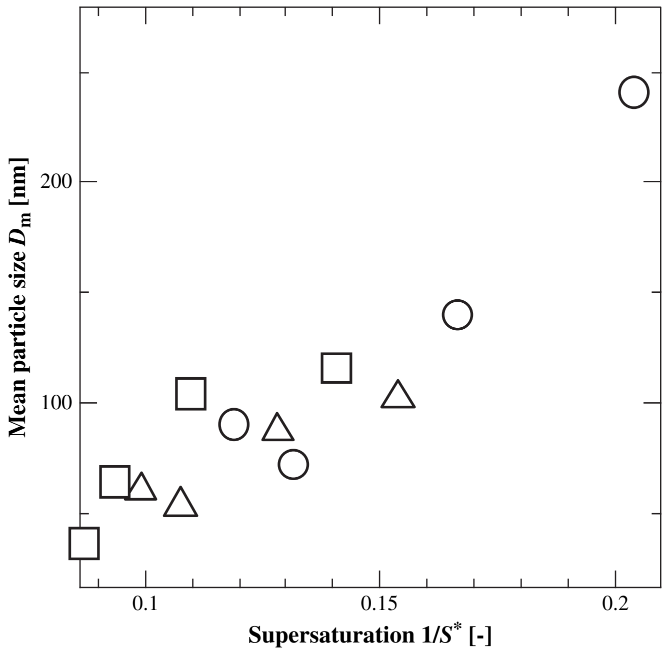

Fig. 5. Comparison between mean particle size and supersaturation at given saturation temperature. Circle, triangle and square denote the saturation temperatures of 523 K, 548 K, and 573 K, respectively.

4. Conclusions

Quinacridone nanocrystals could be produced using hot compressed water recrystallization method. The effects of saturation temperature and cooling water flow rate on particle size were analyzed on the basis of supersaturation and it was found that small nanocrystals with a mean diameter of 36 nm were obtained at a supersaturation ($1/S^*$) value < 0.09.

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