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Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
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Mass-Production of Pigment Nanocrystals by the Reprecipitation Method and their Encapsulation

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Version of record first published: 23 Aug 2006

To cite this article: Kento Ujiiye-Ishii, Koichi Baba, Zhong Wei, Hitoshi Kasai, Hachiro Nakanishi, Shuji Okada & Hidetoshi Oikawa (2006): Mass-Production of Pigment Nanocrystals by the Reprecipitation Method and their Encapsulation, Molecular Crystals and Liquid Crystals, 445:1, 177/[467]-183/[473]

To link to this article: http://dx.doi.org/10.1080/15421400500367082

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Mol. Cryst. Liq. Cryst., Vol. 445, pp. 177/[467]–183/[473], 2006
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400500367082

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Quinacridone nanocrystals with controlled size and morphology were readily fabricated by using a pump as an injection apparatus of the reprecipitation method for mass-production and injecting concentrated N-methyl-2-pyrrolidinone solution. Encapsulation of quinacridone nanocrystals using polymer was

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achieved and quite improved dispersibility was confirmed for the encapsulated nanocrystals.

Keywords: encapsulation; mass-production; nanocrystals; pigment; polystyrene; quinacridone; the reprecipitation method

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INTRODUCTION

Pigments are used to attach colors to various materials. Their history stretches back to ancient times. The roots can be found in the wall paintings in the caverns of Altamira and Lescaux. Here human artists drew animals with fur and wings using paints made by tempering ground minerals and the fat or blood of hunted animals. Between the 13th and 18th centuries, methods of manufacturing several pigments from mineral and other sources were developed. By the second half of the 19th century, ways to make many of organic pigments currently in use had been discovered [1]. In the present age, technologies related to pigments have grown and made remarkable progress. Almost paints and ink are now used in a dispersion state. Controlling the dispersibility, storage stability, and functionality are key technical factors to obtain higher quality pigments. Fabrication of fine-particle pigments and their excellent dispersibility are the important technical breakthroughs.

In this connection, we have applied the reprecipitaion method [2] to pigments. This method is a easy and convenient technique to fabricate organic nanocrystals in general, and we found several interesting size-dependent properties of these nanocrystals [3,4]. However, only limited amount (about several-tens ml) of nanocrystal dispersion was able to be prepared at once. To overcome this problem, in this study, we introduce a pump as an injection apparatus of the reprecipitation method for mass-production of pigment nanocrystals with controlled size and morphology. Also, in order to improve dispersibility of nanocrystals, we studied encapsulation of pigment nanocrystals with polystyrene-based polymer, which is often used to fabricate spherical colloidal crystals [5] by soap-free emulsion polymerization [6,7].

EXPERIMENTAL

The compounds used in this study are quinacridone and *N,N′*-dimethylquinacridone, which are well known as red pigments. Generally, pigments are not so soluble in common organic solvents.

However, we found that *N*-methyl-2-pyrrolidinone (NMP) was a good solvent to prepare the highly concentrated quinacridone solution up to 20 mM. As shown in Figure 1, quinacridone NMP solution (500 ml, 20 mM) was injected into 4.5 l of water using a pump at a pace of 100 ml per minute. At a result, violet-red dispersion of quinacridone nanocrystals was obtained.

In order to prepare core (pigment)-shell (polymer) nanocrystals, the soap-free emulsion polymerization of styrene and divinylbenzene in quinacridone dispersion was performed as the similar procedure described in the literature [7]. At first, quinacridone nanocrystals were fabricated by the reprecipitation method. The emulsion polymerization was carried out in a 500 ml flask. After styrene monomer (50 mg) in divinylbenzene (1.2 ml) were put into 100 ml of concentrated quinacridone nanocrystal dispersion, nitrogen was bubbled for 30 min with magnetic stirring. Then a catalytic amount of potassium peroxide sulfate was added to initiate the polymerization. The reaction lasted under nitrogen atmosphere for 10 h at 82°C.

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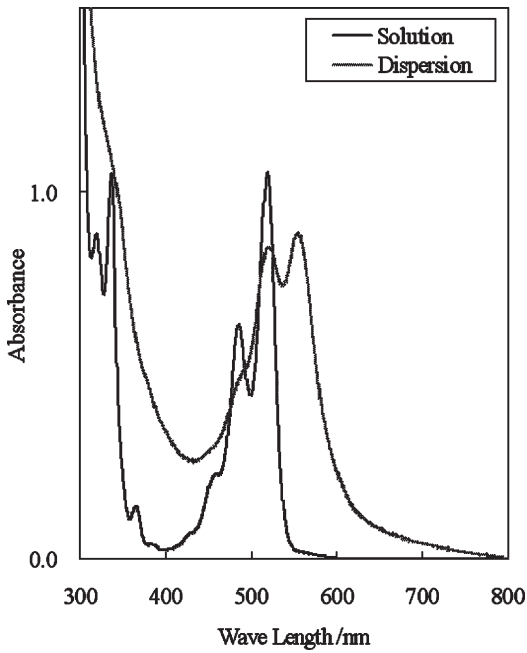

FIGURE 1 Experimental set-up of the injection-pump-assisted reprecipitation method.

RESULTS AND DISCUSSION

For mass-production, most efficient conditions of the reprecipitation method are highly concentrated solution injection and high injection rate. The former condition was achieved by using NMP and the latter was realized by using a high flow-rate pump. Using the injection-pump-assisted reprecipitaion method in this study, the amount of obtained nanocrystals in dispersion was 700 mg per minute at maximum. We obtained 3.5 g of quinacridone nanocrystals in one experiment. This value is about 17,500 times larger than that obtained by the conventional reprecipitation method with manual injection.

Figure 2 shows absorption spectra of quinacridone in NMP solution and in nanocrystal dispersion prepared. The solution spectrum showed sharp peaks while the dispersion spectrum was slightly broadened and the absorption maximum shifted to longer wavelength. Quite similar dispersion spectrum was observed when quinacridone nanocrystals were prepared by the high-temperature and high-pressure liquid

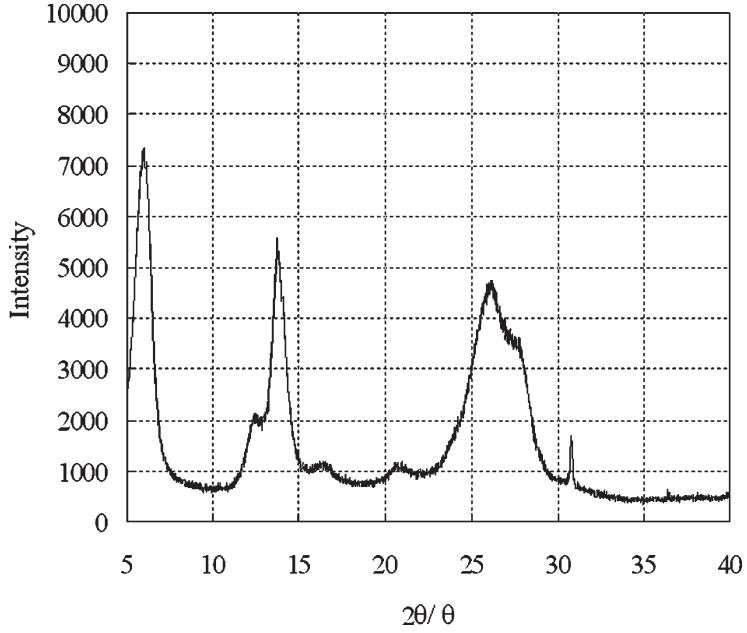

FIGURE 2 UV-visible absorption spectra of quinacridone in NMP solution and the nanocrystal dispersion. The solution spectrum was recorded for the saturated solution by using a 0.1-mm thickness cell. The dispersion spectrum was obtained for the diluted one with three-times volume of water.

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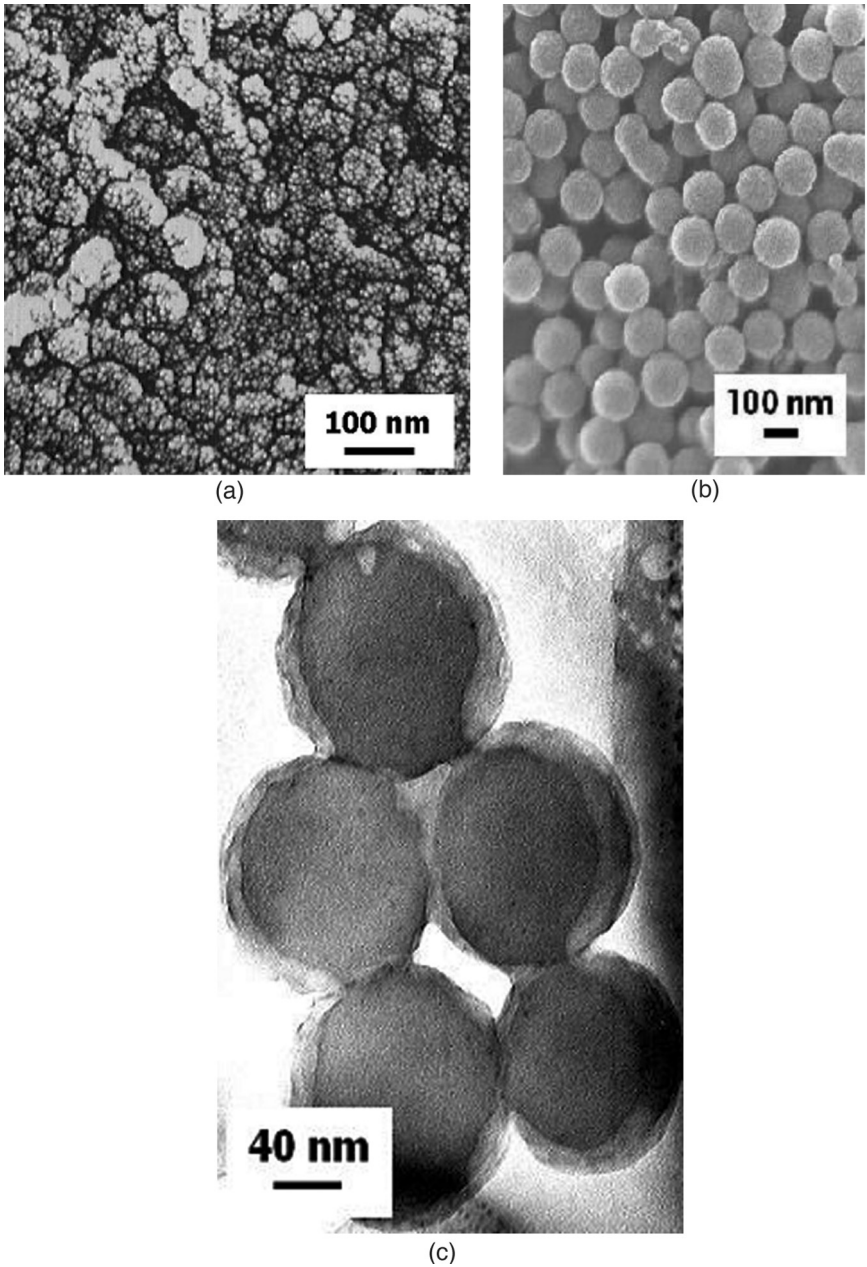

FIGURE 3 SEM images of (a) quinacridone nanocrystals, (b) quinacridone nanoparticles encapsulated by polymer, and (c) TEM image of quinacridone nanoparticles encapsulated by polymer.

crystallization method [8,9]. The size of quinacridone nanocrystals fabricated was 25–80 nm, which was confirmed by observation using a scanning electron microscope (SEM; Fig. 3(a)). From the powder X-ray diffraction data, only α-type nanocrystals were found to be obtained [10].

In the encapsulation experiments, the dispersion color changed from violet-red to light pink in the course of polymerization. After the reaction, oligomeric residue as the floating mass was partially produced, which could be easily removable. It was found that the quinacridone nanocrystals were changed into spherical particles with an increased size (about 100 nm), as shown in the SEM image (Fig. 3(b)). From the transmission electron microscope (TEM) image (Fig. 3(c)), their core-shell structure, i.e., quinacridone nanocrystals covered with a polymer layer, was clearly observed. Shell thickness was about 10–25 nm. Almost all particles observed by TEM contained a core nanocrystal. The obtained encapsulated nanoparticles well dispersed in water even after more than 3 months. This is contrast to the original nanocrystal dispersion showing precipitates after 2 weeks from the preparation. Long dispersion stability of encapsulated particles was caused by the nature of polystyrene-based polymer, which showed high dispersibility in the particle form.

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SUMMARY

We demonstrated the reprecipitaion method assisted by an injection pump for mass-production of organic pigment nanocrystals. Its maximum yield was 700 mg per minute. We succeeded to fabricate encapsulated pigment nanocrystals by soap-free emulsion polymerization. The dispersibility was quite improved by polymer encapsulation. Since many kinds of applications such as ink, OPC, and color filters, are expected for pigment nanocrystals, further investigation will be focused on optimization of mass-production and encapsulation conditions based on the present experiments.

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