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Dispersion control of perylene fluorophores in a polystyrene microsphere

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ABSTRACT

Polystyrene (PS) microspheres embedding perylene fluorophores have been fabricated by the two kinds of encapsulation method; (A) seed polymerization of styrene using perylene nanocrystals as a seed, and (B) emulsion polymerization of perylene-styrene solution. In both methods, the PS microspheres formed were ca. 200 nm in size, roughly larger than bare perylene nanocrystals. Interestingly, the fluorescence peak positions in both the PS microspheres were located between those of solution and nanocrystal states. These facts suggest that the dispersion state of perylene fluorophores in PS microspheres would be changed to be intermediate between solution and nanocrystal states during the polymerization process.

KEYWORDS

Organic nanocrystals; perylene; reprecipitation; polymer microspheres; encapsulation

Introduction

Organic nanocrystals usually show the size distribution to some extent, and the shape is not spherical but intrinsically anisotropic (e.g., rectangular, rod-like, and fibrous). Many researchers have already fabricated ordered array nano- and micro-structures using nano- and micro-particles such as polymer and metal etc., while nonspherical and nonuniform organic nanocrystals have not been employed to form ordered array nano- and micro-structures. To avoid and overcome these problems, encapsulation of organic nanocrystals is very effective and useful. The apparent shape becomes almost uniform and spherical by encapsulating nonspherical and nonuniform organic nanocrystals with polymer shell, which would lead to the easy arrangement process on a substrate [1].

On the other hand, a competitive microphase separation with nanocrystallization of fluorophores inside polymer microspheres has been attracting attention from the viewpoints of controlling the dispersion state and emission properties of fluorophores. Actually, emission properties of perylene are strongly dependent on dispersion states, e.g., monomer and excimer emission in solution state [2], self-trapped exciton (STE) emission in bulk crystal [3], and size-dependent of weak free exciton (FE) and strong STE emission in nanocrystal state [4]. In other words, these behaviors would be useful as a probe to investigate the dispersion state of perylene.

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In the present study, perylene fluorophores have been embedded and dispersed inside polystyrene (PS) microspheres, and their optical properties were investigated, relating to the dispersion state.

Experimental method

Materials

Perylene (sublimed 99.5+ %) was purchased from SIGMA-ALDRICH. Styrene and potassium persulfate (KPS) (special grade chemical) were purchased from Wako Co. Ltd., and used without further purification. Water was purified up to 18.2 MΩ cm using Arium 611UV (Sartorius Mechtronics Japan K.K.).

(A) Soap-free seed encapsulation

Perylene-embedded PS microspheres have been fabricated by the encapsulation of perylene nanocrystals with PS, where aqueous dispersion liquid of perylene nanocrystal was fabricated by injecting 5 mL of perylene-acetone solution (2 mM) into 50 mL of stirred pure water at 0°C. Especially, in order to remove acetone and promote nanocrystallization, perylene nanocrystal dispersion liquid was exposed to microwave (2.45 GHz, 500 W) for 50 s three times [5] and furthermore condensed under reduced pressure. A 1 mL of styrene monomer and 5 mg of KPS as a radical initiator were added to 30 mL of perylene nanocrystal dispersion liquid, and the mixture was stirred and heated at 80°C for 5 h [1].

(B) Soap-free emulsion encapsulation

Perylene-embedded PS microspheres were alternatively fabricated by soap-free emulsion polymerization of perylene-styrene solution: A 1 mL of perylene-styrene solution (6 mM) and 5 mg of KPS as a radical initiator were added to 30 mL of stirred pure water. The mixture was stirred and heated at 80°C for 5 h [6].

Measurement

Perylene nanocrystals and perylene-embedded PS microspheres were observed using a scanning electron microscope (SEM; JSM-6700F, JEOL). Fluorescence spectra were measured with a fluorescence spectrometer (F-7000, Hitachi). The excitation wavelength was 400 nm for all measurements.

Results and discussion

The obtained PS microspheres were spherical, and the average size was ca. 200 nm in both encapsulation methods (Fig. 1(a) – 1(c)), which size is roughly larger than that of bare perylene nanocrystals. In addition, rectangular perylene nanocrystals were not completely observed, except for spherical PS microspheres. In other words, all perylene would be contained inside PS microspheres successfully.

According to fluorescence spectra (Fig. 2), the fluorescence peak positions in both PS microspheres prepared by soap-free seed and emulsion encapsulations were located between those of perylene solution and nanocrystal states. That is to say, the dispersion state of perylene fluorophores would be different from those of both molecular and nanocrystal states, and perylene fluorophores inside PS microsphere would be in the intermediate dispersion state

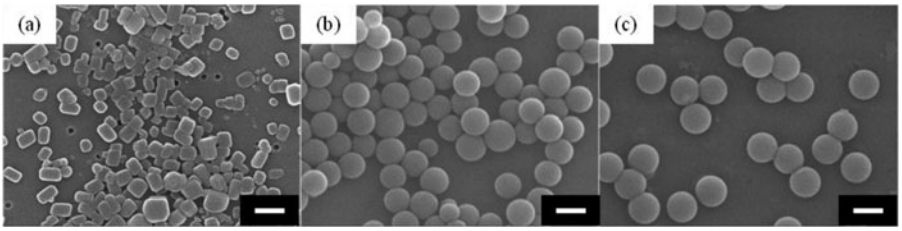

Figure 1. SEM images of (a) peylene nanocrystals, and perylene-embedded PS microspheres fabricated by (b) soap-free seed encapsulation and (c) soap-free emulsion encapsulation. The scale bars indicate 200 nm in size.

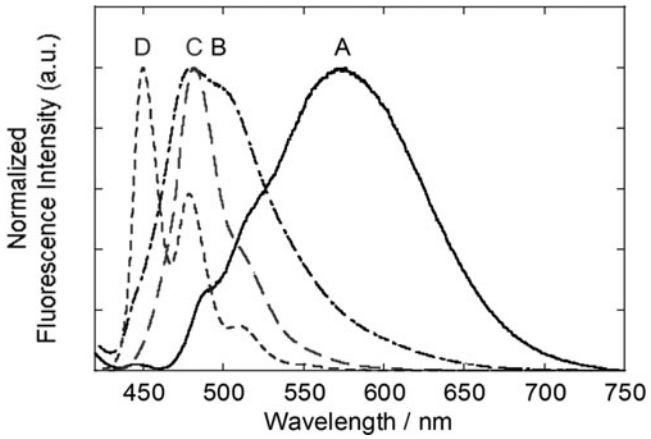

Figure 2. Fluorescence spectra of (A) perylene nanocrystals, perylene-embedded PS microspheres by (B) soap-free seed encapsulation and (C) soap-free emulsion encapsulation, and (D) perylene-styrene solution.

between solution and nanocrystal states. In addition, the fluorescence spectra from these PS microspheres fabricated by soap-free seed and emulsion encapsulations were different each other.

So, the polymerization processes have been investigated by monitoring the changes of fluorescence spectra in the course of polymerization time (Fig. 3(a) and 3(b)). In the soap-free seed encapsulation, the original STE emission peak position was gradually shifted to short

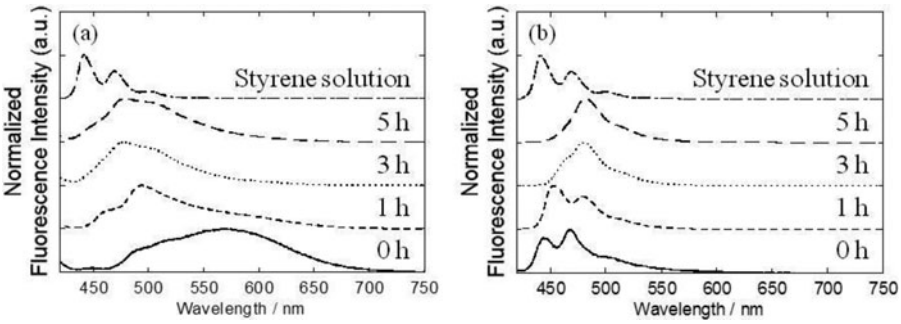

Figure 3. Fluorescence spectral change of perylene fluorophores during (a) soap-free seed encapsulation and (b) soap-free emulsion encapsulation processes. The fluorescence spectra were measured 0, 1, 3, and 5 h after the starting point of encapsulation.

wavelength region, which suggests that encapsulation of perylene nanocrystals was competitive with dissolution and recrystallization/microphase separation of perylene fluorophores inside a PS microsphere, due to, at least, the existence of styrene at the initial stage of polymerization. On the other hand, in the soap-free emulsion encapsulation, monomer emission of perylene fluorophores dissolved in styrene was shifted to long wavelength region, which suggests that perylene fluorophores would be precipitated and competitively undergo a microphase separation with PS. Anyway, the dispersion state of perylene fluorophores inside PS microspheres would be changed gradually to intermediate state different from both molecular and nanocrystal states through competitive microphase separation with nanocrystallization of perylene fluorophores in PS microsphere.

Conclusion

PS microspheres, in which perylene was embedded, have been fabricated successfully by using soap-free seed and/or emulsion polymerization. It was found from the fluorescence spectral changes that the dispersion state of perylene fluorophores inside PS microspheres would be intermediate between molecular and nanocrystal states, and would be formed gradually through competitive microphase separation with nanocrystallization of perylene fluorophores in PS microsphere.

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