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SHORT COMMUNICATION

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Functional fluorescent microspheres

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Abstract Novel functional microspheres encapsulated with tris(8-hydroxyquinolinolato) aluminum were synthesized by dispersion polymerization. They were characterized by scanning electron microscopy (SEM) and electrical conductance titration. The average diameter and size distributions (SDs) of these microspheres were determined by laser diffraction size analysis. The microspheres show good fluorescence.

Keywords Fluorescent · Functional · Microspheres

Introduction

Microsphere-based analytical assays and recognition principles are an important research direction in analytical chemistry. They are used for localized recognition and a number of different readout formats. For example, the incorporation of fluorescent molecules in small particles intensified the development of molecular probes that have application in living cell biology, flow tracing, and fluid mechanics [1]. Recently, the preparation and application of fluorescent microspheres were often reported [2, 3, 4, 5]. The fluorescent chromophores consisted usually of functionalized and polymerizable organic molecules that became a part of the polymer backbone. Fluorescent microspheres were prepared with many inorganic pigments that were dispersed by ultrasound [6, 7]. Almost all of them, however, are often produced by emulsion polymerization yielding nanosized latex particles. In addition, many micrometer-sized fluorescent microspheres were produced by solvent extraction [8, 9]. Although these methods are convenient, the products always had a broad size distribution.

Tris(8-hydroxyquinoline) aluminum (Alq_3) is widely used in modern organic light-emitting diodes (OLEDs) because of its excellent stability and electroluminescent properties. Since 1987, high-luminance, low-voltage-driven devices based on Alq_3 have opened the route to the design of low-cost, large-area displays and illuminators. Despite the large number of studies on this material, very little is known about its application in fluorescent microspheres.

Experimental

Materials

Methylmethacrylate (MMA) was extracted with a mixture of 20%NaCl and 5%NaOH, washed twice with distilled water, dried with $CaCl_2$, and stored at 4°C until use. Tris(8-hydroxyquinolinolato) aluminum (Alq_3) was kindly provided as a gift from Xiaoqin Lin. Benzoyl peroxide (BPO), methanol, poly(vinylpyrrolidone) (PVP) and other reagents were of analytical grade. Water was doubly distilled.

Synthesis

Fluorescent microspheres containing aldehyde groups were prepared by polymerization of MMA (8.0 g) with acrolein (1–4 mL) and benzoyl peroxide (0.1 g) as initiator in methanol (80 g) in the presence of Alq_3 (0.05 g). PVP (1.2 g) was added as stabilizer for the microspheres. The reaction was performed in a 100-mL round-bottomed flask equipped with a reflux condenser, and was carried

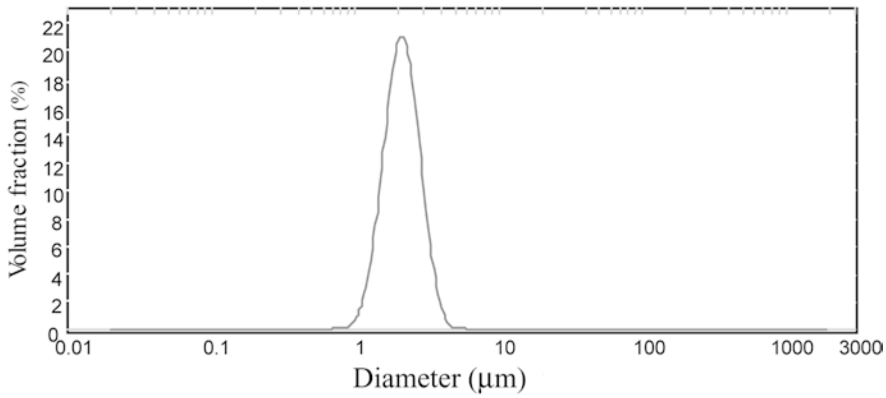

Fig. 1 Size distribution of the fluorescent microspheres

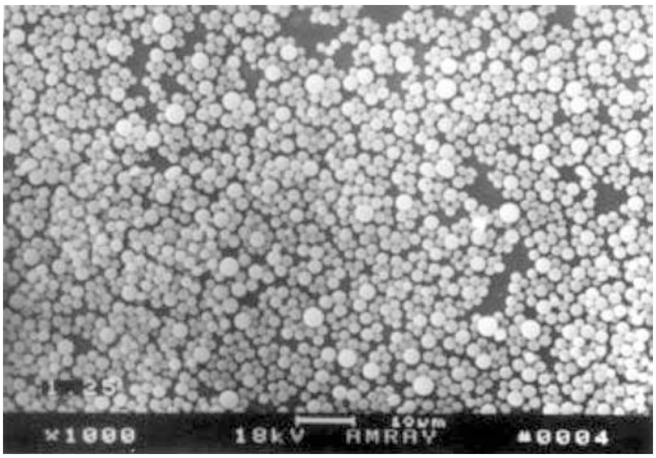

Fig. 2 SEM photograph of the fluorescent microspheres

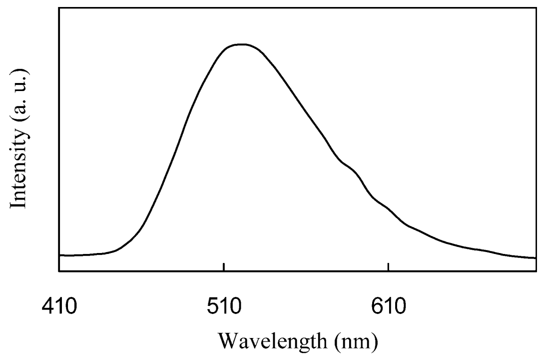

Fig. 3 Emission spectra (Alq_3) in CH_2Cl_2 excited at 395 nm

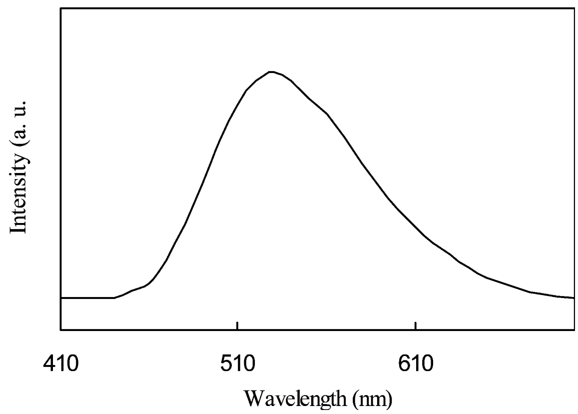

Fig. 4 Emission spectra of the fluorescent microspheres in CH_2Cl_2 excited at 395 nm

out at 70°C for 24 h under an N_2 atmosphere. The resulting microspheres were purified by repeated washing with methanol and water, and dried at 40°C for 8 h in vacuum.

Characterization

The surface morphology of the microspheres was observed by using an AMRAY-1000 scanning electron microscopy at accelerating voltage of 15 kV. The size and its distribution in aqueous dispersions were determined by laser diffraction size analysis (Mastersize 2000, UK). The fluorescence properties of the fluorescent microspheres and Alq_3 were determined with a fluorescence spectrophotometer (Hitachi 650–60, Japan).

The CHO content was determined by electrical conductance titration with a DDS-11A electrical conductance titrator at room temperature. Water (40 mL) was added to a known quantity of the microspheres. After stirring for 30 min, a known excess of (2%) hydrochlorinated hydroxy amine (0.5 mL) was added. The mixture was back-titrated with standard 0.01 N NaOH [10].

Results and discussion

The average diameter of the microspheres was 2.3 μm. The size distribution was typically Gaussian (Fig. 1). The surface was smooth and without noticeable defects (Fig. 2), which minimizes reflection of the fluorescence caused by surface anomalies, thus maximizing the fluorescence signal. The emission spectra of Alq_3 and the microspheres were recorded from 410 to 700 nm with an excitation wavelength of 395 nm (Figs. 3 and 4). The maximum was shifted from 522 nm for Alq_3 in dichloromethane to 533 nm for the fluorescent microspheres.

Table 1 Influence of aldehyde concentration on the size and size distribution (SD) of the fluorescent microspheres

Sample	1	2	3	4
Aldehyde (mmol g^{-1})	1.32	2.31	2.42	1.41
Size (μm)	2.29	2.63	3.72	3.73
SD	0.23	0.26	0.39	0.41

Thus, the microstructure of the spheres had little effect on the emission behavior.

The content of –CHO groups in the microspheres varied between 1.32 and 2.42 mmol g^{-1} (Table 1). In samples 1 and 2, the microspheres were not aggregated, but gelation was observed for samples 3 and 4. These results indicated that gelation was controlled by the content of acrolein. The interaction between aldehyde and Alq_3 may be related to the red shift observed in the fluorescence spectrum. The aldehyde groups still present in the shell provide the field of further application. Future work will include studying the solid-state properties of the fluorescent microspheres and their application in enzyme immobilization.

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