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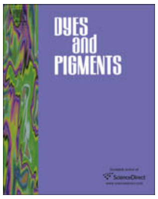

The preparation of copolymerized fluorescent microspheres of styrene using detergent-free emulsion polymerization

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A B S T R A C T

The polymerisable fluorescent monomer, 4-ethoxyl-*N*-allyl-1,8-naphthalimide, was synthesized from 4-bromo-1,8-naphthalic anhydride and characterized using FT-IR spectra, ^{1}H NMR and fluorescence spectra. A copolymer of styrene and 4-ethoxyl-*N*-allyl-1,8-naphthalimide was prepared by detergent-free emulsion polymerization and characterized using fluorescence spectra, SEM and fluorescence microscopy. The fluorescence spectrum of the copolymer displayed excitation at 365 nm and emission at 435 nm in acetone. SEM revealed that the copolymers were microspheres, with smooth surfaces and displayed intense blue fluorescence.

1. Introduction

During recent years, luminescent materials have become a focus of investigation. In this context, 1,8-naphthalimide derivatives have been extensively applied in many fields, such as fluorescent dyes [1], sensors [2], organic light emitting diodes (OLEDS) [3], fluorescent probes [4] and photochemical DNA studies owing to their high fluorescent quantum yield [5]. Polymerisable 1,8-naphthalimides and their copolymers have also enjoyed attention [6–10]; copolymers containing a fluorescent structural unit have good film forming ability, heat-durability, solvent resistance and high fluorescent quantum yields.

Copolymers of 1,8-naphthalimide with vinyl monomers have been obtained using free radical mass polymerization [11], cation solution polymerization [12] and condensation polymerization [13]. However, little published work concerns the preparation of fluorescent microspheres using soap-free emulsion polymerization. Xu et al. prepared fluorescent nanospheres via the emulsifier-free, emulsion copolymerization of styrene with a naphthalimide derivative [14]. In traditional emulsion polymerization, as a result of using an emulsifier, the purity and performance of the polymer often becomes poor. Soap-free emulsion polymerization can overcome these drawbacks and should result in polymer microspheres with a clean surface.

In this paper, the soap-free emulsion polymerization of a 1,8-naphthalimide fluorescent monomer and its copolymers with styrene (St) is reported. Microspheres with narrow dispersity and which displayed blue fluorescence were obtained.

2. Experimental

2.1. Materials

4-Bromo-1,8-naphthalic anhydride (Liaoyang Lian-gang Chemical Ltd.) and allyl amine (Shandong Lu-yue Chemical Ltd.) were used as received. Styrene and potassium persulfate were used after purification. All other reagents were used as received.

2.2. Analysis and measurement

FT-IR spectra of the fluorescent monomers were determined (KBr pellet) on a Bruker Vector 22 spectrophotometer, melting point was measured on X-6 melting point apparatus, and ^{1}H NMR spectra were recorded on a Bruker AV300 instrument. UV–vis absorption spectra of monomer and copolymer were measured on a Shimadzu UV-2501PC spectrophotometer. The fluorescence excitation and emission spectra were measured with an Edinburgh Instruments

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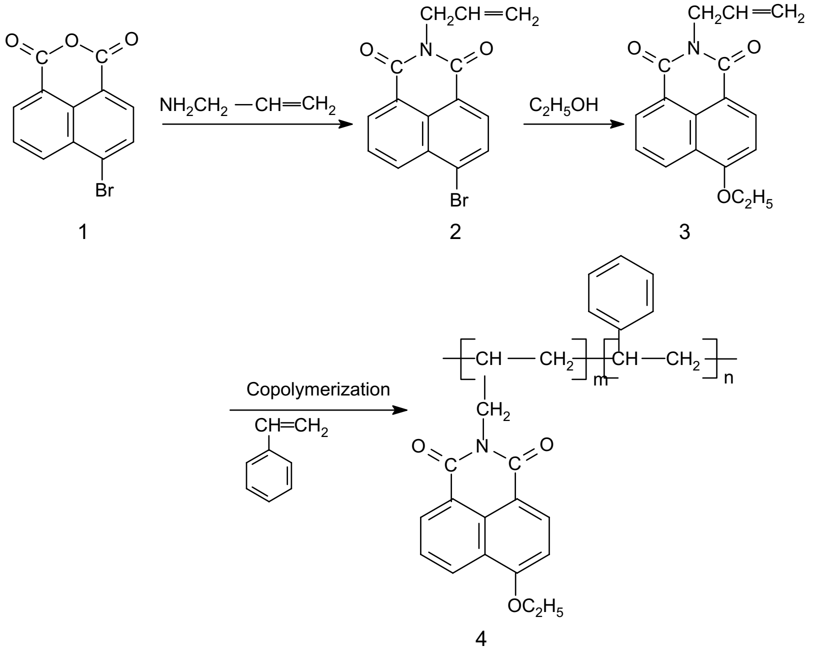


Scheme1. Synthesis of monomer **3** and copolymer **4**.

F900 spectrophotometer. Copolymer microspheres were characterized by Shimadzu SSX-550 scanning electron microscope (SEM), particle diameter and size distribution were measured on Brook Haven Zeta PALS hondrometer. The fluorescence microphoto was obtained by OLYMPUS BX51 fluorescence microscope.

2.3. *Synthesis of 4-ethoxyl-*N*-allyl-1,8-naphthalimide* ***3***

The monomer (**3**) was synthesized with Grabchev's method (Scheme 1) [15].

4-Bromo-1,8-naphthalic anhydride (1, 2.2 g) and allyl amine (0.6 ml) were placed into a 250 mL three-necked flask with a condenser and absolute ethanol (100 mL) was added. The reaction mixture was heated under reflux with stirring for 2.5 h. After cooling to room temperature, the yellow precipitate was filtered off and washed with absolute ethanol. A pale-yellow powder (**2**) was obtained. Compound **2** (1.2 g) and KOH (0.26 g) were placed into a 250 mL three-necked flask with a condenser and absolute ethanol (50 mL) was added. The reaction mixture was heated under reflux with stirring for 4.5 h. Then cooled solution was filtered and washed with distilled water. A pale-yellow solid (**3**) (1.0 g, yield = 90%) was obtained. Mp: 132.7–134.1 °C. ^{1}H NMR (CDCl$_3$) δ ppm: 1.6 (t, 3H), 4.3 (q, 2H), 4.8 (d, 2H), 5.1–5.3 (t, 2H), 6.0 (m, 1H), 7.0–8.6(m, 5H).

2.4. *Synthesis of fluorescent copolymer microsphere* ***4***

Sodium bicarbonate (0.06 g), potassium persulfate (0.05 g) and ultrapure water (100 ml) were added in a 250 mL three-necked flask with a condenser and a N_2 gas inlet, and a mixture (4 g) of 1% monomer **3** dissolved in styrene was added. The reaction mixture was maintained at 80 °C with stirring for 11 h. Emulsion of styrene copolymer was obtained.

3. Results and discussion

3.1. *Characterization of fluorescent monomer* ***3***

The FT-IR spectra of 4-Br-1,8-naphthalic anhydride and monomer **3** are shown in Fig. 1. The bands at 1696 cm^{-1} and 1660 cm^{-1} are assigned to the stretching vibration of C=O in amide compounds. The bands at 1270 cm^{-1} and 1099 cm^{-1} are assigned to the stretching vibrations of the C–O–C bond. The absorption band at 1623 cm^{-1} is characteristic for the $\upsilon_{C=C}$ vibrations from the allyl group. The bands at 2956, 2854, 1462 and 1390 cm^{-1} are assigned to vibrations of the bond C–H in the CH_3 group. As compared with compound **1**, characteristic peaks at 1780 and 1730 cm^{-1} of $\upsilon_{C=O}$ in 1,8-naphthalic anhydride disappeared. Monomer **3** has no absorption band at 563 cm^{-1} for $\upsilon_{C\text{–}Br}$.

The ^{1}H NMR spectrum of monomer **3** is displayed in Fig. 2. The chemical shifts of methyl proton were found at 1.6 ppm. The peaks at 4.3 ppm are assigned to the methylene protons of ethoxyl. The double peaks at 4.8 ppm belong to the methylene protons adjacent to the nitrogen atom. The peaks of methylene protons in vinyl are at 5.1–5.3 ppm. The methine proton peaks appear at 6.0 ppm. The absorption peaks at 7.0, 7.7 and 8.6 ppm are assigned to the protons on naphthalene ring in 1,8-naphthalimide.

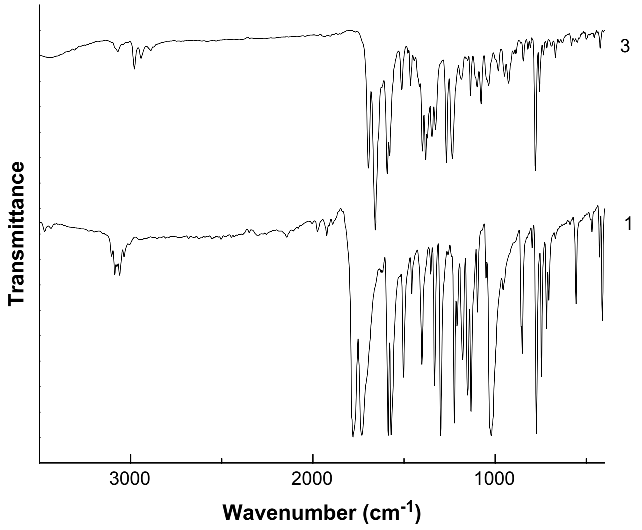
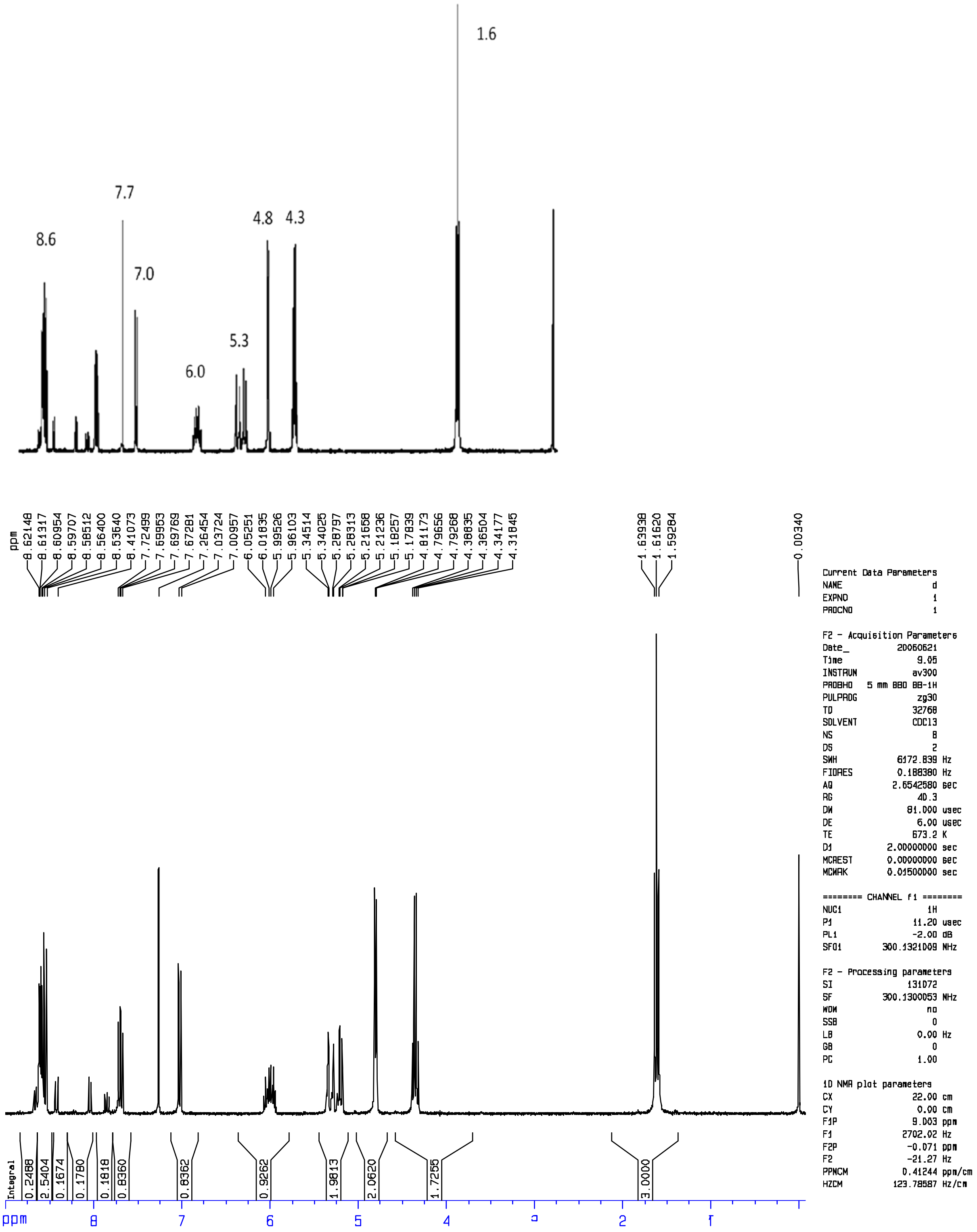


Fig. 1. FT-IR spectra of **1** and **3**.



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MCWRK       0.01500000 sec

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PL1              -2.00 dB
SFO1       300.1321009 MHz

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CY                0.00 cm
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F1             2702.02 Hz
F2P             -0.071 ppm
F2              -21.27 Hz
PPMCM          0.41244 ppm/cm
HZCM         123.78587 Hz/cm
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Fig. 2. ^{1}H NMR spectra of monomer **3**.

Fluorescence excitation and emission spectra of different concentrations of monomer **3** in acetone are shown in Fig. 3. The maximum excitation wavelength (λ_A) was observed at 366 nm. But the maximum emission wavelength (λ_F) was 5 nm blue-shifted upon decreasing the concentration of monomer **3** 10-fold. Owing to low concentration, the fluorescence emission intensity is weak (1×10^{-6} mol/L). Whereas the concentration is high (1×10^{-4} mol/L), fluorescence emission intensity decreased because of fluorescent quenching.

3.2. Characterization of copolymer

The fluorescence spectra of the untreated and treated copolymer are shown in Figs. 4 and 5. The former were obtained by drying an emulsion of the polymer and dissolving in acetone to obtain solutions of different concentrations. For the latter, the copolymers were purified by precipitation, filtration and washing with ethanol before dissolution in acetone.

The absorption maximum for the untreated copolymer was in the range $\lambda_A = 367$–403 nm. The fluorescence spectra of the untreated copolymer in acetone solution showed maxima at $\lambda_F = 431$–436 nm (Fig. 4). Comparison of Fig. 4 with Fig. 5, λ_A (and λ_F) shows that the copolymer before and after purification was virtually identical.

Fig. 6 shows the fluorescence spectra of different concentrations of copolymer emulsion. In the case of the emission spectrum of 0.1 g/L copolymer solution in Figs. 4–6, it is obvious that the emission spectra were weaker than the excitation spectra which indicate that concentration quenching occurred in the three types of copolymer solution. The quenching of untreated copolymer solution was remarkable (Fig. 4); when copolymer was dissolved in acetone, the polymeric chains were stretched and the fluorescent units were able to move. Consequently, the interaction of unreacted monomers and the fluorescent units increased quenching, thereby reducing emission intensity.

However, quenching of the copolymer emulsion was not as notable as that of the untreated copolymer solution (Fig. 6), which may be due to the St-copolymer acting as microspheres, with the fluorescent units being fixed within the spheres. As a result, the fluorescent units will not be free to move and therefore, only a few fluorescent units located at the periphery of the sphere surface can participate in quenching and, so, concentration quenching will occur mainly between unreacted monomers. When the concentration was $<10^{-3}$ g/L, quenching was not observed.

The treated copolymers were washed with ethanol to remove the unreacted monomers. The excitation and emission intensities of the treated copolymers solution were equivalent (Fig. 5). Because the unreacted monomers have been removed from copolymers, the quenching only happened between fluorescent units. The results indicate that there are unreacted fluorescent monomers in reaction system, and the reacted monomers are chemically bonded into the polymer macromolecules. Because treated copolymer solution had no unreacted monomers, but it could emit fluorescence, a feature provides evidence for the fluorescent construction unit on the polymer main chain. Fig. 7 shows the influence of emulsion concentration on fluorescence intensity. The excitation and emission intensities of untreated copolymer have more differences when the concentration is high($C > 10^{-3}$ mol/L). But for the lower concentration solution, the difference is inconspicuous($C < 10^{-3}$ mol/L). The appearances of discrepancies were due to concentration quenching when the concentration was higher than 10^{-3} mol/L.

Fig. 8 displays a fluorescence image of copolymer microspheres with an intensive blue fluorescence emission (for interpretation of the references to colour in this figure, the reader is referred to the

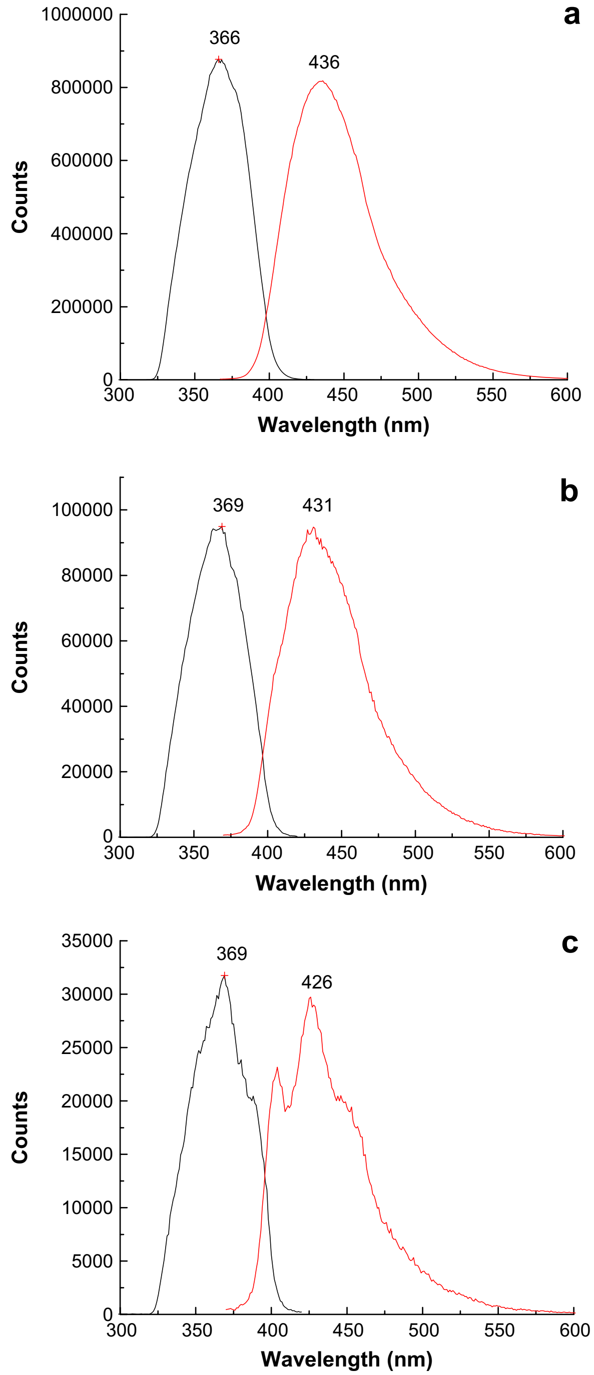

Fig. 3. Fluorescence excitation and emission spectra of monomer **3** in acetone (a: 1×10^{-4} mol/L; b: 1×10^{-5} mol/L; c: 1×10^{-6} mol/L).

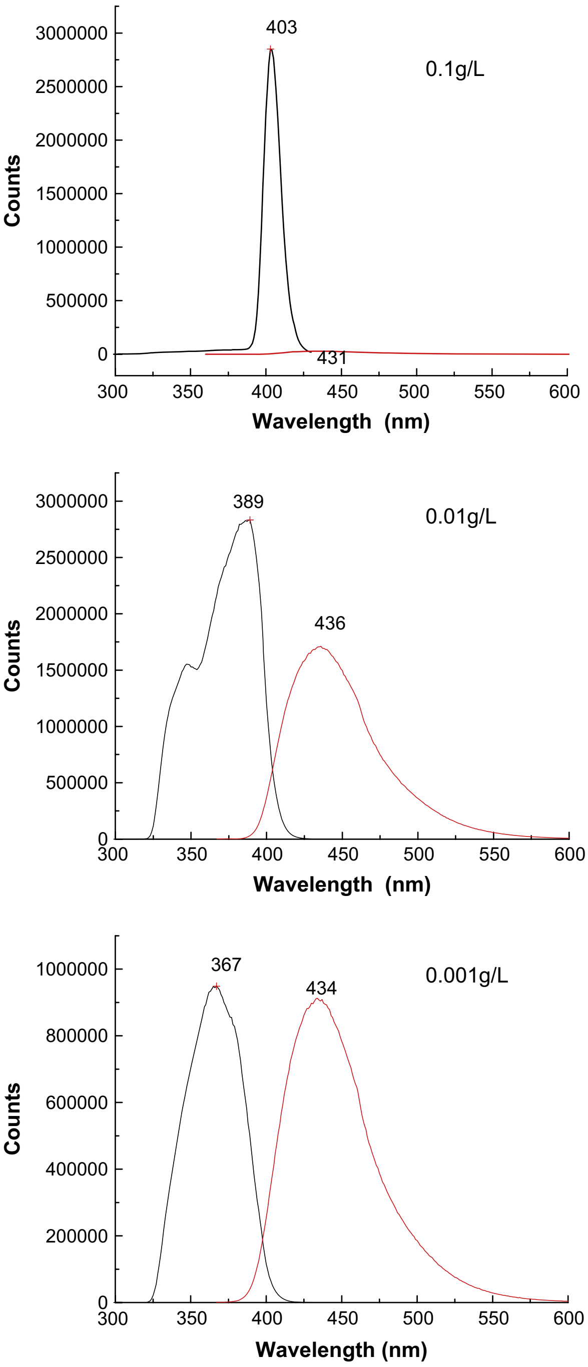

Fig. 4. Fluorescence excitation and emission spectra of untreated copolymer in acetone (different concentrations).

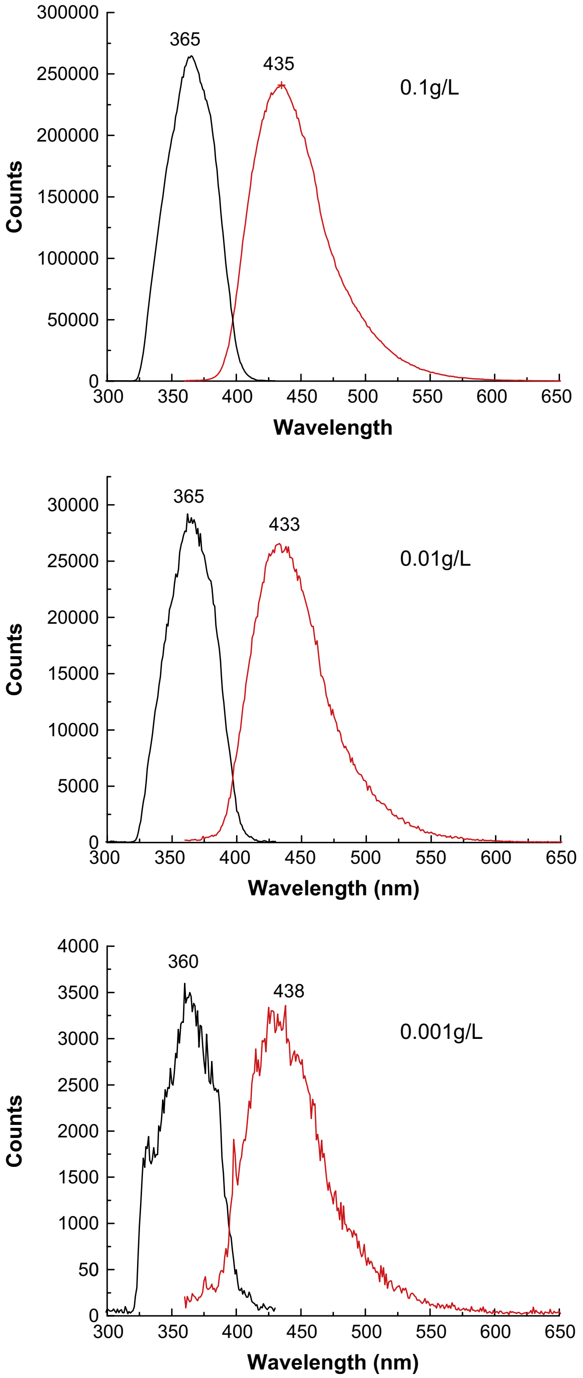

Fig. 5. Fluorescence excitation and emission spectra of treated copolymer in acetone (different concentrations).

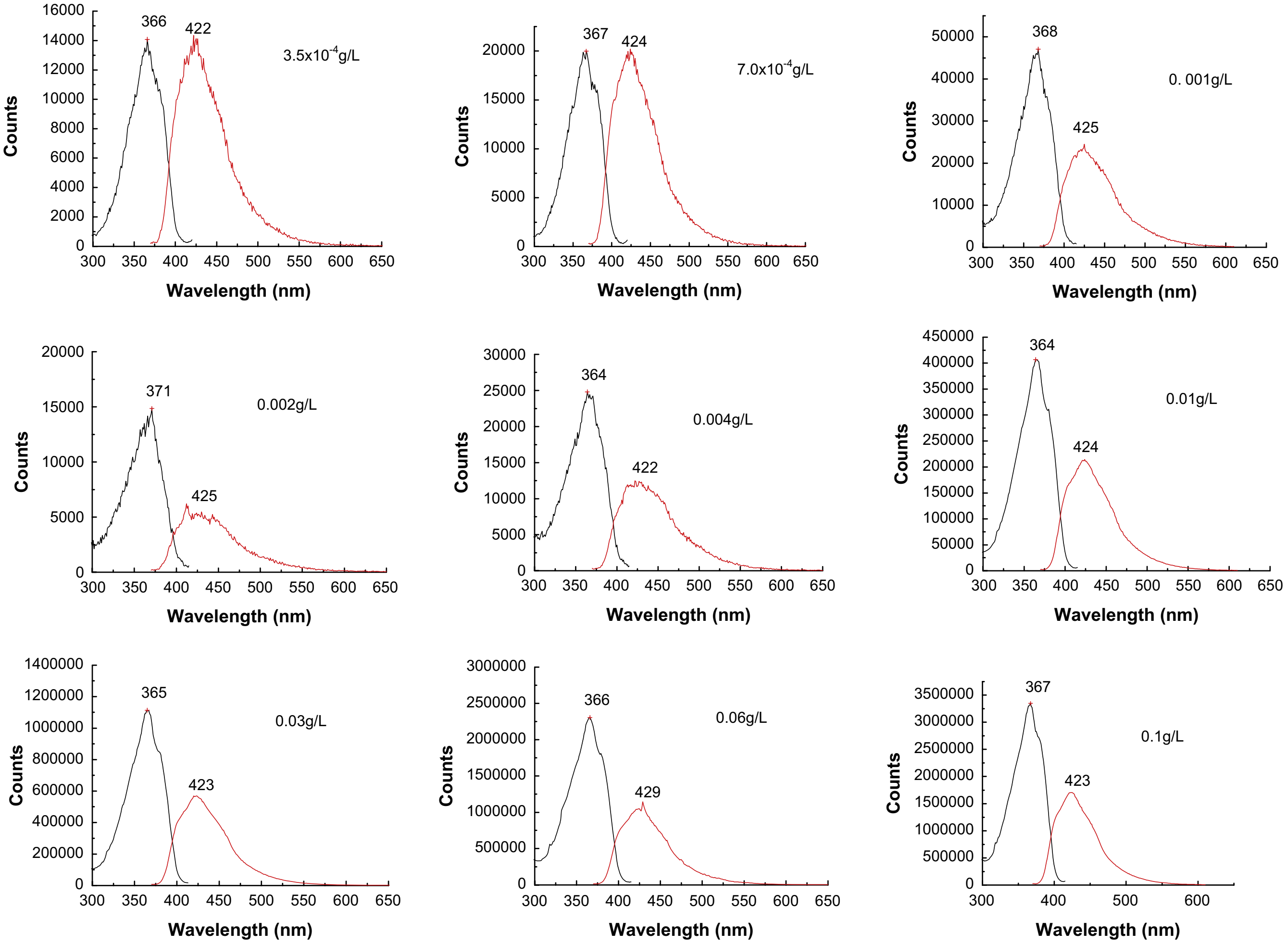

Fig. 6. Fluorescence excitation and emission spectra of copolymer emulsion (different concentrations, the concentration is content of solids in emulsion).

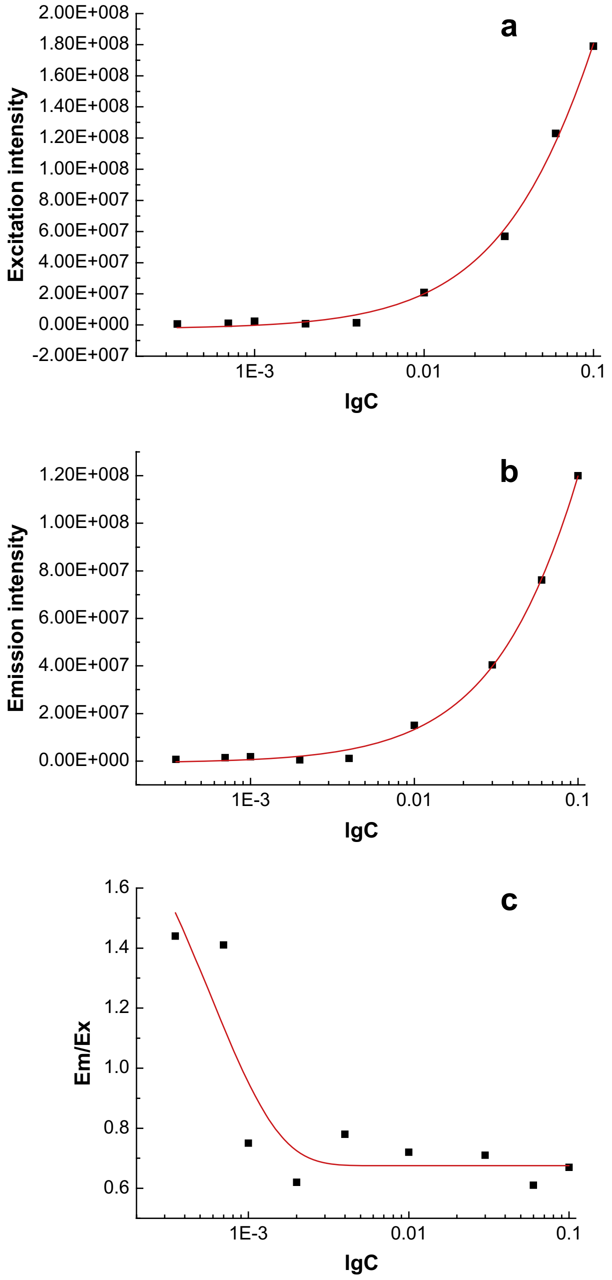

Fig. 7. Curve of excitation intensity–concentration (a), emission intensity–concentration (b), emission intensity/excitation intensity–concentration (c) (copolymer emulsion in water).

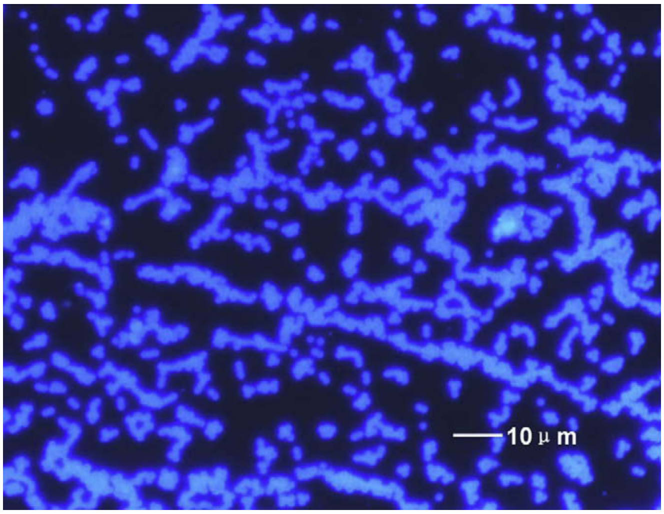

Fig. 8. Fluorescence image of PS copolymer microsphere.

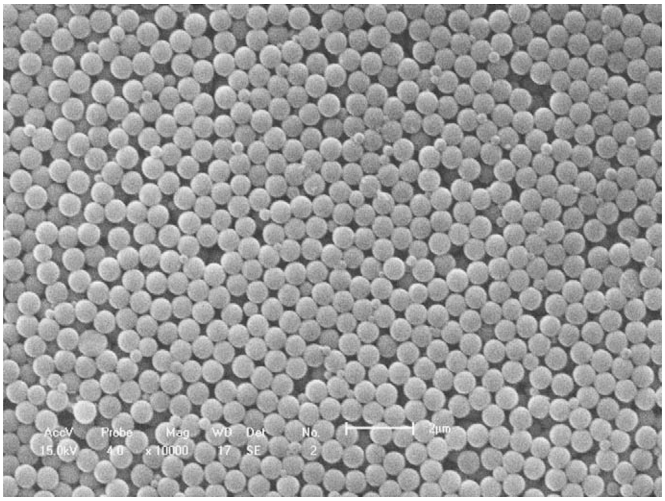

Fig. 9. SEM image of PS copolymer microsphere.

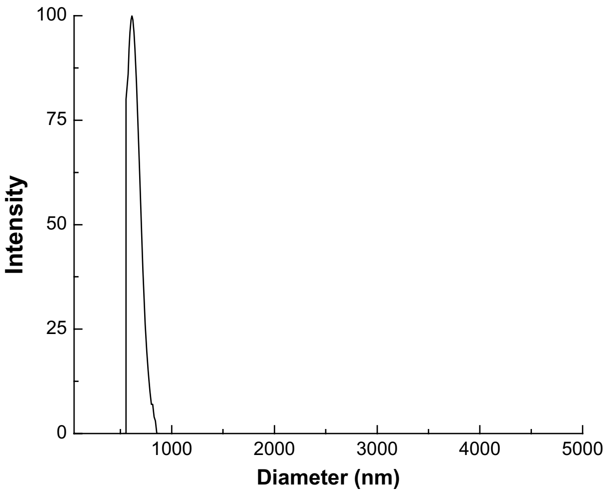

Fig. 10. Diameter and diameter distribution of PS copolymer microsphere.

web version of this article) and Fig. 9 shows SEM photograph of the polymeric microsphere. It can be seen that the microspheres with a diameter of 640 nm are spherical in shape and monodisperse in size. The surfaces of the microspheres are clean and smooth, because there are no emulsifiers in the reaction system. The size distribution curve (Fig. 10) indicates that polydisperse coefficient is 0.036 and average particle diameter is 643 nm.

4. Conclusion

4-Ethoxyl-*N*-allyl-1,8-naphthalimide was synthesized and copolymerized with styrene using detergent-free emulsion polymerization. The fluorescence excitation and emission spectra show that λ_A (λ_F) of the monomer is at 369 nm (431 nm). The results of the polymer characterization and measurements show that the copolymer was prepared successfully. The fluorescent monomer is chemically bonded into the polymer main chain. The copolymers are spherical and monodisperse with intense blue fluorescence.

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