Reactive & Functional Polymers 79 (2014) 59–67

Contents lists available at ScienceDirect

Reactive & Functional Polymers

journal homepage: www.elsevier.com/locate/react

Fabrication of polymer/ZnS nanoparticle composites by matrix-mediated synthesis

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ARTICLE INFO

Article history:
Received 17 April 2013
Received in revised form 6 March 2014
Accepted 29 March 2014
Available online 12 April 2014

Keywords:
Nanoparticle
Dispersion
Polymer composite
Refractive index
Zinc sulfide

ABSTRACT

Zinc sulfide nanoparticles are obtained as primary particles in a polymer matrix by a matrix-mediated synthesis. Two types of matrix polymer are synthesized via the copolymerization of hydrophobic, cation-exchange, and cross-linking monomers. The ZnS nanoparticles are affected by the composition of the matrix polymer, and especially by its hydrophobicity. In a low-hydrophobicity copolymer matrix, aggregates of ZnS nanoparticles are observed in the matrix using transmission electron microscopy (TEM) and X-ray diffraction (XRD). In a high-hydrophobicity cation-exchange copolymer matrix, primary particles of ZnS with 2–5 nm diameters are observed in the matrix by TEM. However, the ZnS pattern is not distinguishable in XRD measurements because the particle sizes are too small to diffract X-rays.

1. Introduction

Recently, inorganic nanoparticles have attracted much interest as they can form quantum dots and are used in photocell [1–3], lasing [4–7], and fluorescent devices [8–11]. Methods for producing quantum dots include electron beam lithography [12–14], molecular beam epitaxy [15–17], and liquid phase synthesis [18–20]. The bulk production of quantum dots using liquid phase synthesis creates aggregates due to the high surface energy of the particles [21,22]. This aggregation changes the dots' character and fluorescence wavelength, and it is therefore important that particles remain dispersed and independent in their medium. Embedding quantum dots in polymers can prevent dot aggregation, and quantum dots/polymer composites have practical applications; however, successfully mixing the quantum dots into the polymer is difficult.

Another application of nanoparticle materials is use as a refractive index modifier of polymers. High refractive index polymers are used in optical applications such as optical communication, organic electroluminescence and light-emitting diodes (LEDs) and, in the future, in optical computers. High refractive index polymers are flexible, light-weight, and easy to micro-fabricate using soft processes. However, the refractive index of organic materials is low relative to inorganic compounds because the main component atom is carbon, which has low atomic refractivity. Many studies have reported on the improvement of the refractive index of polymer materials, and one of the most effective methods is by compositing the polymer with inorganic nanoparticles [23–28]. Zinc sulfide is well known for its high refractive index [21,24,29,30] and fluorescence properties [31–33]. Although this compositing appears to be simple, there are some intractable problems that occur when using nanoparticles. Particularly, the aggregation of particles during the mixing of the nanoparticles and the polymer is major problem. Once nanoparticle aggregates are generated, breaking them down and redispersing the nanoparticles is very difficult. Surface modification of the polymers and the use of surfactants are effective ways to prevent aggregation [27,34–37], however the advantageous effects of nanoparticles are reduced by these additional components.

To solve these problems, the production of nanoparticles in the polymer in situ is effective because the particles are confined in the polymer chain network. Ziolo et al. reported the matrix-mediated synthesis of composites consisting of nanoparticles and polymers using an ion-exchange polymer as the matrix [38]. The γ-Fe_2O_3

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http://dx.doi.org/10.1016/j.reactfunctpolym.2014.03.014
1381-5148/

particles in the polymer matrix were primary particles and the composite was optically transparent and superparamagnetic. This method, therefore, is useful for producing nanoparticles of metal compounds without aggregation. In this study, we modify Ziolo's method to fabricate zinc sulfide/polymer composites.

2. Experimental

2.1. Materials

Methylmethacrylate (MMA, Tokyo Chemical Industry Co., Ltd. Tokyo, Japan) was washed with 5 wt% sodium hydroxide solution and distilled (110 mmHg, 40 °C) before use. 2-Acrylamido-2-methyl-1-propanesulfonic acid (AMPS, Tokyo Chemical Industry Co., Ltd., Tokyo, Japan) was recrystallized from ethanol before use. Trimethylolpropanetriacrylate (TMPTA), sodium styrene sulfonate (NaSS) and trichloro(3,3,3-trifluoropropyl)silane were purchased from Sigma–Aldrich Japan (Tokyo, Japan) and used without further purification. Styrene (St, Wako Pure Chemical Industries, Ltd., Osaka, Japan) was treated with a silica column and distilled (110 mmHg, 40 °C) before use. Divinylbenzene (DVB, Nacalai Tesque, Inc., Kyoto, Japan) was treated with a silica column to remove the inhibitor before use, and α,α′-azobisisobutyronitoryl (AIBN, Nacalai Tesque, Inc.) was recrystallized from ethanol before use. Sodium hydrosulfide (Nacalai Tesque, Inc.) was used without further purification. Zinc chloride and hydrogen peroxide were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan) and used without purification. Methanol and dimethyl sulfoxide (DMSO, Nacalai Tesque, Inc., Kyoto, Japan) were dried with molecular sieves before use.

2.2. Synthesis

2.2.1. Polymerization of matrix polymer

Glass plates (76 × 72 × 1 mm) were immersed in a 1 wt% of trichloro(3,3,3-trifluoropropyl)silane aqueous solution for 2 h, washed well with water and dried. The glass reaction cell (50 × 40 × 5 mm) is assembled by coupling the silane-treated glass plates with a silicone rubber spacer (5 mm).

Two types of copolymers were synthesized, one of which was an MMA, AMPS and TMPTA copolymer and the other was an St, NaSS and DVB copolymer. The monomers were mixed using the ratios given in Tables 1 and 2. A mixture using the monomers and 20 mg of AIBN were dissolved in various amounts of DMSO, as tabulated in Tables 1 and 2, and placed in the glass reaction cell and heated to polymerization for 15 h in an air oven (50 °C). After polymerization, the resulting polymer plate was taken from the reaction cell and immersed in water to extract any unreacted monomer and DMSO. The water was changed three times in a 72-h period. For the St–NaSS–DVB copolymer, the polymer plates were immersed in 1 N HCl for 24 h to protonate the sodium sulfonate moiety in the NaSS, and subsequently washed with water several times. Next, the plates holding the MMA–AMPS–TMPTA and St–NaSS–DVB copolymers were immersed in methanol and the methanol was changed four times in a 12-h period. After this purification, the polymer plates were dried in vacuo at room temperature.

2.2.2. Generation of metal compound nanoparticles

The polymer matrixes were immersed in 0.1 mol dm^{-3} of zinc chloride aqueous solution for 12 h, during which the zinc cation content in the solution was adjusted to match the cation-exchange capacity of the polymer matrix. The polymer matrix containing the zinc ions was immersed in water to remove free zinc ions, and subsequently in methanol to remove the water and dry the matrix. After drying, the polymer plates containing the zinc ions were immersed in 1.0 mol dm^{-3} of sodium hydrosulfide aqueous solution for 12 h for sulfurization. The polymer was then removed from the solution and washed with water several times. After drying, the polymer plates containing zinc sulfide were obtained.

2.3. Characterization

Transmission electron microscope (TEM, JEM-2000FX; JEOL Ltd., Tokyo, Japan) analyses were performed at an accelerating voltage of 200 kV for thin sample sections of 50 nm thickness prepared by microtomy using an ultramicrotome (EM-UC7; Leica Microsystems K.K., Tokyo, Japan) equipped with a diamond knife. The metal content in the composite was estimated by thermogravimetric analysis (TGA, TG/DTA6300S SII NanoTechnology Inc., Tokyo, Japan) under air atmosphere. The polymer sample was prepared for TGA by placing it in platinum pan and heating it from room temperature to 800 °C at a rate of 10 °C/min. The metal content of the residue was estimated to be zinc oxide from the weight of the residue. Fourier transform infrared (FT-IR) spectroscopy (Spectrum One PerkinElmer Japan Co., Ltd., Japan) was performed using

Table 1
Composition ratios of the MMA–AMPS–TMPTA matrix copolymer feed.

Sample	MMA Feed in copolymer[a] (mol%)	AMPS	TMPTA	Monomer concentration wt%	MMA:AMPS ratio (mol)	TMPTA (wt%)	Cation-exchange site (meq/g)
#1	2.00 g (96.7)	– (0.0)	0.200 g (3.3)	66.7	10:0	9.08	0.00
#2	1.617 g (86.7)	0.380 g (9.8)	0.200 g (3.6)	66.6	9:1	9.10	0.84
#3	1.316 g (76.9)	0.680 (19.2)	0.200 g (3.9)	66.6	8:2	9.43	1.49
#4	1.062 g (67.1)	0.940 (28.7)	0.200 g (4.3)	66.7	7:3	9.08	2.06
#5	0.837 g (57.1)	1.16 (38.3)	0.200 g (4.6)	66.6	6:4	9.11	2.55
#6	1.241 g (77.4)	0.680 (20.5)	0.100 g (2.1)	64.8	8:2	4.95	1.62
#7	1.316 g (76.9)	0.680 (19.2)	0.200 g (3.9)	66.6	8:2	9.3	1.49
#8	1.241 g (74.3)	0.680 (19.7)	0.300 g (6.1)	66.9	8:2	13.5	1.48
#9	1.241 g (72.8)	0.680 (19.3)	0.400 g (7.9)	67.8	8:2	17.2	1.41

[a] Monomer mixtures were dissolved in 1 cm^3 of DMSO.