



Synthesis and properties of poly(methyl methacrylate-2-acrylamido-2-methylpropane sulfonic acid)/PbS hybrid composite

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ABSTRACT

The synthesis of a new hybrid composite based on PbS nanoparticles and poly(methyl methacrylate-2-acrylamido-2-methylpropane sulfonic acid) [P(MMA-AMPSA)] copolymer is reported. The chemical synthesis consists in two steps: (i) a surfactant-free emulsion copolymerization between methyl methacrylate and 2-acrylamido-2-methylpropane sulfonic acid and (ii) the generation of PbS particles in the presence of the P(MMA-AMPSA) latex, from the reaction between lead nitrate and thiourea. The composite was studied by scanning electron microscopy (SEM), X-ray diffraction, FTIR spectroscopy, thermogravimetric analysis and differential scanning calorimetry. The microstructure observed using SEM proves that the PbS nanoparticles are well dispersed in the copolymer matrix. The X-ray diffraction measurements demonstrate that the PbS nanoparticles have a cubic rock salt structure. It was also found that the inorganic semiconductor nanoparticles improve the thermal stability of the copolymer matrix.

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1. Introduction

The synthesis of hybrid composites based on organic polymer and inorganic semiconductor nanoparticles has attracted recently much interest because of their potential applications [1,2]. Inorganic semiconductors are easily accessible and in the last decade a great number of these materials were synthesized as nanoparticles. Lead sulfide (PbS) is an important IV–VI semiconductor used in many fields such as Pb²⁺ ion selective sensors, infrared detectors [3] and solar absorbers [4]. In PbS nanoparticles the band gap value of 0.41 eV (at room temperature) is very sensitive to finite size effects, shifting from the near-infrared to visible region as their diameter decreases [5]. Previously, PbS semiconductor nanoparticles were prepared in colloidal solutions [6,7] and embedded in different matrices, such as glasses [8,9], glues [10], lead zirconate titanate [11], zeolites [12] and polymers [13–15]. Thermally stable, easy in processing and transparent to light polymers are an ideal host matrix for inorganic particles. Their presence directly influences the semiconducting crystallite size acting as a size-limiting agent. The most frequent methods used for the preparation of polymer/PbS hybrid composites are: (i) an ion-exchange reaction, when a polymer such as E-MAA (ethylene–15% methacrylic acid copolymer) allows the metal

ions to be introduced into the polymer matrix; afterwards the treatment with H₂S resulting in “in situ” precipitation of the semiconductor compound within the hydrophilic regions of the polymer [15]; (ii) the chemical reaction between a lead salt (lead nitrate or lead acetate) and a sulfur source (H₂S, sodium sulfide or thiourea) in the presence of a hydrophilic polymer (polyacrylamide, polyglycol or polyvinyl alcohol) [13,14,16]; (iii) the simultaneous polymerization of an organic monomer (acrylamide) and formation of semiconductor nanoparticles [17,18].

The present work is focused on the chemical synthesis of a new hybrid composite based on poly(methyl methacrylate-2-acrylamido-2-methylpropane sulfonic acid) [P(MMA-AMPSA)] and PbS nanoparticles. A surfactant-free emulsion copolymerization between the methyl methacrylate and 2-acrylamido-2-methylpropane sulfonic acid is carried out in the first step. Thereafter the PbS nanoparticles were synthesized in the presence of the P(MMA-AMPSA) latex from the reaction between lead nitrate and thiourea. We chose as matrix the P(MMA-AMPSA), a copolymer containing sulfonic acid group, because the anionogen groups present on the colloidal particles surface could fix the lead ions. Thus, the colloidal dispersion offers a suitable reaction media for the growth of the PbS crystals only at the water/copolymer interface. The structural properties and the morphology of the hybrid composite were studied using X-ray diffraction, infrared absorption and scanning electron microscopy (SEM). Also, the thermal properties of the [P(MMA-AMPSA)]/PbS composite were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

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2. Experimental

2.1. Chemicals

2-Acrylamido-2-methylpropane sulfonic acid (AMPSA) was provided by Aldrich and used as received. Methyl methacrylate (MMA) was purchased from Merck and distilled under vacuum at 60 °C and 20 mm Hg to remove inhibitors and stored in a refrigerator. The water-soluble initiator, potassium persulfate (KPS) was purchased from Fluka and purified by recrystallization from water and dried in vacuum.

In the experiment, the PbS nanoparticles were synthesized from the chemical reaction between lead nitrate (Merck) and thiourea (Aldrich).

The non-solvent, methanol (Fluka) and the solvent, N-methyl-2-pyrrolidinone (NMP) (Merck) were used without further purification.

2.2. Synthesis

The P(MMA-AMPSA) copolymer latex was prepared by surfactant-free emulsion copolymerization of MMA with AMPSA using KPS as an initiator. We used the following recipe: 20 ml distilled water, 1 ml (0.94 g) MMA, 0.08 g AMPSA and 0.0513 g KPS. All reactants were dosed into the flask and were then deoxygenated by bubbling with nitrogen for 10 min. The polymerization reaction was carried out at 75 °C for 24 h. The copolymer latex was purified by repeated dialysis in distilled water for at least 1 week, using cellulose dialysis membranes (molecular weight cutoff: 12,000–14,000). After purification, the entire amount of P(MMA-AMPSA) latex was used for the preparation of the hybrid composite. Thus, in the latex were added 0.0062 g $\text{Pb}(\text{NO}_3)_2$ (0.001 M) and afterwards 0.00304 g NH_2CSNH_2 (0.002 M). The reaction was carried out at 80 °C for 24 h. At the end of this reaction the mixture was precipitated in methanol. A black powder product was separated by filtration on a filter paper, washed several times with methanol in order to remove the residual compounds and finally dried. Then, to the composite black powder was added NMP in order to dissolve the P(MMA-AMPSA) copolymer. In this way, the size and morphology of the PbS crystallites obtained after the copolymer removal could be investigated.

2.3. Measurements

The morphology of the latex and powder samples was observed by using a Zeiss Evo 50 XVP scanning electron microscope (SEM). In order to image the samples a droplet of latex was placed on a glass plate and dried in ambient conditions. Further, the samples in latex or powder form were sputtered with a thin layer of gold prior to imaging.

The crystalline phase of the powder samples was identified by X-ray diffraction (XRD) on a Bruker AXS D8 Advance instrument with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). The source was operated at 40 kV and 40 mA and the $\text{K}\beta$ radiation was eliminated using a nickel filter.

The infrared absorption spectra were recorded at room temperature with a Nicolet 6700 FTIR spectrometer in the range of 4000–400 cm^{-1} .

The thermal experiments were performed on a Mettler Toledo TGA/SDTA 851° thermal analyzer, within the temperature range 30–700 °C and a Mettler Toledo DSC 853° differential scanning calorimeter within the temperature range 30–500 °C. The data were recorded in a nitrogen atmosphere with a flow rate of 50 ml min^{-1} , for TG experiments, and 80 ml min^{-1} for DSC ones, and at a heating rate of 10 K min^{-1} . The samples were held in aluminium crucibles for DSC experiments, with a pinhole in the lid (DSC) and alumina crucibles for TG/DTA experiments. The sample

mass ranged between 0.8 and 3 mg for both methods. The content of the inorganic phase was determined as a residue at the end of the degradation process.

3. Results and discussion

The morphology of the samples was observed by SEM. Fig. 1 shows images of P(MMA-AMPSA) microspheres prepared by surfactant-free emulsion copolymerization of MMA with AMPSA. It may be noticed the polydispersity in particles size (400–750 nm). The copolymerization reaction starts in the aqueous phase. At the first step, the thermally dissociating initiator, i.e. KPS, is decomposed under heating (75 °C) to produce sulfate anion-radical. Further the addition of the hydrophilic anion-radicals to the monomer molecules takes place. In the propagation stage, the macroradicals grow and after reaching their limit of solubility (critical chain length, n_{cr}) they precipitate from the aqueous solution. In this way the primary nuclei particles are formed. Being a water-soluble monomer (1.5 g/100 ml water), the number of these nuclei is higher in the case of MMA comparatively with other monomers poorly soluble in water (e.g. styrene). Also, the presence of the hydrophilic AMPSA units in the copolymer chains leads to an increase of the propagation acts until the n_{cr} value is reached. We assume that the nucleation global rate is changed in the same way. So, the diffusion of the MMA, with different concentrations, from the aqueous phase into the nuclei particles (or the copolymer particles) is responsible for the particle size polydispersity.

The next stage in the synthesis of the hybrid composite was the formation of the PbS crystallites on the surface of the colloidal copolymer P(MMA-AMPSA) microspheres. The sulfonic acid groups contained in the copolymer structure could fix the lead ions through the ion-exchange reaction. The possible mechanism reactions (Scheme 1) involved in the chemical synthesis of the hybrid composite can be described as follows. When lead nitrate aqueous solution is added to the copolymer latex Pb^{2+} ions are homogeneously dispersed in the matrix. The $-\text{SO}_3^-$ groups present in the polymer chain interact with the Pb^{2+} ions and stabilize them. On the addition of thiourea aqueous solution the Pb^{2+} ions in the copolymer matrix react with H_2S forming lead sulfide. PbS crystallites are surrounded by polymer chains which provide a limiting effect for grown nanoparticles.

Fig. 2 presents images of the [P(MMA-AMPSA)]/PbS composite latex. It has to be noticed that the particles are agglomerated comparatively with the initial P(MMA-AMPSA) latex. This aggregation can be explained through the attraction of the bivalent Pb^{2+} ions to the monovalent sulfonic acid groups. The relatively big

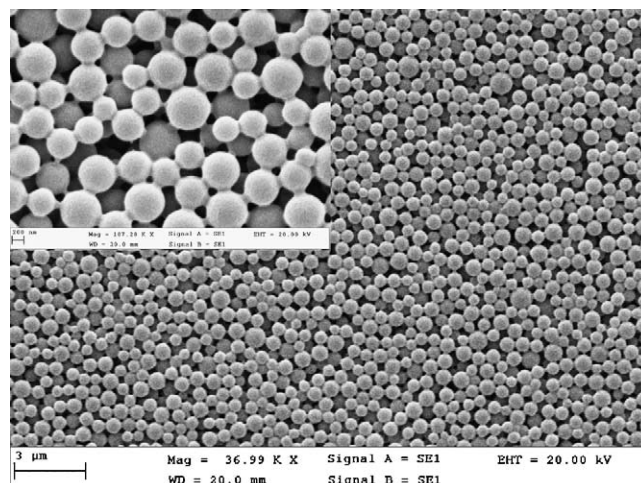


Fig. 1. SEM images of P(MMA-AMPSA) copolymer latex.

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