

# Preparation of Cadmium Sulfide/Poly(methyl methacrylate) Composites by Precipitation with Compressed CO<sub>2</sub>

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**ABSTRACT:** Cadmium sulfide (CdS) nanoparticles and poly(methyl methacrylate) (PMMA) were first synthesized in methyl methacrylate (MMA)/sodium bis(2-ethylhexyl) sulfosuccinate (AOT) microemulsion, in which MMA acts as the solvent and monomer. Then compressed CO<sub>2</sub> was used as an antisolvent to precipitate the CdS and PMMA simultaneously. Using this method, a CdS/PMMA composite was successfully prepared. The CdS nanoparticles dispersed in the polymer matrices were characterized by transmission electron microscopy. The higher pressure is favorable to producing CdS nano-

particles of smaller size. The phase structure of the obtained composite was characterized by X-ray diffraction, which reveals that cubic CdS particles were formed. The FTIR spectra of the composite showed that there is no chemical bonding or strong interaction between CdS and PMMA. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 94: 1643–1648, 2004

**Key words:** poly(methyl methacrylate) (PMMA); CdS; nanoparticles; composites; matrix

## INTRODUCTION

In recent years, nanosized and monodisperse semiconductor particles have been of particular interest because of their size-dependent optic, electric, and magnetic properties compared with those of bulk materials.<sup>1–3</sup> In particular, inorganic nanoparticles such as semiconductors and metals in polymer matrices have attracted much attention because of their variety of applications.<sup>4–10</sup> Different approaches have been used to prepare nanoinorganic/polymer composites.<sup>11–17</sup> Of these approaches, the *in situ* synthesis of inorganic nanoparticles in polymer matrices and the simultaneous polymerization–reduction method have successfully been used. Using these methods, a variety of inorganic/polymer composites have been prepared.

Gas antisolvent technology is becoming more popular in the field of material science. It has been used in different processes such as extraction and fractionation, recrystallization of chemicals, micronization, and precipitation of polymeric particles from solutions.<sup>18–21</sup> In antisolvent technology, CO<sub>2</sub> is commonly used because of its unique properties. Recently, our group successfully recovered the ZnS and Ag nano-

particles synthesized in sodium bis(2-ethylhexyl) sulfosuccinate (AOT) reverse micelles by compressed CO<sub>2</sub>.<sup>22,23</sup> During the recovery, the ZnS or Ag nanoparticles can be precipitated from the reverse micelles, while the AOT remains in solution. The size and amounts of the ZnS or Ag nanoparticles precipitated from the reverse micelles can be easily controlled by varying the CO<sub>2</sub> pressure.

In this work, poly(methyl methacrylate) (PMMA) and cadmium sulfide (CdS) nanoparticles were first synthesized in the microemulsion, and then compressed CO<sub>2</sub> was used as an antisolvent to simultaneously precipitate both the PMMA and the CdS. The PMMA/CdS composite was successfully prepared by this method, and was characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), and FTIR spectra.

## EXPERIMENTAL

### Materials

Methyl methacrylate (MMA, A.R. grade), Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Na<sub>2</sub>S·9H<sub>2</sub>O, and benzoyl peroxide (A.R. grade) were purchased from Beijing Chemical Reagent Factory (China). Sodium bis(2-ethylhexyl) sulfosuccinate (AOT, >99% pure) was obtained from Sigma (St. Louis, MO). CO<sub>2</sub> (99.995% pure) was supplied by Beijing Analytical Instrument Factory (China). Double-distilled water was used in all the experiments.

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### Phase behavior of the CO<sub>2</sub>-expanded microemulsion

The apparatus for determining the expansion curves and the phase behavior of the microemulsion was the same as that used previously to study polymer solutions.<sup>23,24</sup> It consisted mainly of a view cell of 50 mL, a high-pressure pump, a constant temperature water bath, and a pressure gauge. The high-pressure pump was Model DB-80 produced by Beijing Secondary Planet Factory (China), which was used to charge CO<sub>2</sub> into the system. The accuracy of the pressure gauge, composed of a transducer (Foxboro/ICT, San Jose, CA) and an indicator, was  $\pm 0.025$  MPa in the pressure range of 0–20 MPa. The temperature of the water bath was controlled by a Haake D8 digital controller (Haake, Bersdorff, Germany), and the accuracy of the temperature measurement was  $\pm 0.1^\circ\text{C}$ .

The microemulsion was prepared by dissolving the desired amount of AOT and water in MMA. In a typical experiment, a suitable amount of the microemulsion was charged into the view cell (with two quartz windows), which was maintained at 308.2 K in the water bath. CO<sub>2</sub> was then charged into the view cell to a suitable pressure after thermal equilibrium had been reached. A magnetic stirrer was used to enhance the mixing of CO<sub>2</sub> and the microemulsion. The volume of the liquid phase did not change with time after equilibrium was reached. The pressure and the volume at the equilibrium condition were recorded. More CO<sub>2</sub> was added and the volume of the liquid phase at another pressure was determined. The volume expansion coefficients were calculated on the basis of the liquid volumes before and after dissolution of CO<sub>2</sub>. Some surfactant could be precipitated if the pressure of CO<sub>2</sub> was high enough. The pressure at which the surfactant begin to precipitate is called as cloud-point pressure. The cloud-point pressure of the solution was also determined.

### Preparation of microemulsion containing PMMA and CdS

The desired amount of AOT was dissolved in MMA ([AOT] = 0.2M). Then the microemulsion containing, respectively, aqueous solutions of Cd(NO<sub>3</sub>)<sub>2</sub> and Na<sub>2</sub>S were prepared by adding a corresponding aqueous salt solution to the surfactant solution. The water-to-surfactant molar ratio (*w*) was 5 in the microemulsion. Finally, the two solutions containing Cd(NO<sub>3</sub>)<sub>2</sub> and Na<sub>2</sub>S, respectively, were mixed and CdS nanoparticles were formed in the microemulsion. The CdS concentration in the solution was 2.7 mM. Benzoyl peroxide (2% of the total weight of monomer) as the initiator was added to the above solution. The final solution was placed in an oven to polymerize for 20 min at 329.2 K.

### High-pressure UV-vis spectra

A TU-1201 Model spectrophotometer (Shimadzu, Kyoto, Japan) was used to investigate the possibility of precipitating CdS particles from the microemulsion at different CO<sub>2</sub> pressures. The temperature-controlled high-pressure sample cell and experimental procedures were the same as those used previously.<sup>23</sup> The cell was composed mainly of a stainless steel body and two quartz windows, thermostated to  $\pm 0.1^\circ\text{C}$  of the desired temperature by an electric heater and temperature-controlling system. In the experiment, a suitable amount of polymerized solution with CdS nanoparticles was loaded by syringe into the sample cell. The temperature was controlled at 308.2 K. CO<sub>2</sub> was charged into the sample cell by the high-pressure pump until the sample cell was full.

### Recovery of CdS/PMMA composites by CO<sub>2</sub>

The 20-mL water/MMA/AOT microemulsion containing CdS nanoparticles was first polymerized for 20 min in the oven at 329.2 K and then the solution was quickly transferred to an autoclave (without quartz windows). The autoclave was immersed in a water bath at 308.2 K. Then CO<sub>2</sub> was charged into the autoclave by a high-pressure pump until the desired pressure was reached. A stirrer was used (400 rpm) to accelerate the mixing of CO<sub>2</sub> and the solution. After stirring for 0.5 h, the stirrer was stopped and the composites were deposited at the bottom of the autoclave. Then the valve of the outlet of the autoclave was open to release the solution. At the same time CO<sub>2</sub> was continuously charged into the autoclave from the inlet to maintain constant pressure. Finally, CO<sub>2</sub> was released from the autoclave and the product was collected. To remove the residual monomer in the composite, the product was washed several times with ethanol. The precipitated composites might absorb some AOT, which could also be removed by ethanol in the washing process because AOT was soluble in ethanol. Then the product was dried under vacuum at 303.2 K for 4 h and the weights of the product obtained at 4.21, 4.82, and 5.37 MPa were 0.40, 0.51, and 0.59 g, respectively.

### Characterization of CdS/PMMA composites

Molecular weight distribution of the polymer in PMMA/CdS composite was measured using gel permeation chromatography (GPC). The dry polymer was dissolved in THF for the GPC measurement. The morphology of the obtained composite was determined by TEM with a Tecnai 20 electron microscope (Philips, Eindhoven, The Netherlands). The samples were prepared for microtoming by impregnating the

composite with firm-formulation epoxy resin. X-ray diffraction analysis of the samples was carried out using an X-ray diffractometer (XRD, Model D/MAX2500; Rigaku, Tokyo, Japan) with Cu-K $\alpha$  radiation. The IR spectrum was recorded using an IR spectrometer (SENSOR 27; Bruker Optics, Billerica, MA), and each sample was recorded with 32 scans at an effective resolution of 2 cm $^{-1}$ . The concentration of element Na in the CdS/PMMA composite was determined by atomic absorption spectrometry (AAS).

RESULTS AND DISCUSSION

Volume expansion of the CO $_2$ -expanded microemulsion

The solution expanded after dissolution of CO $_2$ . The volume-expansion coefficient  $\Delta V$  [ $\Delta V = (V - V_0)/V_0$ , where  $V$  is the volume of the solution saturated with CO $_2$  and  $V_0$  is the volume of the CO $_2$ -free solution] of the solution at different pressures is a useful parameter for the UV experiments and the recovery process. We determined the  $\Delta V$  of the microemulsion at 308.2 K with  $w = 5$  before and after polymerization for 20 min. The concentration of the AOT in MMA was 0.2M. Figure 1 shows the change of  $\Delta V$  of the solution at different pressures. As we can observe,  $\Delta V$  increases with increasing pressure of CO $_2$ , which is easy to understand because the solubility of the CO $_2$  in the solution increases with increasing pressure of CO $_2$ . Figure 1 shows that the difference in volume expansion of the solutions before and after polymerization was not considerable. This is attributed to the low content of PMMA in the solution. From the volume expansion curves, we can determine the amount of the microemulsion added to the high-pressure cell in the UV study and recovery processes.

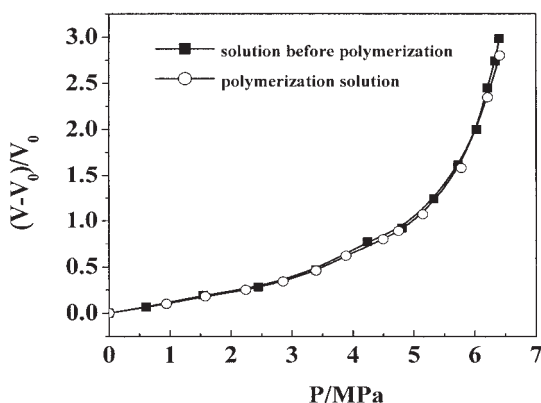


Figure 1 Dependency of the volume expansion of the water/MMA/AOT microemulsion before and after polymerization on CO $_2$  pressure at 308.2 K.

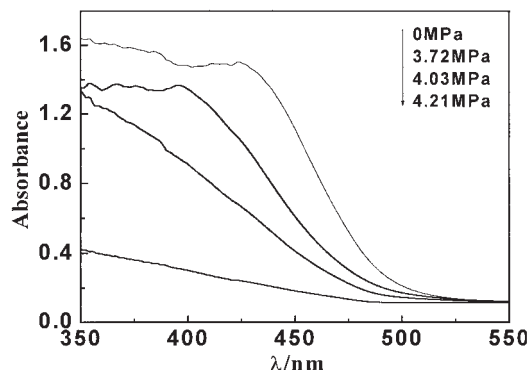


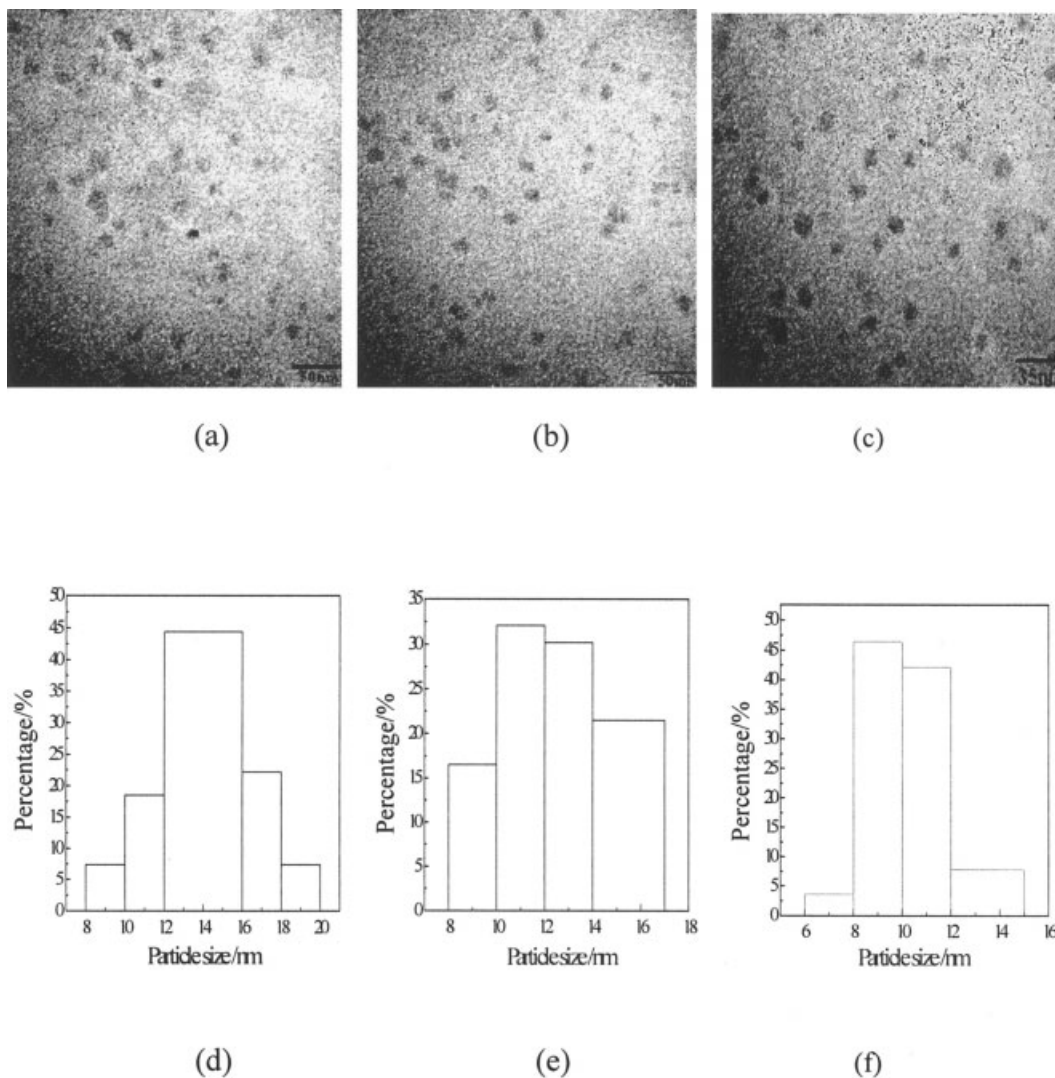
Figure 2 UV spectra of the polymerized solution at 308.2 K and different CO $_2$  pressures.

Phase behavior of the CO $_2$ -expanded microemulsion

If the pressure is high enough, the surfactant can be precipitated from the solution and cause the solution to become cloudy. This pressure is usually denoted as cloud-point pressure ( $P_c$ ). The  $P_c$  of the CO $_2$ /water/MMA/AOT system determined at 308.2 K is 6.30 MPa. All the recovery experiments were conducted at pressures lower than the cloud-point pressure, so the precipitation of the surfactant did not occur.

The dispersed CdS nanoparticles in the solution were a yellow color, and the PMMA solution was colorless. For the polymerized system containing the CdS nanoparticles, it could be seen clearly from the view cell that with the increasing pressure of CO $_2$ , the yellowness of the solution (caused by CdS nanoparticles) gradually becomes less intense, indicating the precipitation of CdS nanoparticles from the microemulsions. As the pressure reached 4.01 MPa, which was much lower than the precipitation pressure of surfactant AOT, the solution became cloudy, which is attributed to the precipitation of PMMA from the solution. As the pressure reached the sufficiently high value of 4.21 MPa, the solution became much more cloudy, and after the complete precipitation for the deposit, it could be found that the solution was colorless, indicating the complete precipitation of CdS nanoparticles from the solution. When CO $_2$  was further charged to the autoclave, it was found that the upper colorless solution became cloudy again, which indicated that not all of the PMMA precipitated with the CdS.

Analysis of the UV-vis spectrum is a commonly used method to characterize the semiconductor nanoparticles in microemulsions. We also used UV-vis spectra to determine the precipitation of the CdS particles from the microemulsion by compressed CO $_2$ . Figure 2 illustrates the UV spectra of the water/MMA/AOT system containing CdS, which was polymerized for 20 min. The broad band is attributed to



**Figure 3** TEM micrographs of CdS in the CdS/PMMA composite obtained at 4.21 MPa (a), 4.82 MPa (b), and 5.37 MPa (c), and the corresponding histogram of particle size distribution (d–f).

absorbance of CdS nanoparticles.<sup>6,17</sup> As we can see from the figure, with the increasing CO<sub>2</sub> pressure the intensity of the absorbance of CdS decreases, indicating the precipitation of CdS nanoparticles from the solutions. As the pressure reaches 4.21 MPa, the absorbance of CdS nearly disappeared, indicating precipitation of all the CdS nanoparticles in the microemulsion. This agrees well with the results obtained by direct observation described above. It also reveals that the precipitation percentage of CdS can be tuned by the pressure, that is, the composition of CdS in the composite can be controlled by varying the pressure of CO<sub>2</sub>.

#### Morphologies, phase structure, and intermolecular interaction of the PMMA/CdS composite

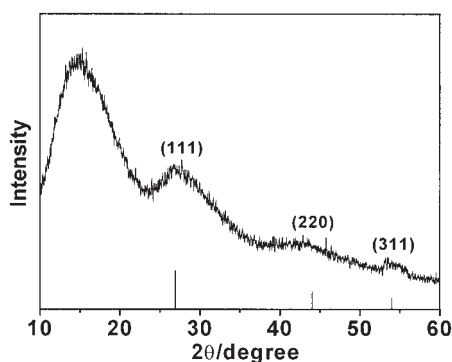
Based on the results of the UV and phase-behavior studies the optimum CO<sub>2</sub> pressures were selected to

prepare the composites. The water-to-surfactant ratio is an important factor for the size of nanoparticles synthesized in the reverse micelles. Generally, the larger the ratio, the larger the particle size. This has been discussed by many researchers. This work focuses on how pressure affects the size of CdS in the composites and morphology of the composites. The TEM micrographs of PMMA/CdS composites, recovered at different pressures of 4.21, 4.82, and 5.37 MPa, are shown in Figure 3(a), (b), and (c), respectively. The particle size and size distribution data were obtained by measuring the diameter of the particles in the micrographs. Figure 3(d)–(f) show the histogram of CdS particle size distribution, respectively, and the figures show a Gaussian distribution with a mean diameter of  $14 \pm 6$ ,  $12 \pm 5$ , and  $10 \pm 5$  nm, respectively, which means that the higher pressure is favorable to produc-

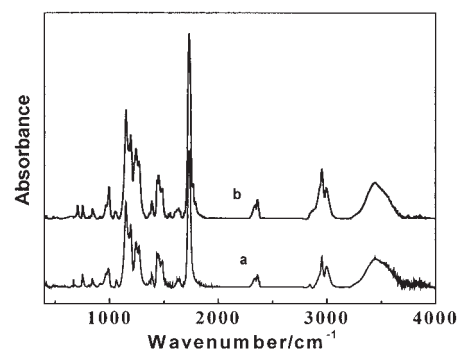
ing the particle with smaller size. This may be attributed to the increased diffusivity and lowered viscosity of the CO<sub>2</sub>-expanded solutions at the higher pressure. The experiments at each pressure were conducted twice, and the obtained TEM results were similar. The TEM images taken from different parts of a sample were also similar.

X-ray powder diffraction (XRD) was used to characterize the phase structure of the obtained composite, which is shown in Figure 4. As we can see from the figure, four peaks appear in the XRD pattern of the composite. The very broad XRD peak at a low diffraction angle, around  $2\theta = 15^\circ$ , indicates amorphous PMMA. The other three peaks correspond to the 111, 220, and 311 planes of cubic CdS.<sup>25</sup> The XRD peaks of CdS are relatively broad, which suggests the small size of CdS in the composite.

FTIR spectra were used to investigate whether there was chemical bonding between CdS nanoparticles and PMMA matrices in the composite. Figure 5 shows the IR spectra of pure PMMA and the obtained PMMA/CdS composite. As we can see from the figure, it is evident that the spectra of pure PMMA and the obtained PMMA/CdS composite are identical, which implies that there is no chemical bonding or strong interaction between CdS and PMMA. The bands at 1730 and 1150, 1195, 1272, and 1242 cm<sup>-1</sup> are assigned to the stretching vibration of the C=O and C—O (symmetric and asymmetric), respectively, which are all typical bands of PMMA. Because the surfactant AOT has a similar group with PMMA, we also performed AAS (Na) to determine whether AOT existed in the composite. The results indicate that Na in the composite is almost not detectable. Therefore, it can be concluded that the amount of AOT in the composites is negligible. The GPC experiment shows that the  $M_w$  of PMMA in the composite is 59,662 ( $M_w/M_n = 2.0$ ). All the above results indicate that the composite is composed of PMMA and small CdS nanoparticles.



**Figure 4** X-ray diffraction pattern of CdS/PMMA composite obtained at 4.21 MPa and 308.2 K. The vertical lines at the bottom indicate the standard positions and relative intensities of cubic CdS.



**Figure 5** IR spectra of the pure PMMA sample (a) and CdS/PMMA composite (b).

## CONCLUSION

In this work, compressed CO<sub>2</sub> was used as an antisolvent to precipitate CdS nanoparticles and PMMA from the polymerized MMA/AOT/water microemulsion. It was found that by controlling the precipitation pressure of CO<sub>2</sub>, the CdS nanoparticles and PMMA can be precipitated simultaneously from the solution, while AOT remains in solution, and the CdS/PMMA composites were successfully synthesized, in which CdS nanoparticles were distributed in the polymer matrices. This method has some potential advantages. It may be easily extended to other microemulsion polymerization systems to prepare inorganic/polymer composites.

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