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Preparation of the Nanoparticles Dispersed in Random Copolymer

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Abstract: Semiconductive nanoparticles are synthesized in thin films of a random copolymer comprised of methylmethacrylate (MMA) and vinylpyrrolidone (VP), which can be called as PMVP. PMVP developed a microphase-separated structure in which the constituent monomer components seemed to be segregated into the respective regions in *nanosize*. The size of the particles synthesized in PMVP films is about a few nm, which is nearly the same as the characteristic spacing of the microphase-separated structure. This microphase-separated structure limits the growth of the particle and prevents the aggregation of the particles. On the other hand, the particles synthesized in films of the polyvinylpyrolidone homopolymer by the similar manner grew much bigger than those in the case of the random copolymer.

Key words: nanoparticle, random copolymer, nanoreactor, microphase-separation

INTRODUCTION

The nanoparticles, particles having diameters of a few nm, are paid much attention, because they exhibit properties significantly different from those in the bulk [1,2]. For example, CdSe nanoparticles show various colors and photoluminescence spectrum, both of which strongly depends on the particle size [3]. CdSe nanoparticles are widely used as fluorescent biological labels, since various fluorophores can be excited by a single wavelength [4,5]. Recent progress in flat panel displays (FPD), such as organic light emitting diodes (OLED) or plasma display panels (PDP) or field emission displays, is owing to the fluorophores of high luminescence quantum yield and long lifetime as well as to the micro-fabrication technology. The nanoparticles may be applied to light-emitting material for FPD.

In order to use the nanoparticles as a light-emitting material, one has to immobilize them in some appropriate matrix. However, it is very difficult to homogeneously disperse the nanoparticles in the matrix since the nanoparticles quite easily coarsen into a large aggregation. The coarsened nanoparticles often deteriorates the quantum yields of the fluorophore [6]. To avoid such aggregation of the nanoparticles, generally two methods have been utilized: one is preparing the nanoparticles in a *monomer* solution and thereafter polymerizing the monomer to fix the nanoparticles homogeneously in the polymerized matrix [7]. The other is synthesizing the nanoparticles by using *nanoreactor* [8]. Block copolymers in which two or more polymer sequences are covalently bound at their chain ends form microphase-separated structure [9,10]. Microdomains of the block copolymers has been used as the nanoreactor for the nanopraticle synthesis [8,11]. However, the size of the microdomains formed in the block copolymers is generally quite larger than that of the nanoparticles. Hence, inside the microdomains, the nanoparticles may coarsen.

In this study, we synthesized the nanoparticles in a random copolymer composed of methylmethacrylate (MMA) and vinylpyrrolidone (VP). The random copolymer was microphase-separated into MMA and VP domains, which have a size significantly smaller than the case of the conventional block copolymers. We will show that the microdomains formed in the random copolymer can be used as a nanoreactor and effectively prevents the aggregation of the nanoparticles synthesized in there.

EXPERIMENTAL SECTION

MMA and VP were purchased from Wako chemicals, Tokyo, Japan, and purified with distillation. Zinc acetate, $Zn(OAc)_2$, and Azobisisobutyronitrile (AIBN) were purchased from Wako chemicals and used without further purification. The random copolymer of MMA and VP, hereafter referred to PMVP, was synthesized by bulk polymerization with AIBN as an initiator [12]. PMVPs were polymerized under N_2 atmosphere at 60 ℃. PMVP was purified by reprecipitation in methanol solution with diethyl ether and deionized water, and dried under vacuum. The composition of MMA in this random copolymer was determined to be 50 mol % by means of ^{1}H-NMR using a JEOL EX-400.

The Films of PMVP were made as follows. 10wt% methanol solution of the PMVP in methanol is spread in a laboratory dish. The samples were dried under vacuum at 60℃ and finally heated to 180℃ in order to remove the solvent completely.

The structure of the random copolymer films was characterized by a Wide-angle X-ray scattering (WAXS) apparatus (M18XHF-SRA, MAC Science Co. Ltd., Yokohama, Japan). The obtained WAXS profiles were corrected for absorption of X-ray beam by the sample, scattering by the air, and smearing effects.

The ZnS nanoparticles were synthesized by the reaction of $Zn(OAc)_2$, which was blended to the PMVP first, and H_2S vapor. The reaction forms ZnS particles in PMVP matrix [11]. PMVP films containing $Zn(OAc)_2$, hereafter referred to ZnPMVP, were prepared from a solution comprised of 1wt% $Zn(OAc)_2$, and 9wt% PMVP in methanol. ZnPMVP films deposited onto the glass slide were dried under vacuum at 60℃ and then heated to 180℃ (same as the PMVP films). Polyvinylpyrrolidone (PVP) films containing $Zn(OAc)_2$, ZnPVP, were also prepared similarly to the case of ZnPMVP films. The dried films containing $Zn(OAc)_2$ were exposed to saturate H_2S vapor for 1h or 2h or 12h in a closed chamber at 25℃. Then, the excess H_2S was removed from the films in vacuum. In this experiment, the H_2S vapor was prepared by the reaction of HCl aqueous solution and NaS. Therefore, the H_2S vapor may be accompanied by some moisture.

UV-vis absorbance were obtained on V-570, JASCO, Japan, spectrophotometer.

RESULTS AND DISCUSSION

Figure 1 shows a WAXS profile measured for the PMVP film prepared in this study.

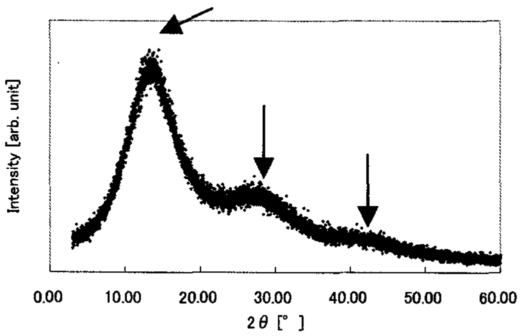

Figure 1. WAXS profile for the PMVP film prepared from the methanol solution.

In Fig. 1 three Bragg peaks at $2\theta = 13°$, $26°$, and $40°$ (indicated by the arrow) are observed. They indicate that the PMVP forms some inhomogeneous structure which has a characteristic spacing of 7 Å. The random copolymer, in macroscopic length scale, seems to behave like a homopolymer. However, hydrophobic MMA and hydrophilic VP are significantly incompatible [13]. The strong repulsive interaction between the two constituents may lead a segregation of MMA and VP, which are randomly bound in the main chain, into the respective domains. In fact, the *microphase-separated structure* has been observed in some random copolymer systems [14,15]. The characteristic spacing of 7 Å observed by WAXS seems to associate with the short-range order of the microphase-separated MMA and VP domains in the PMVP. Although we will not elaborate on the detail of the microphase-separation here, the domain size of MMA and VP is believed to be less than 7 Å.

ZnPMVP films showed the same characteristic spacing in the WAXS profile, though the data is not shown here. Hence, the microphase-separation of MMA and VP is not significantly influenced by blending with the nanoparticle precursor.

Figure 2a shows the absorption spectrum measured for the films of ZnPMVP. Curve A represents the absorption spectrum of the as-prepared film of ZnPMVP. Curve B, C, and D show the absorption spectrum of the sample treated with saturated H_2S vapor for 1hr, 2hr, and 12hr, respectively. Figure 2b shows the difference spectrum of the samples exposed to the saturated H_2S vapor with respect to the unexposed sample (curve A in Fig. 2a).

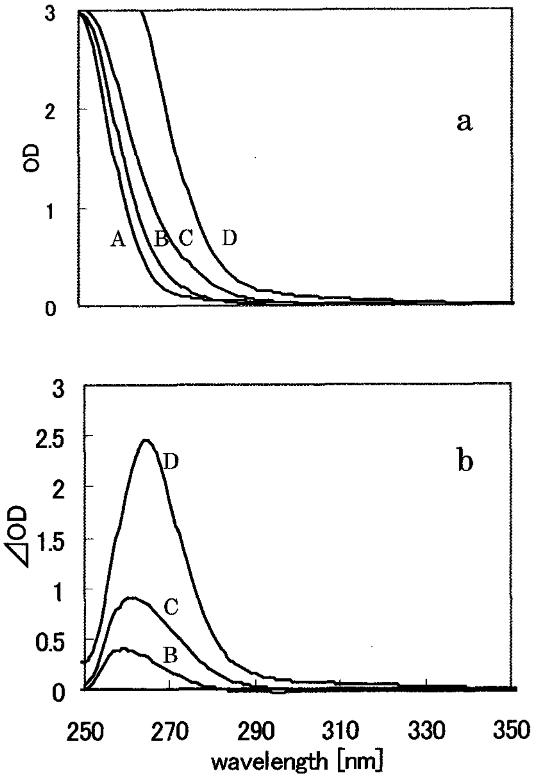

Figure 2. (a) The absorption spectrum for ZnPMVP, (the base film, Curve A), and ZnPMVP treated with H_2S for 1hr (Curve B), 2hr (Curve C), 12hr (Curve D) (b) The difference spectrum of Curve B, C and D relative from Curve A shown in part a.

It is shown that the exposure to H_2S vapor increases the absorbance peak in the range 260-290nm. The peak enhancement is supposed to be attributed by the formation of ZnS particle inside the film. The exciton peaks of ZnS particles are strongly influenced by the particle size [16]. The ZnS particles with the diameter of some 3-4nm show the exciton peak at 275-290nm. The ZnS particles of the larger sizes (>4nm) exhibit the absorbance in the long wavelength region (290nm-380nm). Hence, in our sample, the ZnS particles with the diameter in the range of a few nm are supposed to be formed. The precursor $Zn(OAc)_2$ is distributed selectively in the hydrophilic VP domains [11]. Therefore, the synthesis of the ZnS particle should proceed preferentially in the VP domains. The VP domains

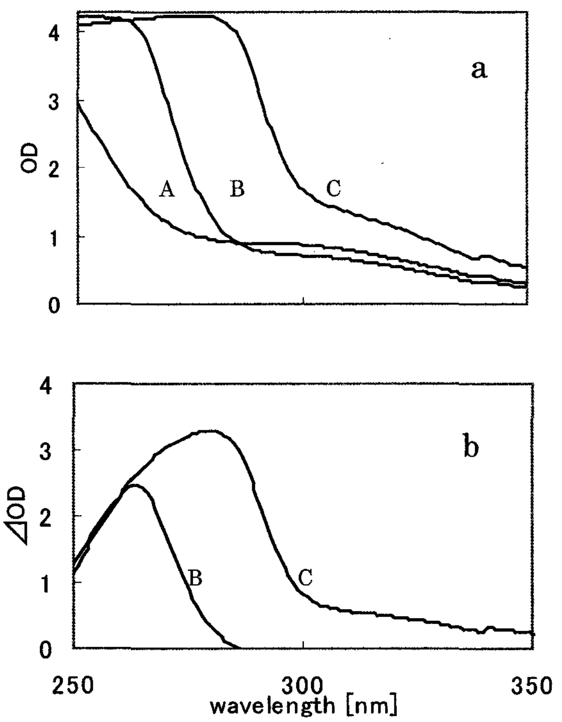

Figure 3. (a) The absorption spectrum for ZnPVP, (the base film Curve A) and ZnPVP treated with H_2S for 1hr (Curve B), 2hr (Curve C) (b) The difference spectrum of Curve B and Curve C relative from Curve A shown in part a.
Note that OD is not saturated in the short-wavelength region in part a.

providing the reaction space are supposed to limit the growth of ZnS particles. Figure 3a shows the absorption spectrum of the homo PVP films containing $Zn(OAc)_2$ or ZnS particles. Curve A represents the absorption spectrum of the as-prepared film of ZnPVP. Curve B and C are the absorption spectrum of the sample treated with H_2S for 1hr, 2hr. In contrast to the case of the random copolymer (see Figure 2a), the long wavelength region (280nm-300nm) of the absorption spectra increases with the exposure time as well as the short wavelength region. It is more clearly represented in the difference spectrum shown in Figure 3b. As the reaction proceeds, the absorbance peak of the sample shifts from 263nm (at the treatment for 1hr) to 280nm (at the treatment for 2hr). Since ZnS particles formed in the homogeneous matrix of PVP, the particles immediately coarsen into the aggregations and formed a bigger ones. This situation is in contrast to the case of the random copolymer in which some discrete phase of the PVP is formed. In this experiment, we didn't continue to set the samples in the H_2S atmosphere in more 2hr due to swelling of the film. As described in the experiment section, some moisture seemed to present in H_2S vapor and caused the swelling of the PVP homopolymer. In PMVP, the hydrophobic glassy domains of MMA seem to inhibit the macroscopic swelling of the film.

The full-width-half-maximum (FWHM) of the absorption spectrum of ZnPMVP treated with saturated H_2S vapor for 12hr, and that of the ZnPVP treated with saturated H_2S vapor for 2hr is 17.5 nm and 38.5 nm, respectively. Qualitatively, the small FWHM of ZnPMVP is interpreted by the narrow size distribution of the ZnS particles synthesized in ZnPMVP film in relative to those synthesized in ZnPVP film.

CONCLUSION

We revealed that the films of the random copolymer comprised of MMA and VP form a microphase-separated structure in which the MMA and VP segregate into the respective domains with a size of less than some 1nm. Then the microphase-separated structure was explored as the reaction space for the ZnS particles. The precursor $Zn(OAc)_2$ was dispersed in the VP regions of the random copolymer and reacted with H_2S vapor in order to form ZnS. The ZnS particles synthesized in the random copolymer showed a sharp exciton peak in the range 257nm-264nm, indicating that their size was in the same range as the microphase-separated structure of the matrix. Furthermore, the size distribution of the particle synthesized in the random copolymer was found to be very narrow. On the other hand, in the PVP homopolymer, the ZnS particles significantly increased their size. These results show that the microphase-separated random copolymers can effectively suppress the aggregation of the inorganic particle synthesized in them and the particles couldn't form bigger than the size of the domain in the random copolymers.

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