

Synthesis of CdS Nanoparticles Dispersed within Amphiphilic Poly(urethane acrylate-co-styrene) Films

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ABSTRACT: CdS nanoparticles were prepared using amphiphilic urethane acrylate nonionomer (UAN) precursor chains having a poly(propylene oxide)-based hydrophobic segment and a hydrophilic poly(ethylene oxide) segment. Cadmium salts were first dissolved in UAN/styrene solutions, and then the solutions were copolymerized to obtain poly(urethane acrylate-co-styrene) films containing dissolved cadmium salts. After reduction with H₂S gas, free-standing films containing CdS nanoparticles were obtained. Transmission electron microscopy images of the films showed that 9.67-nm CdS nanoparticles were dispersed within the poly(urethane acrylate-co-styrene) matrix. The

formation of CdS nanoparticles was also confirmed with UV absorption spectra and photoluminescence emission spectra of the films. Transmission electron microscopy and dynamic mechanical analysis measurements confirmed that hydrophilic/hydrophobic microphase separation in UAN/styrene solutions occurred during the dissociation of the cadmium salts, and the microphase-separated structures were locked in by crosslinking copolymerization. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 97: 2357–2363, 2005

Key words: synthesis; nanoparticles; films

INTRODUCTION

Recently, a lot of research on nanoparticles dispersed within polymer matrices has been carried out because these materials can provide various new properties originating from the combination of properties of inorganic components and polymers. A polymeric matrix provides processability and the flexibility, and inorganic nanosized particles can not only improve the mechanical properties of the host polymer but also give unique properties that differ from those of their bulk materials and atoms. As a result, nanocomposite films, having novel catalytic, magnetic, and optical properties, can be obtained.^{1–7}

Surfactants, amphiphilic block copolymers, and dendrimers have been used as templates for the preparation of inorganic nanoparticles.^{8–11} Template-stabilized nanoparticles are generally obtained as colloidal solutions or polymeric films. In the case of polymer films containing inorganic nanoparticles, most preparation methods are based on *in situ* reactions within amphiphilic block copolymer films, in which hydrophilic nanodomains formed by microphase separation act as nanoreactors. However, amphiphilic block copolymers and dendrimers are very expensive materi-

als and can be obtained only by extremely complicated synthetic processes; this has limited the applications of polymer films containing metal nanoparticles.

In this article, we present the synthesis of semiconductor nanoparticles (CdS) with an amphiphilic oligomer chain, urethane acrylate nonionomer (UAN). Amphiphilic UAN precursor chains can be synthesized via a relatively simple synthetic process, and the price of these UAN chains is much lower than that of amphiphilic block copolymers and dendrimers. The mechanical properties of these urethane acrylate chains can also be freely controlled. We can synthesize freestanding polymer films containing magnetic and silver nanoparticles with crosslinked UAN films.^{12–14} The size and morphology of magnetic nanoparticles dispersed within these matrices can be controlled through variations in the degree of hydrophilic/hydrophobic nanophase separation in amphiphilic UAN through variations in the type of solvent used and the weight ratio of the hydrophobic monomer to UAN in the synthesis of the polymeric matrices.

For the synthesis of inorganic nanoparticles with amphiphilic polymers or dendrimers, in many cases a solvent has been used for dissolving the metal precursor or amphiphilic copolymers in the following ways:

1. In the presence of a solvent, metal precursors, dissolved in the solvent, are taken up by swollen polymer films; this is followed by a reduction process after the removal of the solvent.

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2. A solution containing the dissolved metal precursors and polymer is prepared, and the reduction is subsequently performed in the solution.
3. The solution containing the metal precursors and polymer is deposited onto a substrate, and the reduction is carried out after the removal of the solvent.

In this study, freestanding polymer films containing CdS nanoparticles were prepared through a new consecutive two-step process without a solvent. In the first step, cadmium salts were dissolved in UAN/styrene solutions, and in the second step, the solutions containing dissolved cadmium salts were directly converted into freestanding polymeric films via a crosslinking polymerization process without the evaporation process of a solvent, followed by a reduction process. In this article, we present the synthesis of CdS nanoparticles dispersed within poly(urethane acrylate-co-styrene) films synthesized through the copolymerization of amphiphilic urethane acrylate precursor chains and a hydrophobic monomer (styrene). The formation of CdS nanoparticles in the polymer matrix was confirmed with transmission electron microscopy (TEM) measurements, ultraviolet-visible (UV-vis) absorption spectroscopy, and photoluminescence spectroscopy. The mechanical properties of the nanocomposite films, examined with an Instron measurement and a dynamic mechanical analyzer, are also presented with respect to the induced microphase separation anticipated for nanocomposite films.

EXPERIMENTAL

Materials

In the synthesis of amphiphilic UAN precursor chains, poly(propylene oxide triol) (PPO triol; molecular weight = 1000; Korea Polyol Co.), 2,4-toluene diisocyanate (TDI; Aldrich Chemical Co., Milwaukee, WI), 2-hydroxyethyl methacrylate (2-HEMA; Aldrich Chemical Co., Milwaukee, WI), and poly(ethylene glycol) (PEG; weight-average molecular weight = 1500; Aldrich Chemicals) were used. PPO triol and PEG were dried and degassed at 80°C and 3–5 mmHg for 2 days. Styrene, 2,2'-azobisisobutyronitrile (AIBN), cadmium acetate, and dimethylacetamide (DMAc) were purchased from Aldrich Chemical Co. and used as received.

Synthesis of the UAN chains

Amphiphilic UAN precursor chains were synthesized with an established three-step process described in previous publications.^{12–14} Each reaction was performed with a 500-mL, four-necked vessel equipped with a stirrer, a thermometer, and an inlet system for

nitrogen gas. The TDI/PPO triol/2-HEMA/PEG molar ratio was 3/1/2/1. The synthesis procedure for the UAN chains was described in detail in our previous reports.^{12–14} The molecular weight of the UAN precursor chains was measured with a model 410 gel permeation chromatograph equipped with a Styragel HR1-4 column (Waters Associates) at 25°C. The flow rate of the carrier solvent, tetrahydrofuran, was 0.5 mL/min. The polystyrene equivalent molecular weight of the synthesized UAN chains was a weight-average molecular weight of 6700; the polydispersity was 1.93. A characterization of the synthesized UAN chains based on ¹H-NMR spectra was reported in previous articles.^{12–14} The expected molecular structure of the UAN chains is schematically illustrated in Figure 1.

Synthesis of the nanocomposite films

The UAN chains were first dissolved in styrene to form homogeneous solutions with 3/3, 3/6, and 6/3 weight ratios of UAN to styrene. Then, cadmium acetate (0.5 wt %) was added and mixed with UAN/styrene mixtures at room temperature. Although cadmium acetate salts could not be dissolved but were instead dispersed in the hydrophobic monomer (styrene), the crystal vanished while the mixture was stirred; this directly indicated that the cadmium acetate salt was dissociated by the UAN chains. After the cadmium acetate salts completely vanished, the radical initiator, AIBN (0.005 g), was added and mixed with the solutions. The solutions were poured into a silicone-packed mold, and then crosslinking copolymerization was carried out at 85°C for 3–4 h to obtain polymer films 0.05 mm thick. After the copolymerization, the transparent solutions became cured transparent films, which were reacted for 5 h in a closed flask with dry H₂S at atmospheric pressure and 25°C to form CdS nanoparticles within the films. The color of the films changed to yellow, and this indicated the formation of CdS nanoparticles. After the reaction, the films were left *in vacuo* in a desiccator overnight to remove excess H₂S.

Measurements

A transmission electron microscope (JEM 2020CX, JEOL), with an acceleration voltage of 200 kV, was used to clarify the nanostructures of the composites films. The nanocomposite films were embedded in an epoxy resin (Epon-812) supplied by SPI. Ultrathin sections of the nanocomposite films, approximately 70 nm thick, were prepared at –60°C with an Ultracut R ultramicrotome from Leica. Carbon was vacuum-evaporated onto the thin sections to prevent the accumulation of electrons during the TEM observations. The particle sizes were determined with a comparator on the basis of the measurement of at least 150 parti-

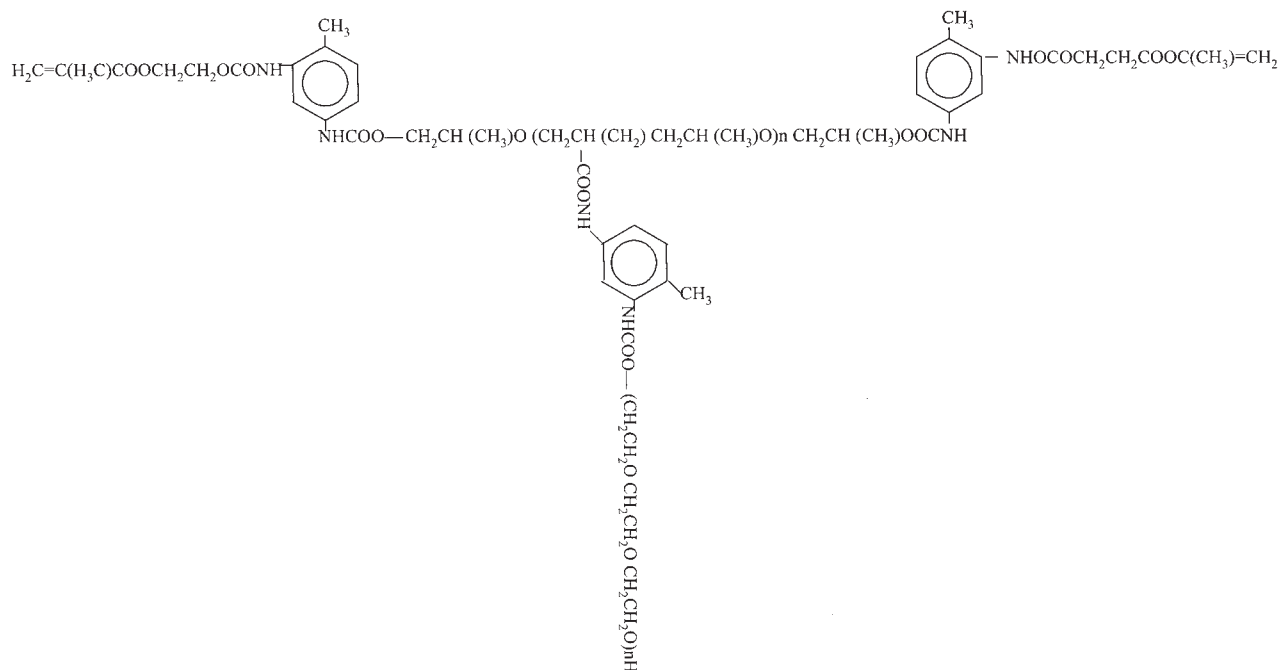


Figure 1 Schematic presentation of the UAN chains.

cles. Neat poly(urethane acrylate-*co*-styrene) films were immersed in OsO_4 (2 wt %) aqueous solutions for 1 day and rinsed with water to stain the hydrophilic domains of the films.

The tensile properties of the films were measured with a Hounsfield Instron R10001231 instrument. The cross-head speed was 1 mm/min. All samples were measured five times. Dynamic mechanical measurements of the dry networks were performed with a DMA 2980 (TA Instruments, Inc., New Castle, DE) in the extension mode at 1 Hz and at a heating temperature of $2^\circ\text{C}/\text{min}$ in the temperature range of $20\text{--}200^\circ\text{C}$. UV spectroscopy measurements of the obtained composite films were also performed with a Shimadzu 3210 instrument between 190 and 900 nm. Steady-state fluorescence spectra were obtained on a Shimadzu RF-5301PC fluorescence spectrophotometer by the measurement of the CdS/polymer nanocomposite films. The excitation wavelength was 360 nm, and the bandwidths were 5 nm for excitation and emission.

RESULTS AND DISCUSSION

Formation of the nanoparticles within the poly(urethane acrylate-*co*-styrene) matrix

Semiconductor nanoparticles have unique size-dependent chemical and physical properties. In particular, CdS has a particle-size-dependent electronic spectrum; that is, the size of the semiconductor particles decreases to the nanoscale, the band gap of the semiconductor increases, and this causes a blueshift in the UV-vis absorption spectra.^{6,7,10,15-17} Therefore, the

blueshift in the absorption edge is direct evidence of the formation of nanosized CdS particles. According to the literature, bulk CdS materials exhibit absorption onset at 515 nm,¹⁵⁻¹⁷ so absorption onset at a shorter wavelength indicates the formation of CdS nanoparticles. Figure 2 shows the UV-vis spectra of the nanocomposite films. The films show an absorption onset around 490 nm. This indicates the formation of CdS nanoparticles within the poly(urethane acrylate-*co*-styrene) films. With a change in the weight ratio of

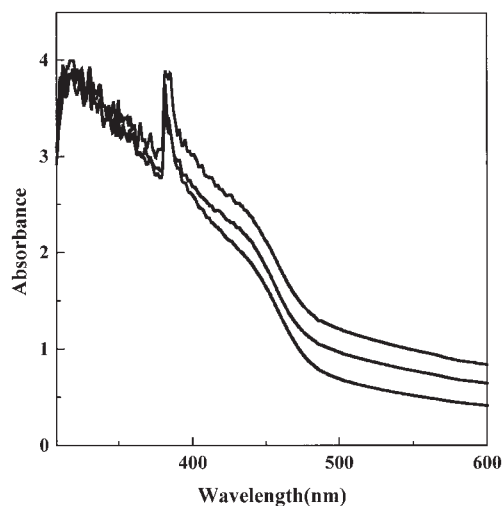


Figure 2 UV-vis spectra of poly(urethane acrylate-*co*-styrene) films, containing CdS nanoparticles, prepared with different UAN/styrene weight ratios: (a) 3/3, (b) 3/6, and (c) 6/3.

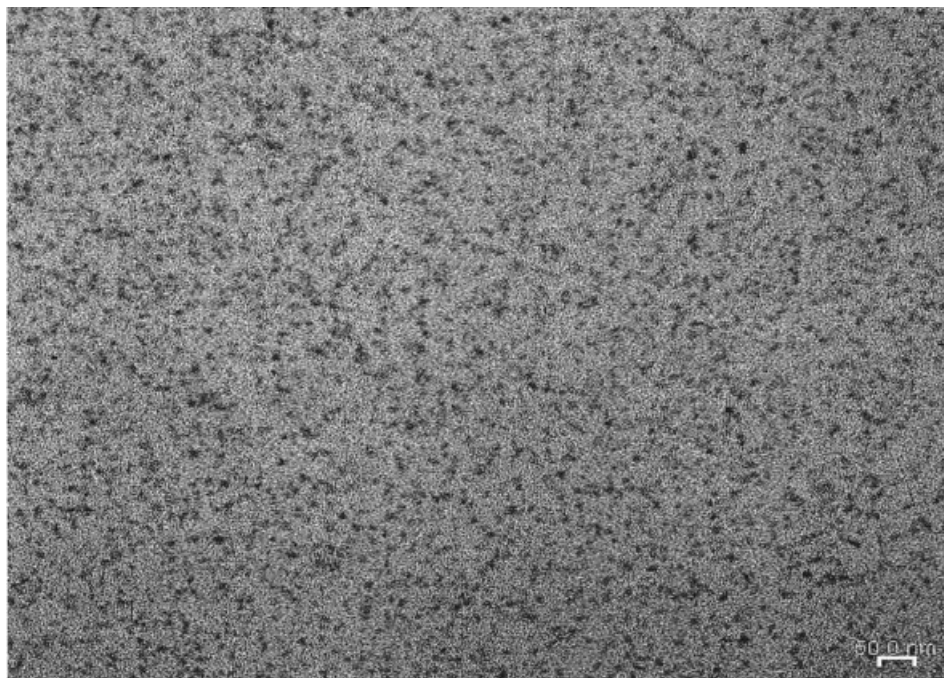


Figure 3 TEM micrograph of a poly(urethane acrylate-*co*-styrene) film containing CdS nanoparticles.

UAN to styrene, the nanocomposite films show an absorption edge at almost the same wave length, and this indicates that the CdS nanoparticles that formed in the crosslinking polymerized UAN/styrene film have almost the same size. TEM measurements have been used to observe CdS nanoparticles in the crosslinking polymerized UAN/styrene film. As shown in Figure 3, 9.67-nm CdS nanoparticles are dispersed in the crosslinking polymerized UAN/styrene matrix.

The formation of the CdS nanoparticles can also be confirmed with photoluminescence spectroscopy because nanosized CdS particles exhibit light-emitting behavior at a specific wavelength.^{6,7,10,15–17} Figure 4 shows the emission spectra for the nanocomposite films containing CdS nanoparticles. The nanocomposite films, synthesized with different weight ratios of UAN to styrene, exhibit photoemissions at about 490 nm; this indicates the formation of CdS nanoparticles within the poly(urethane acrylate-*co*-styrene) films.

Microphase separation in the poly(urethane acrylate-*co*-styrene) network

For the synthesis of polymer films containing inorganic nanoparticles based on amphiphilic block copolymers, nanoparticles and polymeric films with hydrophilic nanodomains are obtained with a separate process.^{1–7} Microphase-separated polymer films are first prepared and then immersed in metal salt solutions to form metal/polymer complexes within their hydro-

philic nanodomains, and the formation of nanoparticles via a proper reduction process follows.

For our system, the formation of salt/amphiphilic UAN precursor chains is first carried out by the mixing of cadmium salt with a UAN/styrene solution; this is similar to the process for the preparation of metal nanocolloidal solutions stabilized by amphiphilic polymers or surfactants. It can be postulated that upon the mixing of cadmium acetate with UAN/styrene mixtures, cadmium acetate salts are dissociated

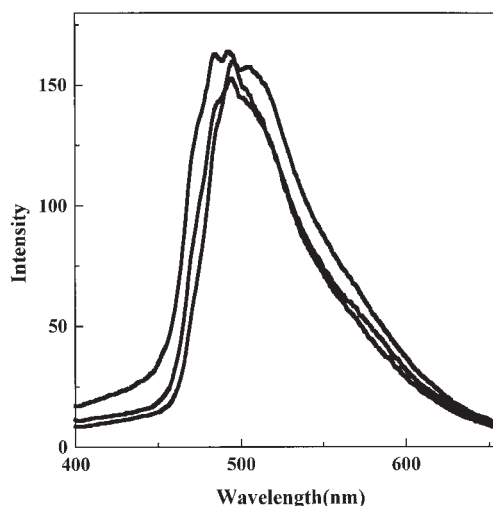


Figure 4 Photoluminescence emission spectra for poly(urethane acrylate-*co*-styrene) films, containing CdS nanoparticles, prepared with different UAN/styrene weight ratios: (a) 3/3, (b) 3/6, and (c) 6/3.

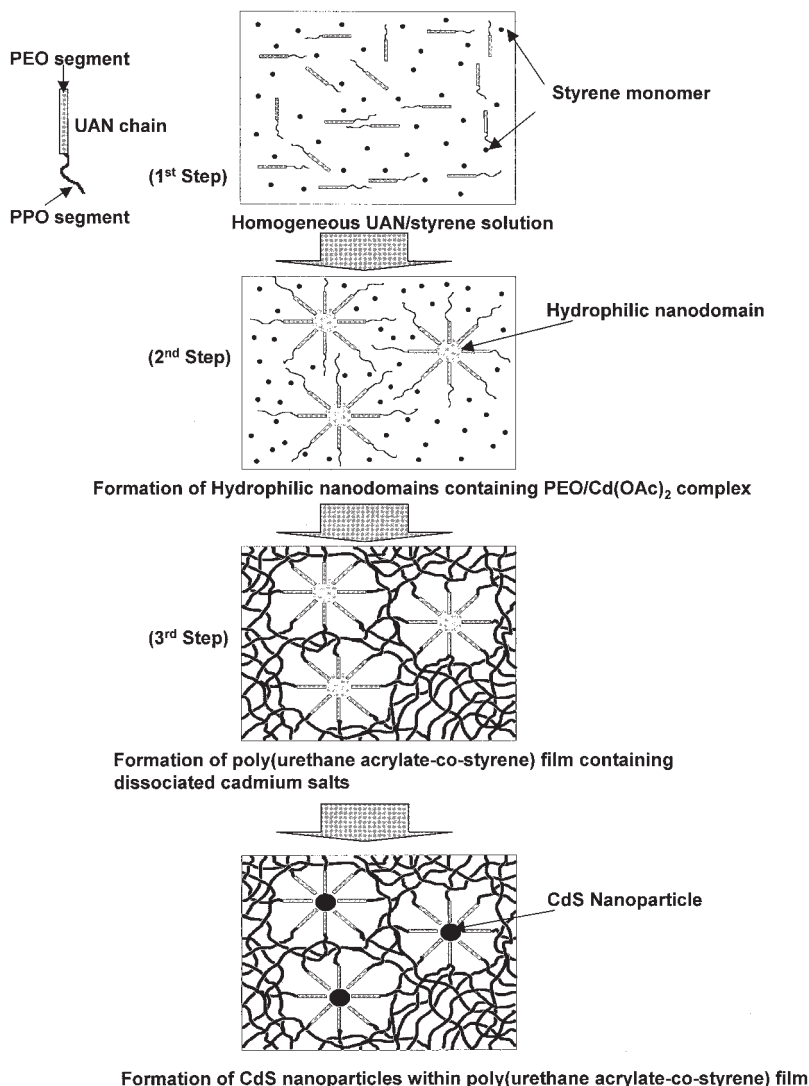


Figure 5 Schematic presentation for postulated microstructures of a UAN/styrene solution containing cadmium salts and a poly(urethane acrylate-co-styrene) film containing CdS nanoparticles.

through the formation of complexes with poly(ethylene oxide) (PEO) segments in the UAN chains, whereas hydrophobic PPO-based segments in UAN and styrene monomers are homogeneously mixed with one another to form continuous hydrophobic domains. Through a polymerization process, the microphase-separated structure of UAN/styrene solutions containing dissociated cadmium salts is locked in by crosslinking polymerization, and this results in the solutions being converted into transparent poly(urethane acrylate-co-styrene) films containing dissociated cadmium salts. Through the reaction of the films with H₂S gas, the films containing dissociated cadmium salts are converted into films containing CdS nanoparticles. Postulated microstructures of UAN/styrene solutions containing cadmium salts and poly(urethane acrylate-co-styrene) films containing CdS nanoparticles are schematically illustrated in Figure 5.

Figure 6 shows a TEM image of a crosslinking polymerized UAN/styrene film stained by an OsO₄ aqueous solution. Because the OsO₄ aqueous solution is absorbed only by hydrophilic PEO segments, the dark spots (ca. 10 nm) dispersed within the matrix represent the hydrophilic domains. It can be confirmed by this result that PEO segments of UAN are microphase-separated with the PPO-based hydrophobic segment of UAN and styrene and form their own hydrophilic domains. By comparison with the TEM image of Figure 3, we find that the number of dark spots is much lower than that of CdS nanoparticles dispersed within the matrix. This result indicates that the hydrophilic segments of the UAN chains are slightly microphase-separated from the hydrophobic segments and styrene; this may be due to the amphiphilic character of the ethylene oxide repeating units of PEO in the UAN chains.^{18,19} Therefore, the degree of microphase separation of PEO segments

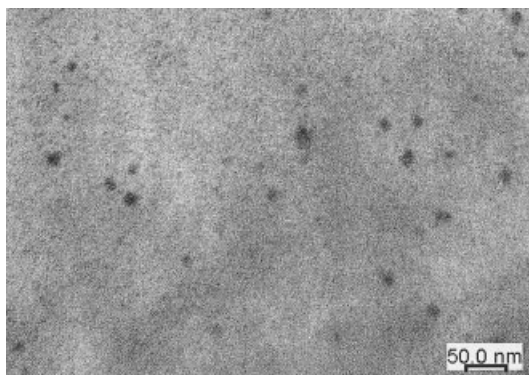


Figure 6 TEM micrograph of an OsO_4 -stained poly(urethane acrylate-*co*-styrene) films.

from hydrophobic segments is increased by the dissociation of cadmium salts within UAN/styrene solutions. In other words, because the cadmium salt can be dissociated only by PEO chains of UAN, a larger number of PEO chains are microphase-separated to make complexes with cadmium salts by the dissociation of the salts. This causes the degree of hydrophilic/hydrophobic microphase separation to increase.

It has been reported that microphase separation in crosslinked urethane acrylate films strongly influences the mechanical properties of the films.^{20–22} Unlike macrophase separation, the tensile strength, elongation, and glass-transition temperature of crosslinked polyurethane films increase as the degree of microphase separation between hydrophilic and hydrophobic segments or between soft and hard segments increases. This is because the microphase separation causes increased chain entanglement in each segment, and microphase-separated hydrophilic or hard segments act as physical fillers. Therefore, we examined the mechanical properties of a neat poly(urethane acrylate-*co*-styrene) film and its nanocomposite film with a dynamical mechanical analyzer and an Instron instrument to investigate the microphase separation behavior in poly(urethane acrylate-*co*-styrene) films.

Three types of poly(urethane acrylate-*co*-styrene) films were synthesized. The first film was a neat poly(urethane acrylate-*co*-styrene) film synthesized with a UAN/styrene solution. The second film was a nanocomposite poly(urethane acrylate-*co*-styrene) film containing CdS nanoparticles. The third film was synthesized by the crosslinking polymerization of a UAN/styrene solution containing dissociated cadmium acetate. This film was immersed in DMAc for 1 day to remove dissociated cadmium acetate from the film.

Figures 7 and 8 show the storage modulus and $\tan \delta$ of the three types of films as a function of temperature. Although the third film was synthesized through the copolymerization of a UAN/styrene/cadmium acetate solution, dissolved cadmium acetates in the poly(urethane acrylate-*co*-styrene) networks were re-

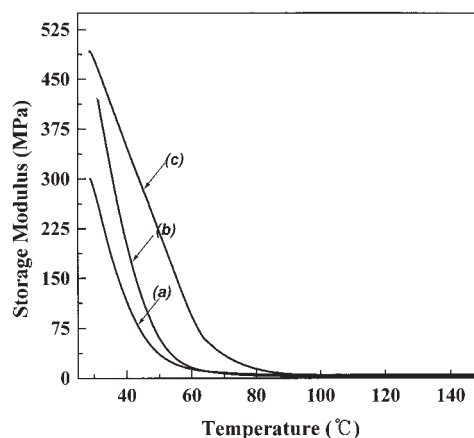


Figure 7 Storage modulus of three types of poly(urethane acrylate-*co*-styrene) films prepared under different conditions as a function of temperature: (a) neat poly(urethane acrylate-*co*-styrene) film, (b) poly(urethane acrylate-*co*-styrene) film containing cadmium salts that was immersed in DMAc to remove cadmium salts, and (c) poly(urethane acrylate-*co*-styrene) film containing CdS nanoparticles.

moved by immersion in DMAc; therefore, the first and third poly(urethane acrylate-*co*-styrene) films had the same chemical composition. However, the third film (curve b) exhibited a higher storage modulus and the maximum $\tan \delta$ at a higher temperature in comparison with the first film (curve a); this may be due to the higher degree of hydrophilic/hydrophobic microphase separation of the third film. That is, the dissociation of cadmium salts and the formation of hydrophilic domains increased the degree of hydrophilic/hydrophobic microphase separation of the networks, causing the storage modulus and temperature of max-

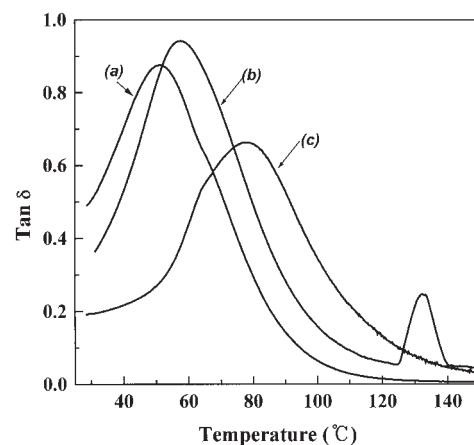


Figure 8 $\tan \delta$ of three types of poly(urethane acrylate-*co*-styrene) films prepared under different conditions as a function of temperature: (a) neat poly(urethane acrylate-*co*-styrene) film, (b) poly(urethane acrylate-*co*-styrene) film containing cadmium salts that was immersed in DMAc to remove cadmium salts, and (c) poly(urethane acrylate-*co*-styrene) film containing CdS nanoparticles.

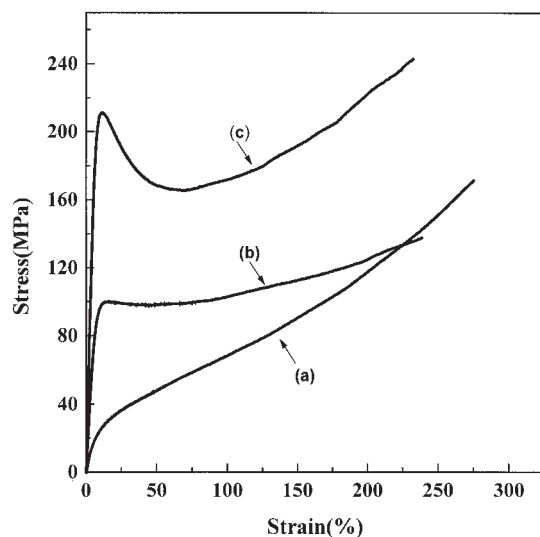


Figure 9 Stress–strain curves for three types of poly(urethane acrylate-*co*-styrene) films prepared under different conditions as a function of temperature: (a) neat poly(urethane acrylate-*co*-styrene) film, (b) poly(urethane acrylate-*co*-styrene) film containing cadmium salts that was immersed in DMAc to remove cadmium salts, and (c) poly(urethane acrylate-*co*-styrene) film containing CdS nanoparticles.

imum $\tan \delta$ of the film to increase. The poly(urethane acrylate-*co*-styrene) film containing CdS nanoparticles (curve c) exhibited a greater storage modulus and the maximum $\tan \delta$ at a higher temperature in comparison with the first and third films. This result may be due to hydrophilic/hydrophobic microphase separation within poly(urethane acrylate-*co*-styrene) and the inclusion of CdS nanoparticles acting as nanosized inorganic fillers.

The tensile mechanical properties of three types of poly(urethane acrylate-*co*-styrene)s are also presented in Figure 9. Just like the dynamic mechanical analysis results, the poly(urethane acrylate-*co*-styrene) film containing CdS nanoparticles [Fig. 9(c)] showed higher tensile strength than the other films. The third poly(urethane acrylate-*co*-styrene) film [Fig. 9(b)] also exhibited higher tensile strength than the neat poly(urethane acrylate-*co*-styrene) film [Fig. 9(a)]. Therefore, the higher tensile strength of the films containing CdS nanoparticles may also be due to hydrophilic/hydrophobic microphase separation in poly(urethane acrylate-*co*-styrene) networks and the inclusion of CdS nanoparticles.

CONCLUSIONS

Unlike conventional processes, freestanding films containing CdS nanoparticles can be prepared through the polymerization of UAN/styrene solutions without

a solvent. The overall mechanism for the formation of poly(urethane acrylate-*co*-styrene) films containing CdS nanoparticles can be proposed as follows. Upon the mixing of cadmium acetate with UAN/styrene mixtures, PEO chains in UAN are microphase-separated to form complexes with the cadmium salt, and the hydrophobic PPO-based segment in UAN and styrene monomers are homogeneously mixed with each other to form continuous hydrophobic domains. As a result, hydrophilic nanodomains formed by the creation of the PEO/cadmium acetate complex are dispersed in a hydrophobic continuous phase. This colloidal solution is converted into microphase-separated polymeric films through the copolymerization of UAN and styrene. By reacting with H_2S , the cadmium cations located in the hydrophilic domains of poly(urethane acrylate-*co*-styrene) networks are converted into CdS nanoparticles dispersed in the polymeric films. The formed CdS nanoparticles and microphase separation within poly(urethane acrylate-*co*-styrene) films can increase the mechanical strength of the films.

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