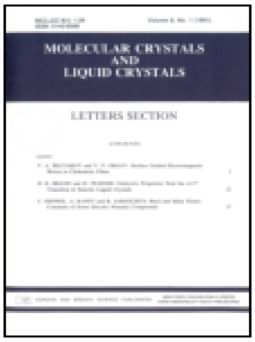

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Synthesis and Characterization of Bridged Polysilsesquioxane Nanoparticles and Their Nanocomposites with Polycaprolactone by UV Irradiation

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Spherical bridged polysilsesquioxane nanoparticles with thiol groups (BPS-SH) were prepared by the reduction of BPS with disulfide groups after the base-catalyzed hydrolysis and condensation reaction of bis(triethoxysilylpropyl)disulfide. The average size of BPS was around 100~300 nm. Hydroxyethyl methacrylate (HEMA)-initiated polycaprolactone (PCL) was synthesized by ring-opening polymerization of caprolactone under the co-initiation of HEMA and $Sn(Oct)_2$*. New nanocomposites of BPS-SH and HEMA-PCL were fabricated by the photo-induced chemical reaction under a photoradical generator and ultraviolet light. BPS was fully and continuously covered with PCL, which resulted in the rough surface of BPS nanoparticles as well as the connected BPS nanoparticles together.*

Keywords Bridged polysilsesquioxane; Polycaprolactone; Nanocomposites; UV Irradiation

Introduction

Bridged polysilsesquioxane (BPS) is a unique organic-inorganic hybrid material formed by the sol-gel polymerization of silane monomers with two or more trialkoxysilyl groups attached to an organic bridging group [1]. By varying the organic bridging groups incorporated as an integral component of the silica network, it is easy to modulate various properties of BPS such as physical, chemical, and mechanical properties [2-4]. Furthermore, the introduction of reactive bridging groups on the chemical or UV reaction not only gives function to BPS but also provides the opportunity to design the new hybrid materials [5-7]. We have already explored composites of spherical BPS nanoparticles and Pd nanoparticles via ionic interactions. BPS containing sulfonic groups through the chemical reaction of bridging groups in the silica network was successfully prepared without templates or surfactants to make particle-particle composites with positively charged Pd-POSS nanoparticles [8]. Here, we describe the first fabrication of hybrid BPS-polymer nanocomposites by UV irradiation. The used polymer is polycaprolactone (PCL) which has been increasingly interest

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in materials science for applying to the drug delivery system, tissue engineering scaffolds, and so on [9-10]. Spherical BPS nanoparticles containing thiol groups (BPS-SH) were reacted with hydroxyethyl methacrylate (HEMA)-initiated PCL (HEMA-PCL) through the photo-induced chemical reaction by UV irradiation. UV irradiation was applied to make BPS covered with PCL by the reaction of thiol groups in BPS-SH and double bond in HEMA-PCL. The incorporation of PCL to BPS with a diameter of 100∼300 nm caused the bumpy surface of BPS as well as the linked BPS to each other because BPS was fully surrounded by PCL. In addition, the melting temperature of HEMA-PCL was disappeared in BPS-PCL due to the effect of BPS covered by PCL. The thermal stability of BPS-PCL was increased as compared to that of HEMA-PCL because of the hybridization between silica-based BPS and PCL through the chemical bonding. BPS-PCL was fully characterized by FT-IR, DSC, TGA, SEM, TEM, EDX. It is unique and interesting method to prepare new BPS-polymer hybrid system by incorporating polymer to BPS through the photo-induced reaction between the reactive bridging groups of BPS and polymer. Various polymers can be introduced to BPS by the chemical or UV reaction between bridging groups of BPS and polymer. To my knowledge, this is first example of hybrid BPS incorporated with polymer by UV irradiation.

Experimental

Materials

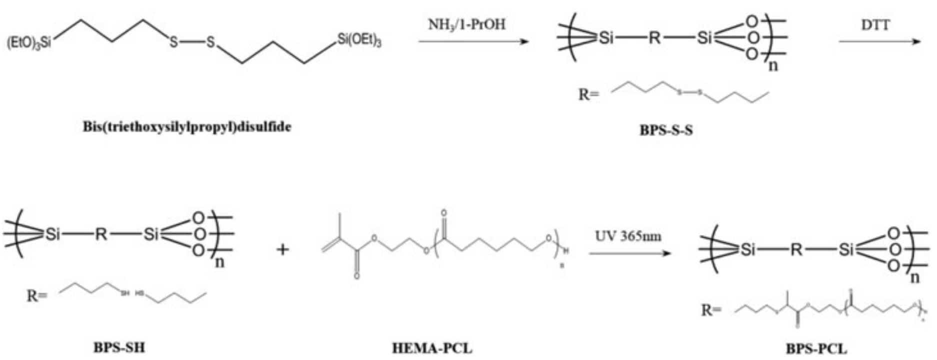
Hydroxyethyl methacrylate (HEMA) and ε-caprolactone were vacuum-distilled and stored under nitrogen prior to use. Stannous octoate ($Sn(Oct)_2$), dithiothreitol (DTT), 2,2-dimethoxy-2-phenylacetophenone, dichloromethane, and 1-propanol was purchased from Aldrich and used as received. Bis(triethoxysilylpropyl)disulfide and ammonia solution were obtained from Gelest and Junsei, respectively and used as received.

Characterization

^{1}H-NMR spectra (400MHz AVANCE 400FT NMR, BRUKER) and FT- IR spectra (Nicolet IR200, THERMO) were used to analyze the structure of BPS-SH, HEMA-PCL, and BPS-PCL. The thermal behavior was examined with DSC (DSC2010, TA Instruments) and TGA (TGA S-1000, SCINCO) under a nitrogen atmosphere. The morphologies and compositions were observed by TEM (Libra 120, Carl Zeiss), SEM (JSM-6700, JEOL), and EDX.

Spherical BPS with Thiol Groups (BPS-SH)

The solution of water (3.4 mL), ammonia solution (18 mL), and 1-propanol (5.6 mL) were heated at 60°C for 30 min. To the solution was added bis(triethoxysilylpropyl)disulfide (1 mL). The solution was vigorously stirred and heated at 60°C for 24 h. After cooling to room temperature, water (1 L) was added to the solution and stirred for 12 h. The solution was filtered and dried under vacuum to obtain BPS-S-S. BPS-S-S was immersed in a dithiothreitol (DTT) solution and the mixture was stirred at room temperature for 12 h to break the disulfide bond into thiol groups. The solution was filtered and dried under vacuum to obtain the BPS-SH [8].



Scheme 1. Synthesis scheme of BPS-PLC by UV irradiation.

HEMA-initiated PCL (HEMA-PCL)

HEMA (0.44 mL), ε-caprolactone(7.76 mL), and $Sn(Oct)_2$ (0.23 mL) were added to a flask with nitrogen gas. The solution was heated at 140°C for 24 h with vigorous stirring. The crude products were dissolved in dichloromethane and precipitated in an excess of methanol. HEMA-PCL was dried in vacuum oven. HEMA-PCL was analyzed by GPC ($M_w = 6{,}800$ g/mol).

Nanocomposites of BPS-S-H and HEMA-PCL (BPS-PCL)

HEMA-PCL and BPS-SH were dissolved in dichloromethane (100 mL). To the solution was added 2,2-dimethoxy-2-phenylacetophenone as a photoradical generator. The clear solution was then irradiated with UV light at a wavelength of 365 nm for 1 h. After UV Irradiation, the mixture was filtered and dried in vacuum oven.

Results and Discussion

The total synthesis routes for BPS-PCL are presented in Scheme 1. The synthesis of BPS-S-S under the base-catalyzed hydrolysis and condensation reaction of bis(triethoxysilylpropyl)disulfide was followed by the reduction reaction of BPS-S-S to prepare BPS-SH using DTT as a reducing agent.

HEMA-PCL was prepared in solution using HEMA as the initiator and $Sn(Oct)_2$ as the catalyst. The peaks of double bond at 6.1 and 5.6 ppm and the new peaks derived from PCL at 3.6, 2.3, 1.6, and 1.2 ppm were observed in ^{1}H-NMR spectrum of HEMA-PCL. UV irradiation was used to incorporate HEMA-PCL into BPS-SH through the chemical reaction between thiol groups in BPS nanoparticles and HEMA groups in HEMA-PCL. Figure 1 shows FT-IR spectra of BPS-SH, HEMA-PCL, and BPS-PCL. The spectrum of BPS-PCL shows Si-O-Si peak at 1100 cm^{-1} and $C = O$ peak at 1730 cm^{-1} which derived from BPS-SH and HEMA-PCL, respectively.

Figure 2 shows SEM images of BPS-SH, HEMA-PCL, and BPS-PCL. The size of BPS particles could be controlled by the monomer concentration, alcohol content, and reaction time. BPS-SH shows the smooth surface of spherical shape with the average size of 100∼300 nm. But, BPS-PCL incorporated with HEMA-PCL through the photo-induced reaction shows rough and uneven surface because BPS is well covered with PCL.

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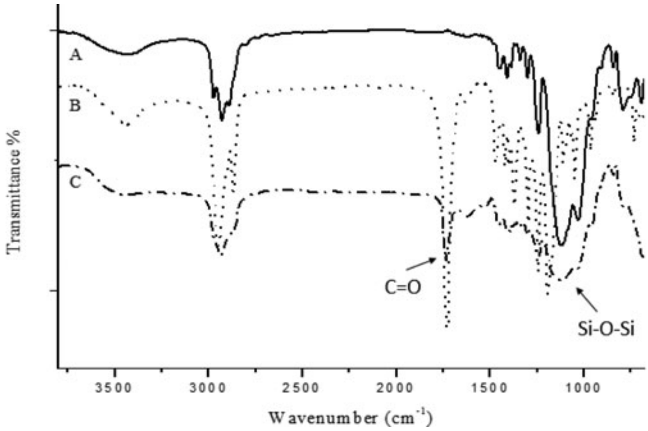

Figure 1. FT-IR spectra of (A) BPS-SH, (B) HEMA-PCL, and (C) BPS-PCL.

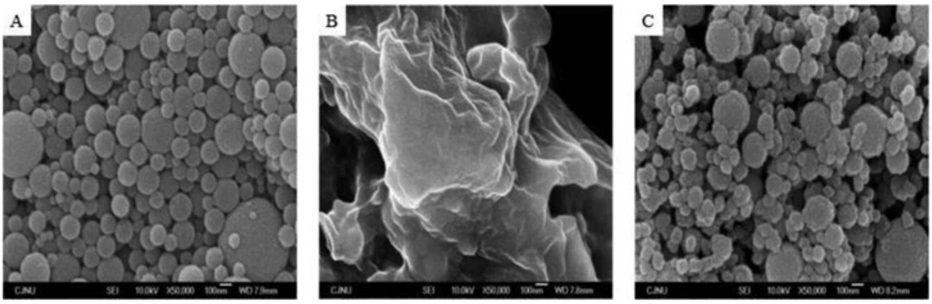

Figure 2. SEM images of (A) BPS-SH, (B) HEMA-PCL, and (C) BPS-PCL.

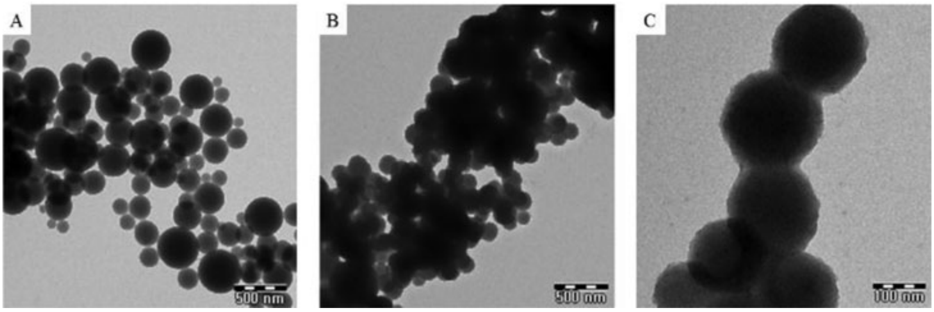

Figure 3. TEM images of (A) BPS-SH, and (B, C) BPS-PCL.

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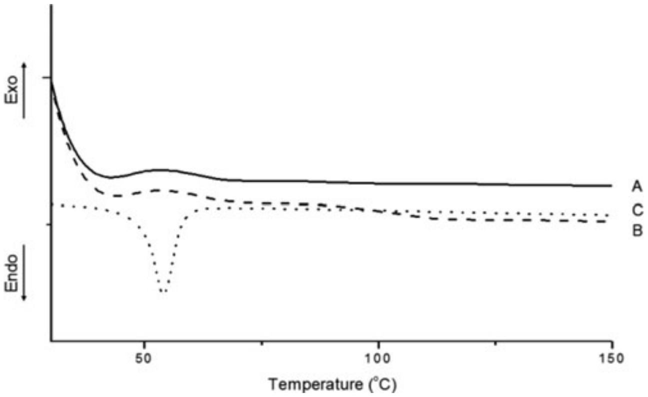

Figure 4. DSC curves of (A) BPS-SH, (B) HEMA-PCL, and (C) BPS-PCL.

This result is more clearly confirmed by TEM images as shown in Figure 3. BPS-PCL shows that BPS nanoparticles are continuously linked together due to the incorporation of PCL into BPS while BPS-SH is separately dispersed.

Figure 4 shows DSC curves of BPS-SH, HEMA-PCL, and BPS-PCL. HEMA-PCL shows melting temperature around 54°C derived from PCL chains. In case of BPS-PCL nanocomposites, melting temperature is totally disappeared due to the rigidity of silica-based BPS-SH. Generally, polymer-silica hybrid nanocomposites present the disappearance or increase of glass transition temperature or melting temperature of polymer due to the silica based inorganic materials [11-12].

The enhanced thermal stability of BPS-PCL as compared to that of HEMA-PCL was confirmed by TGA as shown in Figure 5. HEM-PCL was completely decomposed when the temperature is increased up to 600°C. The residual content of BPS-PCL is larger than that of HEMA-PCL because of silica-based BPS nanoparticles. These results indicate that BPS nanoparticles are successfully covered with PCL by UV irradiation.

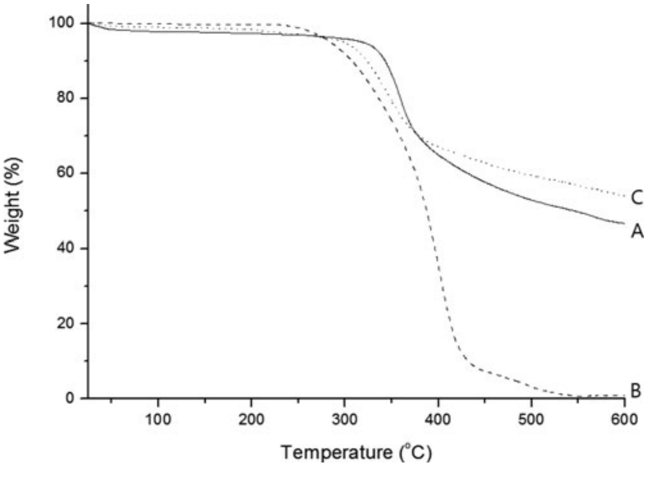

Figure 5. TGA curves of (A) BPS-SH, (B) HEMA-PCL, and (C) BPS-PCL.

Conclusions

Hybrid BPS-PCL nanocomposites were successfully prepared by the photo-induced reaction of BPS-SH and HEMA-PCL through simple UV irradiation. BPS nanoparticles with the average size of 100∼300 nm were well covered with PCL, which resulted in the continuous linkage of BPS nanoparticles together. BPS-PCL showed no melting temperature and enhanced thermal stability due to the effect of the rigid silica-based BPS nanoparticles surrounded by PCL.

Acknowledgments

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