

Synthesis of Amphiphilic Triblock Copolymers for the Formation of Magnesium Fluoride (MgF₂) Nanoparticles

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Received 8 February 2011; accepted 18 January 2012

DOI 10.1002/app.36844

Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A series of amphiphilic poly(2-hydroxyethyl methacrylate)-*b*-polydimethylsiloxane-*b*-poly(2-hydroxyethyl methacrylate) (pHEMA-*b*-PDMS-*b*-pHEMA) (A-B-A) triblock copolymers were synthesized from three different carbinol-terminated polydimethylsiloxanes with varying molecular weight. A carbinol-terminated polydimethylsiloxane was modified with 2-bromoisobutyryl bromide to obtain a macroinitiator. The block copolymers were characterized by NMR, GPC, and dynamic light scattering (DLS). Reverse micelles of a copolymer were formed in mixture of benzene/methanol solution which served as nanoreactors for the synthesis of magnesium fluoride (MgF₂) nanoparticles. The MgF₂ was prepared via chemical precipitation using magnesium chloride and potassium fluoride as reactants. The MgF₂-triblock copolymer composites were

synthesized as a function of MgF₂-weight ratio (0.5, 5, and 10 wt%) in copolymer. The MgF₂ colloids were dissolved in three organic solvents: methanol, *isopropanol*, and tetrahydrofuran. The polymer nanoparticles were characterized by DLS, transmission electron microscopy, thermogravimetric analysis, and X-ray diffraction (XRD) analysis. The formation of MgF₂ crystals was observed by XRD. Particle size and particle size distribution showed significant changes in different solvents. The thermal stability of MgF₂ colloids increased as the amount of nanoparticle increased in polymeric matrix. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: block copolymers; inorganic materials; nanoparticle; polysiloxanes; micelles

INTRODUCTION

Polymer nanoparticle composites have wide usages in coatings, sealants, drug delivery vesicles, damping applications, catalysts, optoelectronic, and magnetic devices.^{1,2} Nanoscale morphology of polymer nanoparticle composites allows one to tune several physical properties due to the high surface area of nanoparticles. Nanoparticles in the polymer matrix can enhance mechanical strength, catalytic activity, optical, and magnetic properties.³ The physical properties of polymer nanoparticle composites depend on several parameters such as size and type of nanoparticle, polymer structure, and compatibility between phases.^{4,5}

Polymer nanoparticle composites can be prepared by several methods including dispersion,^{6,7} immersion,^{8,9} and deposition.^{10,11} In the dispersion route, the metal precursors are mixed with a polymeric stabilizer, and then the metal precursors are reduced into metal nanoparticles. In the immersion route, a polymeric template is immersed in an inorganic precursor. After swelling polymer matrix with an inorganic precursor, the precursor is reacted into

inorganic nanoparticles. The deposition route uses a mixture of inorganic precursors and polymer matrix which is deposited onto a substrate. Reduction of the inorganic precursor into metal nanoparticles occurs after solvent evaporation by either thermal or photochemical decomposition.

Amphiphilic block copolymers were frequently used to synthesize nanoparticles.^{12,13} Stabilization of nanoparticles by amphiphilic copolymers can be based on electrostatic or steric stabilization. The electrostatic stabilization is provided by Columbic repulsions.^{4,14} In solvents, amphiphilic copolymers can undergo self-assembly where insoluble block forms a core and soluble block forms a corona.¹⁵ As a result, these copolymers can be used as nanoreactors for precipitation of inorganic nanoparticles.¹⁶ Since inorganic nanoparticles are typically polar, the nanoparticles are stabilized in reverse micelles.¹⁷ Many authors reported synthesis of metal nanoparticles with amphiphilic copolymers as stabilizers. Zinc sulfide nanoparticles were synthesized in poly(4-vinylpyridine)-polystyrene-poly(4-vinylpyridine) triblock copolymers by chemical precipitation.¹⁸ Poly(dimethylsiloxane-*b*-(3-cyanopropylmethyl-siloxane-*b*-dimethylsiloxane) was used to synthesize cobalt nanoparticles in toluene.¹⁹ Gold nanoparticles were synthesized in the presence of poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) surfactant.²⁰

Magnesium fluoride (MgF₂) has unique optical properties with a high transparency from 132 nm to

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3 μm due to a high energy gap. MgF_2 can be employed as antireflective coatings due to these superior properties.²¹ MgF_2 exhibits high scratch, weather resistance, and high thermal stability. MgF_2 is highly birefringent and positive uniaxial crystal with tetragonal unit cells. MgF_2 has the lowest refractive index (1.38) among inorganic crystals.²² An easy preparation procedure of MgF_2 dispersion was previously reported by reacting NaF and MgCl_2 .²³ MgF_2 was used in several applications such as infrared windows, multilayer displays, radiation resistant highly reflective coatings, antireflective coating for aluminum films.²² Additionally, the MgF_2 was used as support for several kinds of catalysts for decomposition of nitrogen oxide,²⁴ hydrodechlorination of chlorofluorocarbons (CFC),²⁵ and hydrodesulphurization of thiophene.²⁶

In this article, amphiphilic pHEMA-PDMS-pHEMA triblock copolymers were prepared. After which, MgF_2 nanoparticles were synthesized and stabilized within the amphiphilic block copolymer. Reverse micelles of copolymers were formed in mixture of benzene and methanol. The MgF_2 nanoparticles were precipitated from methanolic magnesium chloride and potassium fluoride. Polymer stabilized nanoparticles were dispersed in methanol, tetrahydrofuran, isopropanol. The particle size, distribution, and morphology were analyzed by dynamic light scattering (DLS) and transmission electron microscopy (TEM). The thermal stability of triblock copolymers and MgF_2 -triblock copolymer composites was conducted by thermogravimetric analysis (TGA).

EXPERIMENTAL

Materials

Carbinol-terminated PDMS (DMS-C15, $M_n \sim 1400$ g/mol, DMS-C21, $M_n \sim 3700$ g/mol, and DMS-C23, $M_n \sim 7800$ g/mol) was obtained from Gelest. 2-hydroxyethyl methacrylate (HEMA) was obtained from Aldrich and purified as reported.²⁷ 2-hydroxyethyl methacrylate (HEMA) was passed through the neutral silica column eluted with 30/70 benzene/ethyl acetate solvent mixture followed by vacuum distillation. Silica gel (200 mesh), copper (I) chloride, 2-bromoisobutyl bromide, bipyridine, methyl ethyl ketone (MEK), 1-propanol, tetrahydrofuran, isopropanol, methanol, benzene, ethyl acetate, potassium fluoride and magnesium chloride were purchased from Aldrich. Reagents were used as received without a further purification. Copper TEM grids coated with Formvar and carbon were purchased from Ted Pella.

Instruments

Nuclear magnetic resonance (NMR) of samples was taken in CDCl_3 and/or CD_3OD solvent in Varian

Mercury 300. The dynamic light scattering was obtained from a Brookhaven Instruments BI-200SM system equipped with He-Ne laser operated at 632.8 nm with 1 mm entrance aperture. TGA was performed on TA Instruments, High Res TGA 2950. Atomic force microscopy (AFM) images were obtained from a Veeco (Digital Instruments) A Bruker AXS X-ray generator equipped with a two dimensional wire detector was operated at 40 kV and 40 mA and the collimated X-ray beam was monochromatized to $\text{CuK}\alpha$ radiation from 5 to 35° (2θ angle) was used to obtain WAXD data. The TEM pictographs were obtained from a Philips Tacnai-12 model with a combination of high-resolution imaging scanning was equipped with 120 kV illumination system, maximum magnification of 500 K, and maximum resolution of <1 nm.

Synthesis of PDMS macroinitiator

Carbinol-terminated PDMS was modified with 2-bromoisobutyl bromide (BrBBBr) to obtain macroinitiator. The PDMS, (7.12 mmol) was first dissolved in 300 mL of dichloromethane placed in a one-neck flask. Then, triethylamine (42.9 mmol) was added into it. The flask was placed into an ice-bath and cooled to 0°C. 2-bromoisobutyl bromide (42.9 mmol) was added drop wise through a dropping funnel into the flask in an inert atmosphere. The mixture was stirred for 16 h. Then, the dichloromethane was removed *in vacuo* and excess methanol was added to remove triethylamine bromide salt (by-product of esterification of carbinol-terminated PDMS and BrBBBr). The product was washed in methanol (3×150 mL) to remove any residual salt. The methanol remaining in the macroinitiator solution was removed *in vacuo* at room temperature.

Synthesis of pHEMA-PDMS-pHEMA (ABA) triblock copolymer

The macroinitiator (1.85 g, 0.5 mmol) was charged with a MEK/1-propanol (70/30 v/v) solvent mixture into a 100-mL flask. Bipyridine (bpy) (0.156 g/1 mmol) was added into the solution, and the mixture was purged with nitrogen gas for 15 min. HEMA monomer (9.65 g, 75 mmol) and copper (I) chloride (0.0495 g, 0.5 mmol) were charged into the vessel with additional solvent (10 g of 70/30 v/v). The mol ratio of the components was HEMA/macroinitiator/ CuCl/bpy : 150/1/1/2. The flask was sealed with a rubber septum and the reaction was heated to 60°C and held constant for 24 h. The reaction was quenched by exposing the solution to air and diluting with the solvent mixture (70/30 v/v). The mixture was eluted from silica column using the 70/30 solvent mixture to remove the catalyst. The

solvents were removed under vacuum and then polymer was precipitated in *n*-hexane (150 mL). The precipitation sequence was repeated for three times to remove the unreacted HEMA monomer. The theoretical number average molecular weight (M_n) of pHEMA block was changed by varying mole ratio of HEMA/macromonomer to synthesize series of triblock copolymers with the following²⁸: ¹H-NMR (CDCl₃, CD₃OD): δ 0.15 (Si-CH₃), 1.24 (CH₂-C(-CH₃)-C(=O)-CO), 1.56 (C(=O)-CH₂-CH₂-CH₃-, carbinol) 1.97 (-CH₂-C(-CH₃-), 3.85 (CH₂-CH₂-OH), 4.13 (CO-CH₂-CH₂-OH), 4.91 (CH₂-CH₂-OH).

Synthesis and stabilization of MgF₂ colloids

The pHEMA-PDMS-pHEMA (0.06 g) copolymer with theoretical molecular weight 10 K-4 K-10 K g/mol was dispersed in 3 g of a benzene/methanol (80/20 v/v) mixture. After 24 h of stirring, a methanolic solution of MgCl₂ (0.5 mL, 0.01M) was added into polymer dispersion and resultant mixture was stirred for another 7 days at room temperature. Finally, a methanolic KF (0.5 mL, 0.02M) was added into this solution and the reactants were mixed for 3 days at room temperature. This resulted in a 0.5 wt% dispersion. The polymer-nanoparticle composites of 5 wt% (pHEMA-PDMS-pHEMA, 0.60 g; MgCl₂, 5.0 mL; KF 5.0 mL) and 10 wt% MgF₂ (pHEMA-PDMS-pHEMA, 1.20 g; MgCl₂, 10.0 mL; KF 10.0 mL) colloids were synthesized using the same method. Benzene/methanol mixture was evaporated at room temperature. The mixture was dispersed into deionized water at 80°C for 3 h. After cooling to room temperature, the solution was centrifuged for 10 min. The potassium chloride, by-product, in supernatant was removed. The process was repeated three times. For characterization the MgF₂ nanoparticles were dispersed in organic solvents.

Sample preparation for characterization

The NMR experiments to derive M_n (H97S3, H92S8, H96S4) were carried out by dissolving the block copolymers in *d*-methanol (CD₃OD) for the copolymers with the smaller PDMS blocks and a solvent mixture of *d*-chloroform and *d*-methanol (1/1 w/w) for the copolymers with larger PDMS blocks (H67S33 and H56S44). Before addition of catalyst, an aliquot of polymerization mixture was taken and dissolved in CDCl₃. A NMR of this aliquot was taken and compared to the polymers after beginning of reaction by using the ratio of the resonance intensity at $\delta \sim 5-6$ ppm (double bond, HC=, from HEMA) and $\delta \sim 0$ ppm (-CH₃ from PDMS). This ratio decreased as the conversion increased. From the comparison of intensity ratio of the above-

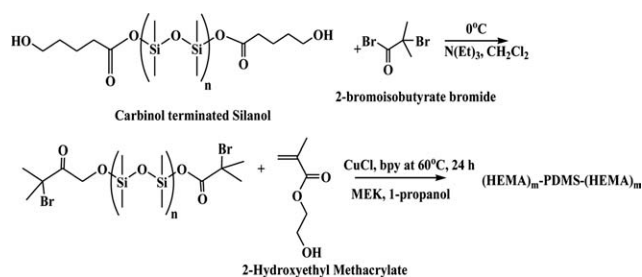
mentioned resonances at the initial time and throughout the reaction, monomer conversion was calculated. Number average molecular weight (M_n) of pHEMA was calculated after purification of aliquots from unreacted HEMA. Integration ratio of the peak resonances at $\delta \sim 0$ ppm (6 H, -CH₃ from PDMS) and $\delta \sim 4.2$ ppm (2H, -COOCH₂, from HEMA) was used to determine M_n of pHEMA. This ratio was multiplied by M_n of PDMS. Block copolymer molecular weight was determined by adding the M_n of PDMS and pHEMA. The number-average molecular weight (M_n) and polydispersity index (PDI) of pHEMA-PDMS-pHEMA copolymer were characterized by gel permeation chromatography. The triblock copolymer was diluted in THF for GPC analysis. Molecular weights and molecular weight distributions were measured according to polystyrene standards in high-resolution Waters columns with THF flow rate at 1 mL/min.

The AFMs were obtained in multimode at scan rate (10 μ m/s) under ambient conditions. Samples were diluted to 0.2 wt% in methanol and spin-cast on glass substrate at 3000 rpm for 15 s. with 10°C/min heating rate. Neat amphiphilic triblock copolymer and MgF₂ colloids were dried at vacuum oven at room temperature for 24 h. Wide angle X-ray (WAXD) technique was used to determine the structure of MgF₂ colloids stabilized in amphiphilic triblock copolymers.

Particle size and particle size distribution were characterized by DLS and TEM. The MgF₂-copolymer composites were diluted to 0.1 wt% in methanol, THF, and *isopropanol*. All solutions were filtered with a teflon membrane (0.45 μ m) before analysis. Scattering measurements were carried out at 25°C and 90° angle. The TEM samples were diluted to 0.1 wt% and dropped onto copper TEM grids. Samples were stained with 1 wt% aqueous sodium phosphotungstate and dried at room temperature.

RESULTS AND DISCUSSION

Well-controlled organic/inorganic (acrylic/polydimethylsiloxane) hybrid copolymers were synthesized by ATRP as block or graft-copolymers with varying compositions to determine structure/property relationship for different applications such as impact-resistant materials, thermoplastic elastomers, compatibilizers, emulsifiers, membranes, drug-delivery systems, and biosensors.²⁹⁻³¹ In this study, a series of amphiphilic copolymers of HEMA and PDMS were prepared by ATRP. Out of the series, one (H80S20) was chosen as stabilizer for proof of concept to prepare MgF₂ nanoparticles. It was anticipated that the reverse micelles of the copolymer could function as nanoreactors for precipitation reactions. The stability



Scheme 1 Synthesis conditions of macroinitiator and amphiphilic triblock copolymers.

of reverse micelle and solubility of the reactants were taken into account in the choice of protic and aprotic polar solvents for this study.

Synthesis of pHEMA-PDMS-pHEMA (ABA) triblock copolymer

The synthetic route of triblock copolymers with PDMS (middle block) and pHEMA is outlined in Scheme 1. The block copolymerizations were carried out in a mixture of methyl ethyl ketone and propanol using a PDMS macroinitiator. The solvent mixture was needed to ensure solubility of both the pHEMA and PDMS blocks and resulting copolymers. Nine ABA copolymers were prepared with block size varying from M_n 5,000–15,000 g/mol for the A (pHEMA), and M_n 1,400–8,000 g/mol for the B block (PDMS). The copolymers were characterized by GPC and NMR.

Table I shows the molecular weights and molecular weight distributions of series of pHEMA-*b*-PDMS-*b*-pHEMA triblock copolymers. From the Table I it is clear that there is some evidence of a controlled polymerization. Although there were some differences in molecular determination between the three techniques, this was due to the differences in the hydrodynamic volume of pHEMA and the standard polystyrene.³² Polydispersity indexes (PDI) were high due to broad PDI of the PDMS series used as macroinitiators. The GPCs of PDMS macroinitiator and

pHEMA-*b*-PDMS-pHEMA block copolymers were all unimodal and there was an increase of molecular weight from macroinitiator to block copolymer. The unimodal polymers suggest the living polymerization of HEMA with the PDMS-based macroinitiator.

The kinetic data for the formation of amphiphilic triblock copolymers with three different macroinitiators (M_n 1.4 K, 4 K, 8 K g/mol) were obtained by using NMR. In each case, pHEMA blocks with theoretical number-average molecular weight ($M_n \sim 10$ K g/mol) were grown on three different macroinitiators. The kinetic plots of pHEMA-PDMS-pHEMA are shown in Figure 1. Linear reaction kinetics was observed implying first-order ATRP kinetics.³³ Linear plots were also consistent with a constant number of growing species during polymerization. Macroinitiator with the highest molecular weight (M_n 8 K g/mol) showed the most rapid polymerization whereas other two macroinitiators had almost same reaction rate. All reaction plots indicated behavior consistent with a controlled polymerization. The number average molecular weight and polydispersity index as a function of conversion % for varying macroinitiators were shown in Figure 2. Number-average molecular weight of amphiphilic triblock copolymers increased linearly with conversion (%) and polydispersities decreased from ~ 2 at low conversions to ~ 1.5 at high conversions indicating controlled nature of polymerization.

Nuclear magnetic resonance (NMR) spectroscopy was used to characterize, determine percent conversion as a function of time, and calculate the number average molecular weight (M_n). Overall conversion was around 80% within 1 h. All the block copolymers are dispersible in a mixture of organic and aqueous-organic solvents. In methanol and methanol-water mixtures, block copolymers containing PDMS of $M_n > 3000$ g/mol forms micelles with PDMS core and pHEMA shell. The formation of micelles was determined by the use of NMR spectroscopy. Figure 3 shows the NMR spectra of pHEMA-*b*-PDMS-pHEMA in a pHEMA block selective

TABLE I
Molecular Weight and Molecular Weight Distribution of a Series of Block Copolymers Synthesized by ATRP

	Theoretical M_n	M_n of PDMS	PDI of PDMS	pHEMA/PDMS	M_n (GPC)	M_n (NMR)	M_w/M_n
H80S20 ^a	10K-4K-10K	3,700	1.92	80.0/20.0	19,300	19,700	1.51
H67S33	5K-4K-5K	3,700	1.92	66.7/33.3	13,400	9,300	1.31
H86S14	15K-4K-15K	3,700	1.92	85.6/14.4	35,100	28,900	1.53
H71S29	10K-8K-10K	7,800	2.03	71.4/28.6	27,500	25,300	1.55
H56S44	5K-8K-5K	7,800	2.03	55.6/44.4	21,400	16,400	1.57
H79S21	15K-8K-15K	7,800	2.03	78.9/21.1	41,600	34,600	1.51
H97S3	15K-1.4K-15K	1,400	1.25	97.2/2.8	34,300	22,500	1.46
H92S8	5K-1.4K-5K	1,400	1.25	91.7/8.3	21,200	12,500	1.50
H96S4	10K-1.4K-10K	1,400	1.25	95.7/4.3	31,600	20,500	1.48

^aH, pHEMA; 80, wt % of pHEMA in triblock copolymer; S, PDMS; 20, wt % of PDMS in triblock copolymer.

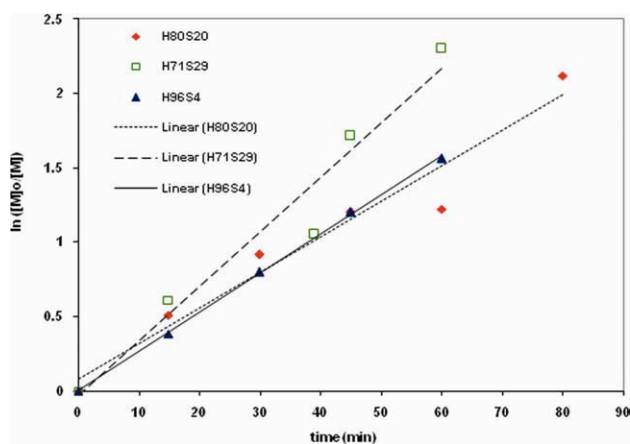


Figure 1 Polymerization kinetic plots of ATRP of pHEMA-PDMS-pHEMA triblock copolymers with varying macroinitiators for M_n , 1.4 K, 4 K, 8 K g/mol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(d-methanol) and a non-selective (mixture of d-chloroform and d-methanol, 1/1 w/w) solvent, respectively. The polymer sample was dissolved in (1 : 1 w/w) CD_3OD and $CDCl_3$ solvent mixture. The intensity ratio of $-CH_3$ moiety from PDMS and $-OCH_2$ moiety from HEMA were used to determine the formation of micelles in a selective solvent. A decrease of $-CH_3/-OCH_2$ intensity ratio from 0.8 to 0.15 was observed when the mixture of solvent (mixture of d-chloroform and d-methanol, 1/1 w/w) was changed to neat methanol. The decrease of intensity of $-CH_3$ relative to $-OCH_2$ suggest aggregation of PDMS part in methanol forming core-shell type of aggregations (micelles). An interesting behavior of the pHEMA-b-PDMS-pHEMA copolymer is the formation of reverse micelles in a PDMS selective solvent such as mixture of d-chloroform and d-meth-

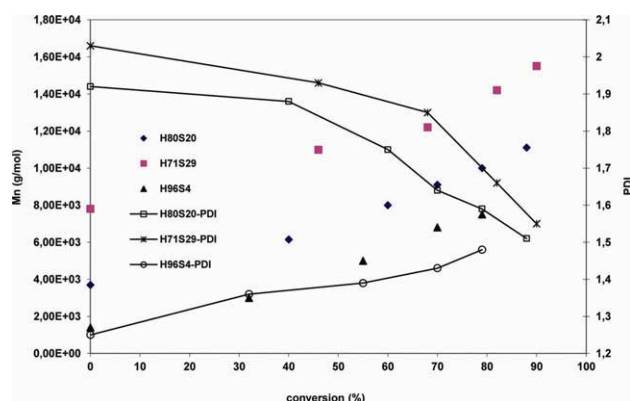


Figure 2 Number average molecular weight (M_n) and polydispersity index (PDI) for three different molecular weight macroinitiator with M_n , 1.4 K, 4 K, 8 K g/mol as a function of conversion %.[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

anol, 4/1 w/w in which pHEMA block was not soluble. Figure 3(c) shows the NMR spectra of the block copolymer in d-chloroform and d-methanol, 4/1 w/w. In this mixture of solvent, the CH_3/OCH_2 intensity ratio increases from 0.8 to 0.9 suggesting formation of reverse micelle with pHEMA as the core and PDMS shell.

The particle size and particle size distribution of copolymer micelles and reverse micelles were obtained and are shown in Table II. The particle size distribution and average size of assemblies were obtained in THF, methanol, and a methanol/water mixture. Scheme 2 shows a depiction of micelles and reverse micelles in methanol and THF. In methanol, the PDMS blocks aggregate in the core and the hydrophilic pHEMA blocks form the shell. With the

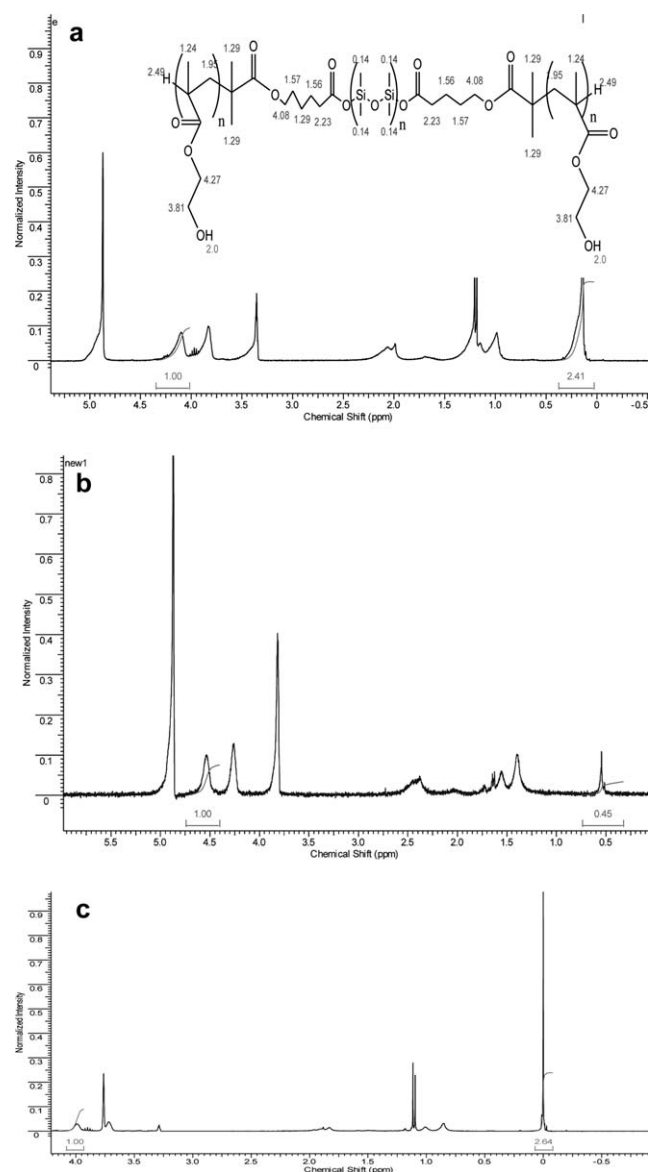


Figure 3 NMR spectra of H67S33 in (a) 1/1: methanol/chloroform, (b) excess methanol, (c) excess chloroform.

TABLE II
Particle Sizes (Mean Diameters Shown) in Methanol, THF, and Methanol/Water Mixture Obtained by DLS

Sample Name	Molecular Weight	PSD in THF (nm)	THF (nm)	PSD in Methanol (nm)	Methanol (nm)	PSD in Methanol/Water (95/5) (nm)	Methanol/Water (95/5) (nm)
H80S20	10K-4K-10K	1.3 ± 0.1	29.8 ± 2.0	1.3 ± 0.4	38.4 ± 2.8	1.2 ± 0.1	44.9 ± 5.3
		17.8 ± 0.3		17.8 ± 0.6		45.9 ± 0.7	
		85.7 ± 0.8		316.2 ± 1.2			
H67S33	5K-4K-5K	1.2 ± 0.2	14.3 ± 6.3	1.3 ± 0.3	26.1 ± 3.1	1.3 ± 0.2	36.3 ± 3.8
		26.7 ± 0.7		17.8 ± 0.9		54.8 ± 2.5	
		183.8 ± 1.5		421.7 ± 1.8			
H86S14	15K-4K-15K	1.2 ± 0.2	35.2 ± 5.8	1.2 ± 0.2	56.4 ± 4.0	1.2 ± 0.1	67.2 ± 5.6
		49.2 ± 0.6		15.8 ± 0.4		70.0 ± 1.6	
				76.6 ± 1.2			
H71S29	10K-8K-10K	48.1 ± 0.6	33.7 ± 5.9	1.1 ± 0.1	53.6 ± 2.6	54.2 ± 0.2	74.8 ± 4.0
		368.1 ± 1.5		25.7 ± 1.8			
H56S44	5K-8K-5K	1.2 ± 0.2	20.7 ± 5.8	1.6 ± 0.2	40.2 ± 3.9	29.7 ± 1.5	59.3 ± 5.7
		13.2 ± 1.1		44.2 ± 1.6		82.8 ± 3.5	
		133.3 ± 1.6					
H79S21	15K-8K-15K	41.6 ± 1.2	39.5 ± 4.2	2.1 ± 0.1	69.3 ± 6.9	9.2	86.1 ± 5.7
				71.9 ± 1.5		69.7 ± 1.7	
						183.2 ± 0.6	
H97S3	15K-1.4K-15K	1.2 ± 0.2	22.6 ± 4.4	1.3 ± 0.3	33.6 ± 2.8	1.2 ± 0.5	39.0 ± 2.8
		83.3 ± 1.8		13.3 ± 1.5		9.8 ± 0.7	
		227.8 ± 2.1		133.3 ± 2.4		36.0 ± 0.8	
H92S8	5K-1.4K-5K	1.42 ± 0.2	10.4 ± 5.6	1.3 ± 0.2	15.6 ± 2.7	1.2 ± 0.6	24.1 ± 4.8
		134.1 ± 1.4		13.3 ± 1.3		16.9 ± 0.4	
				316.2 ± 3.3		143.1 ± 2.3	
H96S4	10K-1.4K-10K	1.3 ± 0.1	31.4 ± 5.6	1.2 ± 0.2	45.4 ± 9.2	14.6 ± 1.4	60.2 ± 5.1
		237.1 ± 1.3		17.6 ± 1.9		178.7 ± 1.5	
				204.7 ± 2.2			

addition of water, i.e., increase of polarity of solvent, larger micelles are formed especially with increasing PDMS content. For THF, a reverse micelle is expected since the pHEMA block is not soluble in THF.

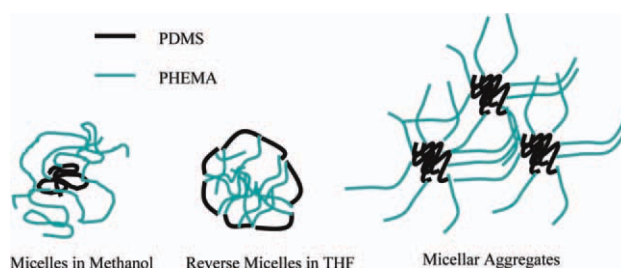
The block copolymer samples that had less PDMS content, i.e., H97S3, H92S8, and H96S4 yielded smaller micelles and micellar aggregates than H80S20, H67S33, and H86S14 in methanol because of low ratio of hydrophobic/hydrophilic content. When the hydrophobic block length is fixed, increasing the hydrophilic block results in a larger micellar diameter. Consequently, the micellar diameter of H80S33, H67S20, and H86S14 (molecular weight of hydrophobic block is 4 K) with the number-average molecular weight of hydrophilic block is 5, 10, and 15 K g/mol were 14, 29.8, and 35 nm, respectively. Similarly, when unilaterally increasing the molecular weight of hydrophobic block (H92S8, H67S33, and H56S44) in series 1.4 K, 4 K, and 8 K g/mol, the micellar diameter was 10.4, 14.3, and 20.7 nm, respectively. Proportional behavior of the block molecular weight with micellar diameter was also observed for the other micelles including the reverse micelles in THF.

It has been previously reported that the critical micelle concentration (CMC) of amphiphilic copolymers are dependent on the ratio of hydrophobic/

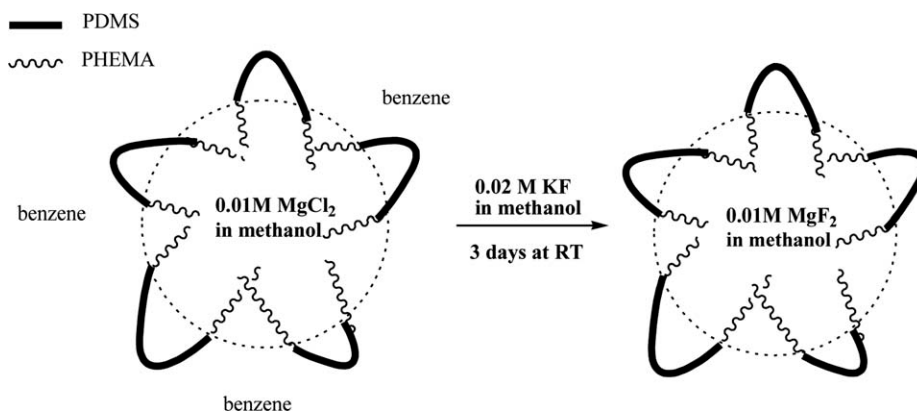
hydrophilic content.³⁴ This can also affect also the micelle size and degree of aggregation. The addition of water into methanol increased the polarity of the medium pushing the aggregation of the PDMS blocks at a lower concentration of amphiphilic triblock copolymer than without the water. For H86S14, this resulted in an increase in micelles diameter from 56 nm in methanol to 67.2 nm in a methanol–water medium.

Precipitation and stabilization of MgF₂ nanoparticles

The amphiphilic triblock copolymer (H80S20) was chosen for a nanoreactor on account of its median



Scheme 2 Possible assemblies formed in organic solvents. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]



Scheme 3 Schematic representation for the synthesis of the MgF_2 colloid in the core of reverse micelles.

size and amenability to the various solvents used in the synthesis. The synthesis of MgF_2 nanoparticles included two steps. First of all, methanolic magnesium chloride was stabilized in reverse micelles of H80S20 at room temperature. This was followed by drop-wise addition of methanolic solution of potassium fluoride. The preparation of the MgF_2 colloids is shown in Scheme 3.

Wide angle x-ray diffraction analysis

The X-ray analysis for thin films of the amphiphilic triblock copolymer and MgF_2 colloids with varying weight percentage is shown in Figure 4. The MgF_2 crystals without the triblock copolymer were also synthesized from same stock solutions used for the synthesis of the stabilized MgF_2 colloids. A strong peak at 27.3° (2θ) was attributed to the 110 reflection of randomly oriented MgF_2 .²¹ This peak was also obtained in the 5 and 10 wt% colloids stabilized in triblock copolymers. On the other hand, the 110 reflection peak was not observed for the 0.5 wt% MgF_2 . This was probably due to concentration limits of the instrument. A broad peak was observed at 12.5° for triblock copolymer due to presence of amorphous PDMS. This broad peak slightly shifted to lower 2θ angle as concentration of MgF_2 increased.

AFM analysis

The film morphology of micelle films and micelle stabilized nanoparticle (MgF_2) composite were investigated by AFM. The AFM images of amphiphilic triblock copolymers and MgF_2 colloids with triblock copolymer stabilizers are shown in Figures 5 and 6. No phase separation was observed for the triblock copolymer film since long pHEMA blocks resulted in chain entanglements and the formation of disordered sphere morphology. MgF_2 colloids with 100 nm diameter were observed. MgF_2 colloids were

organized as loosely packed arrays indicating well-dispersed reverse micelles.

DLS and TEM analysis

Table III shows the particle size and particle size distribution (PSD) of amphiphilic triblock copolymers and copolymer stabilized MgF_2 colloids. The MgF_2 colloids were dispersed in organic solvents such as methanol, THF, and *isopropanol*. The multimodal particle size distribution was observed when THF and *isopropanol* were used which implied poor dispersion. However, a narrower particle size distribution was observed for MgF_2 colloids when dispersed in methanol indicating that the reagglomeration of the colloid was prevented.³⁵

Figures 7–9 show TEM micrographs which show a comparison of triblock copolymers with and without a MgF_2 core cast from methanol, THF, and *isopropanol*. A higher contrast was observed in the TEM micrograph of MgF_2 colloids stabilized with triblock copolymer relative to the amphiphilic triblock

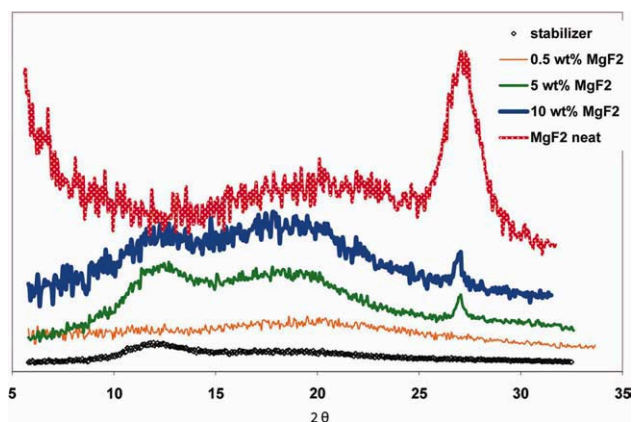


Figure 4 Representation of the XRD pattern for neat triblock copolymer (H80S20) and MgF_2 colloids with varying weight %, 0.5, 5, and 10 wt% in stabilizer (neat triblock copolymer). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.interscience.wiley.com).]

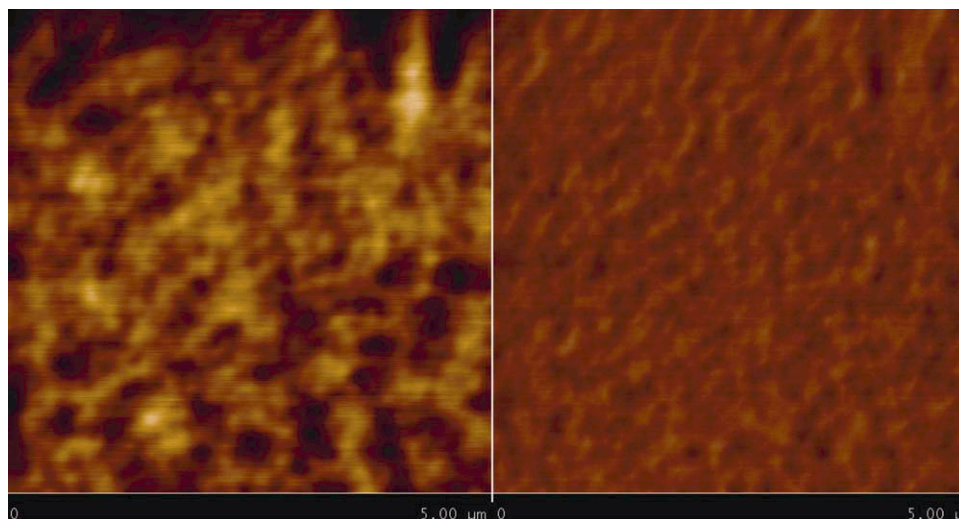


Figure 5 Tapping mode AFM profile of pHEMA-PDMS-pHEMA triblock copolymer (H80S20) cast from methanol, (a) height image, (b) phase image. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

copolymer. The increase in the contrast of MgF_2 colloids could be attributed to metal salt core. Additionally, the particle size of triblock copolymer was observed to increase after the anion metathesis reaction occurred between MgCl_2 and KF.

TGA analysis

TGA of amphiphilic triblock copolymer and MgF_2 colloids with varying weight percentage in copolymer is shown in Figure 10. As expected, the stabilized MgF_2 colloids had better thermal stability than the triblock polymer alone. The decomposition of amphiphilic triblock copolymer started at 290°C with and without the metal salt core. The polymer-

nanoparticle composites with 0.5 wt% MgF_2 had a thermal decomposition at 335°C , whereas the decomposition of 10 wt% MgF_2 colloid was slightly higher at 370°C . It is presumed that the PDMS block decomposed at 530°C as observed most predominately in triblock copolymer without the metal salt core (stabilizer). The triblock copolymer and copolymer with 0.5 wt% MgF_2 colloids were fully decomposed by 650°C . A residue of 15 and 20 wt% remained up to 700°C for the 5 and 10 wt% MgF_2 colloids, respectively. Only the 10 wt% MgF_2 colloid showed a single-step decomposition. In addition, the entire thermogram and hence the decomposition temperature was shifted 50°C higher. This showed some beneficial interaction

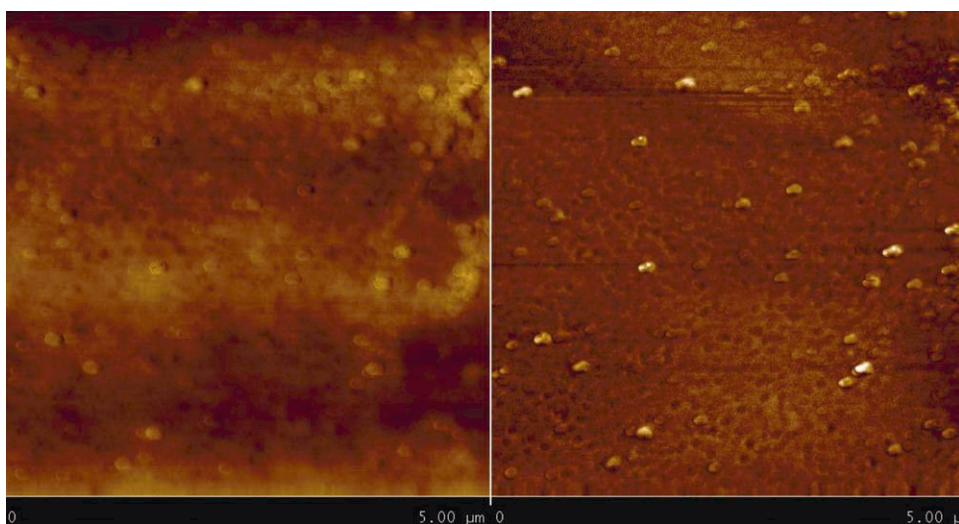


Figure 6 Tapping mode AFM profile of 0.5 wt% MgF_2 colloids stabilized in pHEMA-PDMS-pHEMA triblock copolymer (H80S20) cast from methanol, (a) height image, (b) phase image. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Hydrodynamic Diameter of Neat Amphiphilic Triblock Copolymers and MgF₂ Colloids with Varying Ratio, 0.5, 5, 10 wt % in Triblock Copolymer

Solvent	0.5 wt% MgF ₂ Colloid size by DLS	5 wt% MgF ₂ Colloid size by DLS	10 wt% MgF ₂ Colloid size by DLS
Methanol	36.5 ± 4.6	1.7 ± 0.3 41.7 ± 4.2	3.3 ± 0.1 54.0 ± 5.9
THF	1.4 ± 0.2	1.3 ± 0.2	1.2 ± 0.2
	16.2 ± 2.1	19.1 ± 2.1	5.2 ± 1.7
	79.1 ± 7.8	26.9 ± 3.9	26.9 ± 3.9
Isopropanol	241.2 ± 15.7	53.7 ± 5.8	100.6 ± 14.1
	1.4 ± 0.3	1.3 ± 0.1	1.2 ± 0.1
	33.6 ± 3.4	50.1 ± 5.1	10.2 ± 1.4
MEK	269.8 ± 16.1	105.4 ± 13.4	
0.5 wt% MgCl ₂ in methanol		Not soluble 12.7 ± 2.5 121.9 ± 13.9	

between the metal salt and the triblock copolymer at a 10 wt% ratio.

Stable MgF₂ nanoparticles in the dispersion of pHEMA-PDMS-pHEMA copolymers were successfully synthesized. Reaction between methanolic magnesium chloride and potassium fluoride was expected to occur in reverse micelles of amphiphilic triblock copolymers. The formation of MgF₂ crystals was confirmed by using X-ray diffraction (XRD). A broad peak was observed at 27.3° belong to (110) reflection. This was anticipated due to small crystal size of MgF₂.¹⁸ Rutnakornpituk et al. showed that particle size increased as the concentration of Co₂(CO)₈ increased in the dispersion of triblock

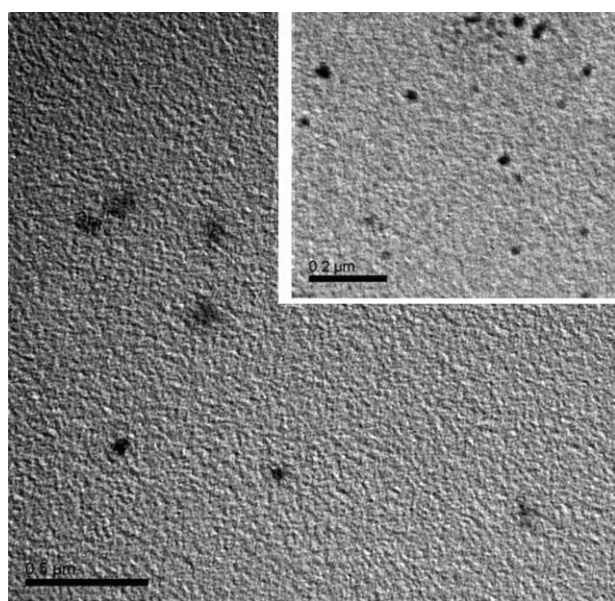


Figure 7 TEM micrograph of 0.5 wt% MgF₂ colloids stabilized in methanol by triblock copolymer (H80S20), inset: triblock copolymer dissolved in methanol without metal salt.

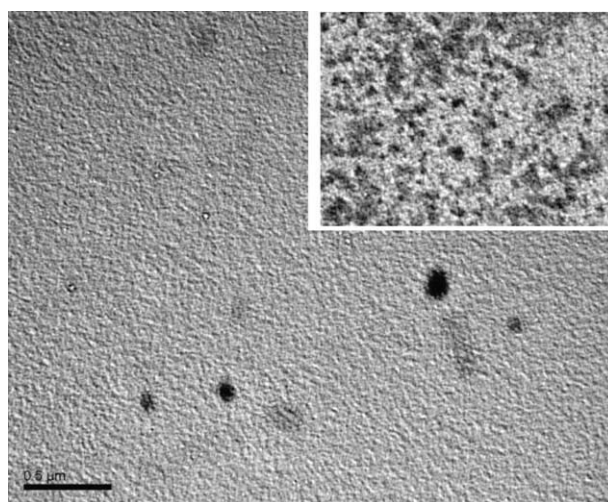


Figure 8 TEM micrograph of 0.5 wt% MgF₂ colloids stabilized in THF by triblock copolymer (H80S20), inset: triblock copolymer dissolved in THF without metal salt.

copolymers.¹⁹ Similarly, as the concentration of methanolic MgCl₂ (0.5, 5, 10 wt%) increased in the reverse micelles, the particle size of MgF₂ colloids dissolved in methanol increased. However, no correlation was found between the particle size of MgF₂ colloids and the concentration of methanolic MgCl₂. Guo et al. attributed this observation to solvent-responsive behavior of block copolymer stabilizers in different organic solvents due to Flory-Huggins interaction parameters between stabilizers and organic solvents.¹⁷

The synthesis of MgF₂ through chemical precipitation in reverse micelles has not been previously reported. The amphiphilic triblock polymers in this study were relatively inexpensive, insulating, and

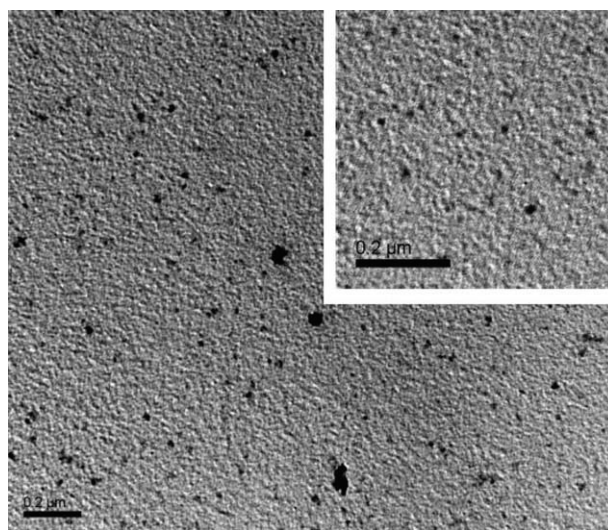


Figure 9 TEM micrograph of 0.5 wt% MgF₂ colloids stabilized in isopropanol by triblock copolymer (H80S20), inset: triblock copolymer dissolved in isopropanol without metal salt.

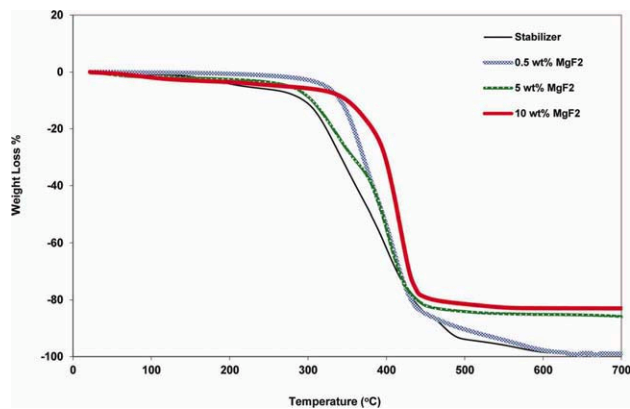


Figure 10 Thermogravimetric analysis of pHEMA-PDMS-pHEMA triblock copolymer (H80S20) and 0.5, 5, 10 wt% of MgF₂ polymer composites. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

transparent. By varying blocks of the polymers, it is envisioned that the 3D organization of nanoparticles,³⁶ polymer–nanoparticle interaction, magnetic,³⁷ and optical³⁸ properties, and processability of nanoparticle–polymer composites can be tuned. The MgF₂ colloids have the potential to be used as optical materials as well as abrasion and scratch resistant coatings.^{39,40}

CONCLUSIONS

A series of pHEMA-*b*-PDMS-*b*-pHEMA amphiphilic triblock copolymers were prepared by ATRP. These block copolymers are well controlled in molecular weight and have low molecular weight distribution as found from GPC and NMR. MgF₂ nanoparticles were successfully synthesized by the chemical precipitation of magnesium chloride and potassium fluoride in reverse micelles of pHEMA-PDMS-pHEMA triblock copolymers. MgF₂ nanoparticles with triblock copolymers were dispersed in organic solvents such as methanol, THF, and *isopropanol*. The MgF₂ colloids were observed to be well-dispersed. In these organic solvents, the DLS analysis showed MgF₂ colloids had different particle size and particle size distribution due to solvent-responsive conformational changes in hydrodynamic volume of triblock copolymers. The formation of MgF₂ was proven by a strong peak at 27.3° (2θ) in XRD. The TGA showed MgF₂ colloids improved thermal stability of pHEMA-PDMS-pHEMA triblock copolymers.

References

- Chiu, J. J.; Kim, B. J.; Kramer, E. J.; Pine, D. J. *J Am Chem Soc* 2005, 127, 5036.
- Tadros, T. F. *Colloid Stability: The Role of Surface Forces*; Wiley-VCH, Weinheim, 2007.
- Rozenberg, B. A.; Tenne, R. *Prog Polym Sci* 2008, 33, 40.
- Mayer, A. B. R. *Polym Adv Technol* 2001, 12, 96.
- Shenhar, R.; Norsten, T. B.; Rotello, V. M. *Adv Mater* 2005, 17, 657.
- Teranishi, T.; Hosoe, M.; Tanaka, T.; Miyake, M. *J Phys Chem B* 1999, 103, 3818.
- Harris, L. A.; Goff, J. D.; Carmichael, A. Y.; Riffle, J. S.; Harburn, J. J.; St. Pierre, T. G.; Saunders, M. *Chem Mater* 2003, 15, 1367.
- Gotoh, Y.; Kanno, T.; Fujimori, Y.; Ohkoshi, Y.; Nagura, M.; Akamatsu, K.; Deki, S. *Polym J* 2003, 35, 960.
- Wang, T. C.; Rubner, M. F.; Cohen, R. E.; *Chem Mater* 2003, 15, 299.
- Glass, R.; Möller, M.; Spatz, J. P. *Nanotechnology* 2003, 14, 1153.
- Macanás, J.; Farre, M.; Muñoz, M.; Alegret, S.; Muraviev, D. N. *Phys. Stat. Sol. (A)* 2006, 203, 1194.
- Balazs, A. C.; Emrick, T.; Russell, T. P. *Science* 2006, 314, 1107.
- Förster, S.; Antonietti, M. *Adv Mater* 1998, 10, 195.
- Müller, H.; Leube, W.; Tauer, K.; Förster, S.; Antonietti, M. *Macromolecules* 1997, 30, 2288.
- Bronstein, L. M.; Chernyshov, D. M.; Timofeeva, G. I.; Dubrovina, L. V.; Valetsky, P. M.; Obolonkova, E. S.; Khokhlov, A. R. *Langmuir* 2000, 16, 3626.
- Huo, Q.; Liu, J.; Wang, L.-Q.; Jiang, Y.; Lambert, T. N.; Fang, E. *J Am Chem Soc* 2006, 128, 6447.
- Guo, Y.; Moffitt, M. G. *Macromolecules* 2007, 40, 5868.
- Nie, W.; Zhu, J.; Renguoxie, N.; Chen, Y.; Jiang, W.; Ji, X. *Nanotechnology* 2006, 17, 3313.
- Rutnakornpituk, M.; Thompson, M.S.; Harris, L. A.; Farmer, K. E.; Esker, A. R.; Riffle, J. S.; Connolly, J.; St. Pierre, T. G. *Polymer* 2002, 43, 2337.
- Sakai, T.; Alexandridis, P. *J Phys Chem B* 2005, 109, 7766.
- Rywak, A. A.; Burlitch, J. M. *Chem Mater* 1996, 8, 60.
- Pilvi, T.; Hatanpaa, T.; Puukilainen, E.; Arstila, K.; Bischoff, M.; Kaiser, U.; Kaiser, N.; Leskela, M.; Ritala, M. *J Mater Chem* 2007, 17, 5077.
- Hsu, W. P.; Zhong, Q.; Matijevic, E. *J Colloid Interface Sci* 1996, 181, 142.
- Wojcichowska, M.; Zielinski, M.; Pietrowski, M. *Catal Today* 2004, 90, 35.
- Malinowski, A.; Juszczak, W.; Pielaszek, J.; Bonarowska, M.; Wojciechowska, M.; Karpinski, Z. *Chem Commun* 1999, 8, 685.
- Wojciechowska, M.; Pietrowski, M.; Czajka, B.; Lomnicki, S. *Catal Lett* 2003, 87, 153.
- Beers, K. L.; Boo, S.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules* 1999, 32, 5772.
- Wang, J. S.; Matyjaszewski, K. *Macromolecules* 1995, 28, 7901.
- Miller, P. J.; Matyjaszewski, K. *Macromolecules* 1999, 32, 8760.
- Shinoda, H.; Miller, P. J.; Matyjaszewski, K. *Macromolecules* 2001, 34, 3186.
- Lutz, J.-F.; Jahed, N.; Matyjaszewski, K. *J Polym Sci Part A Polym. Chem.* 2004, 42, 1939.
- Robinson, K. L.; Khan, M. A.; de Paz Bazez, M. V.; Wang, X. S.; Armes, S. P. *Macromolecules* 2001, 34, 3155.
- Matyjaszewski, K.; Patten, T.; Xia, J. *J Am Chem Soc* 1997, 119, 674.
- Lee, S. C.; Chang, Y. K.; Yoon, J. S.; Kim, C. H.; Kwon, I. C.; Kim, Y. H.; Jeong, S. Y. *Macromolecules* 1999, 32, 1847.
- Rong, M. Z.; Zhang, M. Q.; Liang, H. C.; Zeng, H. M. *Appl Surf Sci* 2004, 228, 176.
- Yusuf, H.; Kim, W.-G.; Lee, D. H.; Aleshyna, M.; Brolo, A. G.; Moffitt, M. G. *Langmuir* 2007, 23, 5251.
- Spada, F. E.; Berkowitz, A. E.; Prokey, N. T. *J Appl Phys* 1991, 69, 4475.
- Underwood, S.; Mulvaney, P. *Langmuir* 1994, 10, 3427.
- Arndt, H.; Jilavi, M.; Mennig, M.; Oliveira, P. W.; Schmidt, H. U. S. Patent Application 2008/0261053, June 07, 2005.
- Maier, R. L.; Sparrow, R. W.; Then, P. M. U. S. Patent Application 2004/0202225, Nov. 18, 2003.