

## Crosslinked Epoxy Microspheres: Preparation, Surface-Initiated Polymerization, and Use as Macroporous Silica Porogen

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**ABSTRACT:** In this article, we report the preparation of crosslinked epoxy microspheres with diameters of 5–10  $\mu\text{m}$  prepared via phase-inverted phase separation induced by polymerization in the thermosetting blend of epoxy and poly( $\epsilon$ -caprolactone). The surfaces of the epoxy microspheres were functionalized to bear 2-bromopropionyl groups, which were further used as initiators to obtain poly(glycidyl methacrylate) (PGMA) grafted epoxy microspheres via the surface-initiated atom transfer radical polymerization approach. The PGMA-grafted epoxy microspheres were then employed to react with 3-aminopropyltrimethoxysilane (APTMS) to obtain the functionalized epoxy microspheres, the surface of which contained a great number of trimethoxysilane groups. A co-sol-gel process between the APTMS-functionalized epoxy microspheres and tetraethoxysilane was performed, and organic–inorganic glassy solids were obtained. The organic–inorganic glasses were used as precursors for accessing macroporous silica materials via pyrolysis at elevated temperatures. The hierarchical porosity of the resulting macroporous silica was investigated by means of field emission scanning electronic microscopy, transmission electronic microscopy, and surface-area Brunauer–Emmett–Teller (BET) measurements. We found that the macroporous silica possessed BET surface areas in the range 183.9–235.2  $\text{m}^2/\text{g}$ , depending on the compositions of their precursors. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

**KEYWORDS:** morphology; porous materials; phase behavior; surfaces and interfaces; thermosets

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### INTRODUCTION

Polymer microspheres with controlled shape and size are a class of important materials, which have found extensive applications in coatings, adhesives, molding compounds, and the modification of existing polymers as active fillers, because of their rheological and reinforcing properties.<sup>1–5</sup> Crosslinked polymer microspheres can further be applied as chromatographic column packing and substrates for medical diagnostics. In general, emulsion or dispersion (and/or suspension) polymerization of vinyl monomers are used to prepare microspheres of poly(methyl methacrylate) (PMMA), polystyrene, and poly(vinyl acetate).<sup>6</sup> Crosslinked epoxy microspheres are of interest because of their thermal, dimensional stability and chemical resistance. More importantly, there are a great number of functional groups (e.g., hydroxyl or amino groups) at the surfaces of epoxy microspheres, which allows further chemical modification to endow the materials with new performance.

Crosslinked epoxy microspheres are generally prepared via dispersion polymerization with polyethers (e.g., polypropylene glycol) (PPG) as solvents.<sup>7,8</sup> As the curing reaction proceeds,

epoxy is demixed out of the initially homogeneous mixtures, which are composed of epoxy precursors and polyethers in the form of crosslinked microspheres. The formation of spherical epoxy particles generally follows a reaction-induced phase separation mechanism (RIPS).<sup>9–15</sup> The driving forces for RIPS are attributable to the following two aspects: (1) the increased molecular weight due to polymerization (viz., the curing reaction), which gives rise to a decreased contribution of mixing entropy to the free energy of mixing, and (2) the alteration of the inter-component interaction parameters ( $\chi$ ) with the conversion of monomers. In this approach, polymeric solvents (e.g., PPG) are used as the major components, whereas epoxy thermosets are a minor component. The use of liquid polyethers can facilitate the isolation of the resulting epoxy microspheres from these mixtures. In addition to the aforementioned direct RIPS technique, crosslinked epoxy microspheres can be alternatively prepared via the so-called phase-inverted reaction-induced phase separation approach. In this approach, the epoxy thermoset is a major component, whereas the thermoplastic polymers are the minor components. This is in marked contrast to the aforementioned RIPS technique. In this approach, crosslinked epoxy

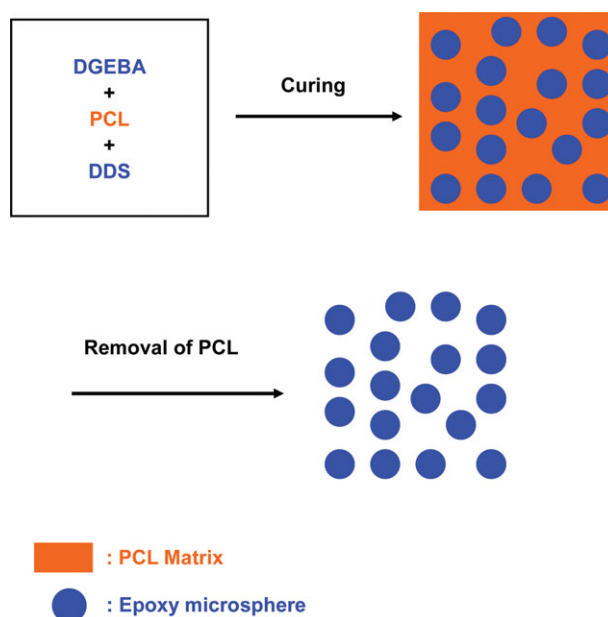
microspheres are formed in a phase-inverted RIPS manner. Hsieh and Woo<sup>16</sup> reported the preparation of crosslinked epoxy micro-particles in thermosetting blends of epoxy with PMMA. It was found that in the thermosetting blends containing up to 30 wt % PMMA, dispersed epoxy microspheres were obtained with diameters of 10–80  $\mu\text{m}$  after continuous PMMA matrices were rinsed via extraction with dichloromethane. The phase-inverted reaction-induced phase separation behavior was interpreted in terms of a spinodal decomposition mechanism in the process of curing, which was involved with several complicated competitive kinetic mechanisms, such as the curing reaction, phase separation, and changes in the viscoelastomeric properties of the component polymers. We realized that the shapes and distribution of size of the resulting epoxy microparticles depended heavily on the composition of the thermosetting blends, the curing conditions, and the viscoelastic properties of the thermoplastic polymers used.

Reaction-induced phase separation in blends of epoxy thermosets containing poly( $\epsilon$ -caprolactone) (PCL) with 4,4'-diaminodiphenylsulfone (DDS) as a hardener has previously been investigated by Chen and Chang<sup>17</sup> and Ni and Zheng.<sup>18</sup> It was found that in the thermosetting blends, phase-inverted phase separation occurred when the content of PCL was 20 wt % or higher.<sup>18</sup> This observation is reminiscent of the preparation of crosslinked epoxy microspheres via the phase-inverted reaction-induced phase separation approach, which to the best of our knowledge, has not been previously reported. In this article, we report the preparation of crosslinked epoxy microspheres via the phase-inverted reaction-induced phase separation approach with this thermosetting system; we also explore the application of the as-prepared crosslinked epoxy microspheres as porogens to access macroporous silica. Toward this end, the surfaces of the crosslinked epoxy microspheres were grafted with poly(glycidyl methacrylate) (PGMA) via a surface-initiated atom transfer radical polymerization (ATRP) approach, and the PGMA-grafted epoxy microspheres were reacted with 3-aminopropyltrimethoxysilane to promote their reactivity with tetraethoxysilane (TEOS). It should be pointed out that the preparation of macroporous silica with crosslinked epoxy microspheres as a porogen is quite different from the hierarchical assembly technique done with the use of closely packed polymer colloidal particles as templates, an approach that is amply represented in the literature.<sup>19–26</sup> In these previous reports, polymer colloidal particles (e.g., PMMA and polystyrene) were generally nonreactive. In this study, the utilization of reactive epoxy microspheres helped to promote the chemical linkages between silica matrices and the porogen, and thus, the macroporosity of silica was modulated. To the best of our knowledge, there have been no reports on the use of reactive epoxy microspheres as porogens in the preparation of macroporous silica. In this contribution, The macroporosity of the resulting silica materials was addressed by field emission scanning electronic microscopy (FESEM), transmission electronic microscopy (TEM), and Brunauer–Emmett–Teller (BET) surface area measurements.

## EXPERIMENTAL

### Materials

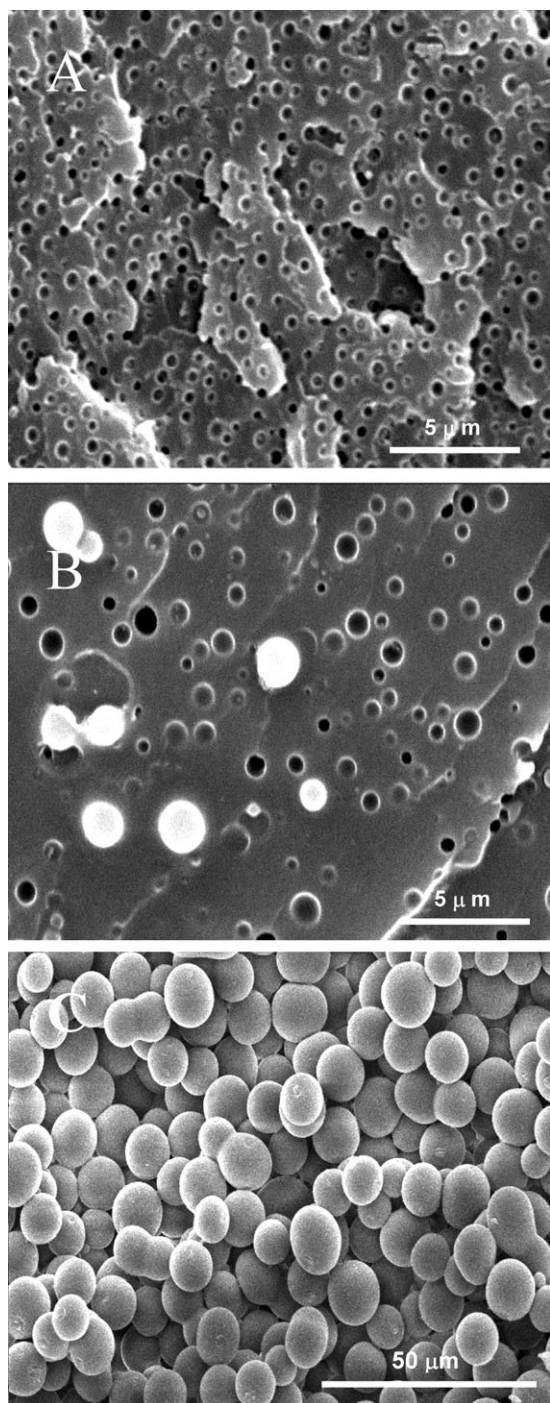
Diglycidyl ether of bisphenol A (DGEBA), with an epoxide equivalent weight of 185–210, was purchased from Shanghai



**Scheme 1.** Preparation of the epoxy microspheres via reaction-induced RIPS in the blends of epoxy resin and PCL. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Resin Co. (China). 4,4-Diaminodiphenylsulfone (DDS) was used as the curing agent. Poly( $\epsilon$ -caprolactone) (PCL) was purchased from Sigma Aldrich Co., and it had a quoted number-average molecular weight ( $M_n$ ) of 80,000. Glycidyl methacrylate (GMA) and 3-aminopropyltrimethoxysilane were of analytical pure grade and were purchased from Shanghai Reagent Co. (China). 2-Bromopropionyl bromide and  $N,N,N',N',N'$ -pentamethyldiethylenetriamine (PMDETA) were purchased from Aldrich Co. and were used as received. Hydrochloric acid (37%) was purchased from Shanghai Reagent Co. The solvents, such as tetrahydrofuran and triethylamine, were obtained from a commercial source. Before use, tetrahydrofuran was refluxed over metal sodium and then distilled; triethylamine was dried over  $\text{CaH}_2$  and was then refluxed with *p*-toluenesulfonyl chloride and distilled. Methyl phenyl ether was dried over  $\text{CaH}_2$  and distilled.

**Preparation of the Epoxy Microspheres (Scheme 1).** Typically, DGEBA (20.000 g) and PCL (11.5600 g) were mixed at 100°C with continuous stirring for a sufficient time until PCL was totally dissolved, and then, DDS (7.000 g, i.e., equimolar with respect to DGEBA) was added to the mixture with continuous stirring until the systems became homogeneous and transparent. The mixtures were cured at 80°C for 2 h, 150°C for 3 h, and 180°C for 2 h to ensure a complete curing reaction. The cured blend of epoxy with PCL was ground and added to a 250-mL flask. Chloroform (50 mL) was charged with vigorous stirring until all of the pellets were dispersed in  $\text{CDCl}_3$ . The mixture was centrifuged to afford the solids. This procedure was repeated three times to rinse PCL. After it was dried in a vacuum oven at 30°C for 24 h, the product (25.120 g) was obtained with a yield of 93.1%. Scanning electron microscopy (SEM) showed that spherical particles with an average diameter of 5–10  $\mu\text{m}$  were obtained [see Figure 1(C)].



**Figure 1.** SEM micrographs of epoxy thermosetting blends containing (A) 10, (B) 20, and (C) 30 wt % PCL ( $M_n = 80,000$ ).

**Functionalization of the Epoxy Microspheres with 2-Bromopropionyl Bromide.** To a flask equipped with a magnetic stirrer, the previous epoxy microspheres (5.50 g), dichloromethane (15 mL), and triethylamine (13 mL) were charged. To attain a fine dispersion, ultrasonic irradiation was exerted onto the system. Thereafter, 2-bromopropionyl bromide dissolved in 10 mL of dichloromethane was added dropwise with vigorous stirring. The reaction was carried out at 30°C for 24 h, and the reacted

epoxy particles were isolated with a centrifuge. The powders were then washed with tetrahydrofuran three times. After being dried *in vacuo* at 30°C for 24 h, the product (6.3700 g, viz., 2-bromopropionyl-functionalized epoxy microspheres) was obtained at a yield of 86.1%.

Fourier transform infrared (FTIR) spectroscopy (KBr,  $\text{cm}^{-1}$ ): 3408 (O—H), 1736 [—OOCCH(CH<sub>3</sub>)Br].

The content of bromine was measured to be 9.85 wt % by means of elemental analysis.

**Synthesis of the PGMA-Grafted Epoxy Microspheres.** To a 25-mL flask equipped with a magnetic stirrer, 2-bromopropionyl-functionalized epoxy microspheres (2.000 g), GMA (2.8707 g, 0.0202 mol), and freshly distilled methyl phenyl ether (10 mL) were charged with vigorous stirring. Thereafter, copper(I) chloride (CuCl; 0.3361 g) and PMDETA (0.6580 mL) were added. The flask was connected to a Schlenk line for degassing via three freeze–pump–thaw cycles to remove traces of oxygen. The polymerization was carried out at 70°C for 10 h. After the system was cooled to room temperature, a great amount of methanol was added to afford the precipitates. The precipitates were redispersed with dichloromethane (12 mL) and reprecipitated with methanol. This procedure was repeated three times until the product became colorless. After it was dried in a vacuum oven at 40°C for 12 h, the product (3.7475 g, i.e., PGMA-grafted epoxy microspheres) was obtained with a conversion of GMA of 60.9%. Each PGMA chain was estimated to have an  $M_n$  of approximately 730 Da in terms of the content of bromine and the conversion of GMA monomer.

**Preparation of the Macroporous Silica.** Typically, to a flask equipped with a magnetic stirrer, the PGMA-grafted epoxy microspheres (1.000 g, 3.2803 mmol with respect to epoxide groups), anhydrous tetrahydrofuran (10 mL), and 3-aminopropyltrimethoxysiloxane (0.5881 g, 3.2802 mmol) were charged, and the reaction was carried out at 60°C for 4 h. After it was cooled to room temperature, the reacted mixture was equally dispatched into four portions and then poured into four poly(ethylene terephthalate) beakers, respectively, each of which contained a magnetic stirrer. Thereafter, 0.1328, 0.2985, 0.5117, and 0.7959 g of TEOS were added, respectively, to these beakers with vigorous stirring, and then 0.08600, 0.1407, 0.2110, and 0.3047 g of deionized water and catalytic amounts of hydrochloric acid were added. All of these beakers were sealed, and the sol–gel process was performed at room temperature for 7 days. The gelled products were obtained after the solvent and other volatile compounds were removed *in vacuo* at 30°C for 24 h. The compositions of the gels are summarized in Table I.

The above gelled samples were placed into a pipe furnace to decompose all of the organic components at high temperatures. Typically, in the air atmosphere, the samples were heated up to 450°C at a heating rate of 1°C/min and were maintained at this temperature for 3 h. Thereafter, the temperature was raised to 550°C at a heating rate of 1°C/min, and the samples were maintained at this temperature for 2 h. In all cases, white solids were obtained.



**Table I.** Results of BET Measurements for the Macroporous Silica

Macroporous silica	Precursor	[APTMS-functionalized epoxy]/[TEOS] (w/w)	$S_{\text{BET}}^{\text{b}}$ ( $\text{m}^2/\text{g}$ )	$V_{\text{pore}}^{\text{c}}$ ( $\text{cm}^3/\text{g}$ )
MS1	EP10TEOS0 <sup>a</sup>	100:0	217.6	0.12
MS2	EP9TEOS1	90:10	227.0	0.14
MS3	EP8TEOS2	80:20	235.3	0.18
MS4	EP7TEOS3	70:30	223.7	0.32
MS5	EP6TEOS4	60:40	183.9	0.19

<sup>a</sup>EP stands for APTMS-functionalized epoxy microspheres.<sup>b</sup>BET surface area.<sup>c</sup>Pore volume.

### Measurement and Characterization

**FTIR Spectroscopy.** FTIR measurements were performed on a PerkinElmer Paragon 1000 FTIR spectrometer. Before the measurements, the specimens were dried *in vacuo* at 60°C for 48 h. The samples were granulated, and the powders were mixed with KBr and then pressed into small flakes for FTIR measurement. All of the specimens used in the study were sufficiently thin to be within a range where the Beer–Lambert law was obeyed. The spectra were obtained at a resolution of 2  $\text{cm}^{-1}$  and are reported as the averages of 64 scans.

**NMR Spectroscopy.** The samples were dissolved (or dispersed) in deuterium  $\text{CDCl}_3$ , and the NMR spectra were measured on a Varian Mercury Plus 400-MHz NMR spectrometer with tetramethylsilane (TMS) as the internal reference.

**Determination of the Bromine Contents.** The contents of bromine were determined by means of a technique of oxygen flask combustion followed by titration with mercuric nitrate. The samples were first combusted in a 1-L oxygen-filled combustion flask containing 0.01M nitric acid. After combustion, the flask was cooled, and the solution was titrated with a dilute standard silver nitrate solution to calculate the content of bromine. The value of bromine content was taken as the average of three measurements with a deviation of 5%.

**Thermogravimetric Analysis (TGA).** A TA Instruments thermogravimetric analyzer (Q-5000) (DE, USA) was used to investigate the thermal stability of the samples. The samples (ca. 5 mg) were heated in a nitrogen atmosphere from ambient temperature to 800°C at a heating rate of 20°C/min in all cases.

**Scanning Electron Microscopy (SEM).** The cured blends of epoxy with PCL were fractured under cryogenic conditions with liquid nitrogen. The fractured surfaces were immersed in dichloromethane at room temperature for 30 min. The PCL phase could be preferentially rinsed with the solvent while the epoxy phase remained unaffected. The etched specimens were dried to remove the solvents. The specimens were examined with a Hitachi S-2150 scanning electron microscope (SEM) (Tokyo, Japan) at an activation voltage of 15 kV. The fracture surfaces were coated with thin layers of gold of about 100 Å. For the morphological observation of macroporous silica, the powder samples were adhered to the surface of acrylic bets, and

the samples were then coated with thin layers of gold of about 100 Å. The SEM micrographs were obtained by means of a JEOL JSM 7401 F FESEM instrument (Tokyo, Japan) at an activation voltage of 5 kV.

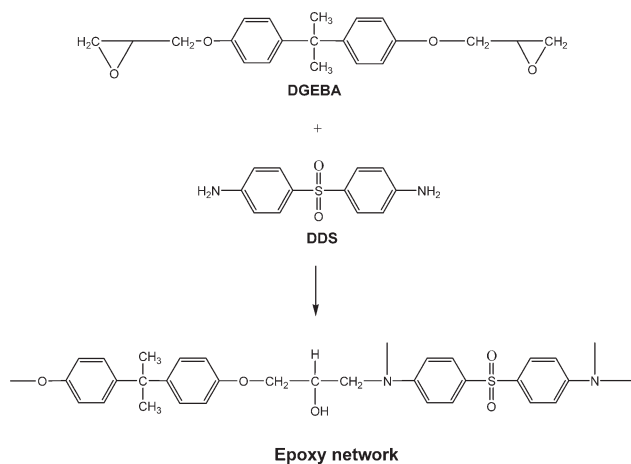
**TEM.** The suspension of macroporous silica in ethanol was dropped on 200-mesh copper grids, and the solvent was slowly evaporated at room temperature. The specimens were then subjected to morphological observation by means of TEM analyses on a JEOL JEM-2010 high-resolution transmission electron microscope at an acceleration voltage of 120 kV.

**Specific Surface Area Analyses.** The surface areas and pore size distributions were determined by nitrogen sorption at 77 K with the volumetric technique on a Micromeritics ASAP 2010 instrument (Norcross, GA). The silica samples were ground and sieved through a 200-mesh sieve and degassed *in vacuo* at 150°C for at least 6 h before measurements. The specific surface areas were calculated with the multipoint BET method with DeltaGraph graphics software (Norcross, GA). The pore size distributions were determined by density functional theory with nitrogen on carbon at 77 K with the slitlike pore model.

## RESULTS AND DISCUSSION

### Synthesis of the Crosslinked Epoxy Microspheres

In a previous article, we reported that phase-inverted reaction-induced phase separation occurred in the thermosetting blends of epoxy and PCL when DDS was used as the curing agent.<sup>18</sup> In this study, this thermosetting blend system was used to prepare crosslinked epoxy microspheres with a fine shape and distribution of size. We prepared the thermosetting blends by starting homogeneous mixtures composed of DGEBA, DDS, and PCL. We observed that as the curing reaction proceeded, the initially transparent mixtures gradually became cloudy; this indicated the occurrence of reaction-induced phase separation (Scheme 1). The driving forces for the reaction-induced phase separation were attributable to two aspects: (1) the increased molecular weight due to polymerization (*viz.*, the curing reaction), which gave rise to the decreased contribution of mixing entropy to the free energy of mixing, and (2) the alteration of  $\chi$  with the conversion of the monomers. The latter may have favored mixing or demixing, depending on whether  $\chi$  decreased or increased with conversion. If a system possesses favorable intermolecular specific interactions (e.g., hydrogen bonding), miscible blends of the thermosets will be obtained.<sup>27–30</sup> If  $\chi$  increases with conversion, the previous collective changes may cause the system to cross thermodynamic phase boundaries, and this will result in a transition from an initial homogeneous to a microphase-separated state. In this case, it was proven that  $\chi$  for the epoxy/PCL blends cured with DDS favored demixing; this was in marked contrast to the blends cured with 4,4'-methylenebis-(2-chloroaniline). The morphologies of the thermosetting blends were investigated by means of scanning electron microscopy (SEM). Heterogeneous morphologies were observed in all the cases. Although the content of PCL was less than 15%, spherical domains with diameters of 0.5  $\mu\text{m}$  were uniformly dispersed in the continuous epoxy matrix [Figure 1(A)]. The spherical domains were attributed to PCL, and the continuous matrices were attributed to the epoxy. It was noted that with increasing



**Scheme 2.** Curing reaction of the epoxy monomers (viz., DGEBA + DDS).

content of PCL, the blends displayed remarkably different morphologies. Although the content of PCL was 20 wt %, some PCL domains became interconnected, and some spherical particles appeared [Figure 1(B)]. The spherical particles were assigned to epoxy because the PCL phase was etched with dichloromethane. We noted that a totally phase-inverted morphology was evident when the content of PCL was 30 wt % or higher [Figure 1(C)]; that is, the epoxy component was transformed into spherical particles. The thermosetting blends were subjected to solubility tests, and we found that the phase-inverted blends were fully dissolved into dichloromethane. After repeated rinsing with dichloromethane, powderlike products were obtained. Shown in Figure 1(C) is the SEM micrograph of the samples prepared from the thermosetting blends containing 30 wt % PCL. Crosslinked epoxy microspheres 5–10  $\mu\text{m}$  in size were successfully obtained. In this study, the cured blend containing 30 wt % PCL was used to prepare crosslinked epoxy microspheres, and these epoxy microspheres were used throughout this study.

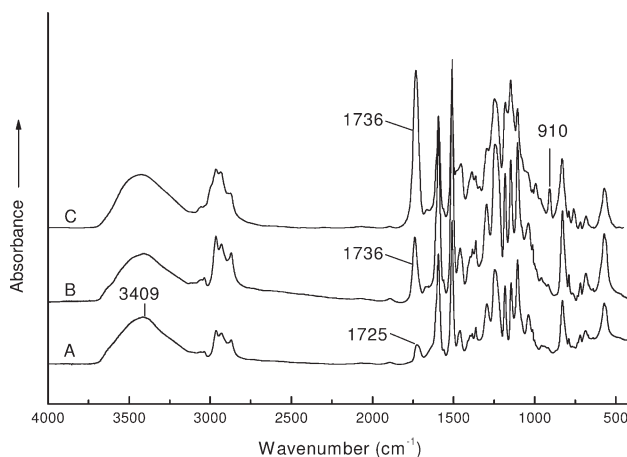
### Surface-Initiated ATRP

The crosslinked epoxy microspheres were functionalized to afford the initiator for the ATRP of GMA via their etherification with 2-bromopropionyl bromide. The surface reaction was carried out between secondary hydroxyl groups of amine-crosslinked epoxy (Scheme 2) and 2-bromopropionyl bromide. Shown in Figure 2 are the FTIR spectra of the control epoxy (curve A) and 2-bromopropionyl-functionalized epoxy (curve B). The control epoxy microspheres were characterized by the band at  $3409\text{ cm}^{-1}$ ; this was assigned to the stretching vibrations of hydroxyl groups in hydroxyl ether structural units of amine-crosslinked epoxy. In addition, a minor band at  $1726\text{ cm}^{-1}$  appeared. This band was ascribed to the carbonyls of a small amount of PCL, which was entrapped in the epoxy microspheres in the process of reaction-induced phase separation. Upon functionalization with 2-bromopropionyl bromide, a new band appeared at  $1736\text{ cm}^{-1}$  apart from the spectral bands assignable to epoxy. This band was assigned to the stretching vibrations of carbonyl groups in the moiety of 2-bromopropionyl groups. FTIR spectroscopy indicated that the surfaces of

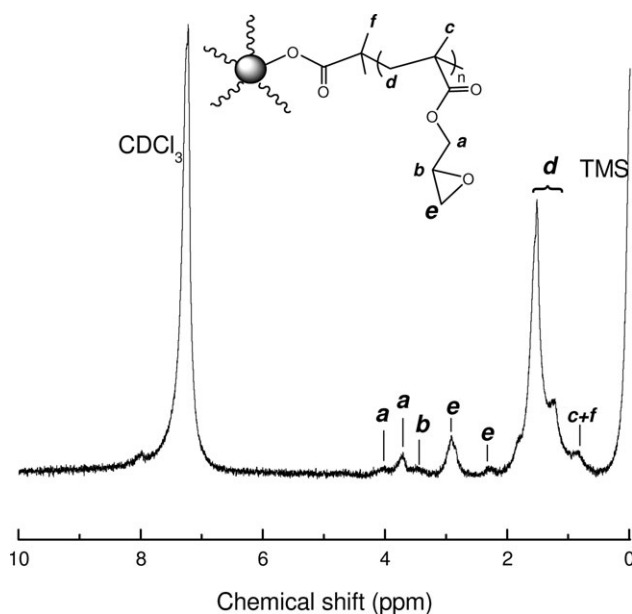
the epoxy microspheres were successfully functionalized with the 2-bromopropionyl groups. The elemental analysis showed that the degree of functionalization was about 0.1199 mol/g. The previous 2-bromopropionyl-functionalized epoxy microspheres were used to initiate the polymerization of GMA in the presence of a complex of copper(I) chloride with PMDETA. The viscosity of the system significantly increased as the polymerization proceeded; this suggested that the surface-initiated ATRP of GMA was efficiently carried out. The FTIR spectrum of PGMA-grafted epoxy microspheres is also presented in Figure 2 (see curve C). We noted that the intensity of the band at  $1736\text{ cm}^{-1}$  was significantly increased. The increased intensity indicated that the surface-initiated polymerization was successfully achieved. In addition, another new band appeared at  $910\text{ cm}^{-1}$ , which was attributable to the epoxide groups of PGMA chains. FTIR spectroscopy indicated that the resulting product combined the structural features from epoxy and PGMA. The PGMA-grafted epoxy was further subjected to  $^1\text{H-NMR}$  spectroscopy, and the  $^1\text{H-NMR}$  spectrum is shown in Figure 3. It was seen that all of the resonance assignable to the PGMA protons was detectable, although the spectral lines were seriously broadened. The broadened spectral lines were responsible for the low mobility of PGMA chains grafted onto bulky epoxy microspheres because the anisotropy of chemical shift could not be efficiently averaged through the Brownian motion of PGMA chains in the  $\text{CDCl}_3$  solution. It should be pointed out that the resonance of the protons assignable to epoxy microspheres could not be detected because of their insolubility in the  $\text{CDCl}_3$  solution. The results of FTIR and  $^1\text{H-NMR}$  spectroscopy indicated that the PGMA-grafted epoxy microspheres were successfully obtained. With the conversion of GMA controlled to be about 60.9%, the length of each PGMA grafted onto the surface of the epoxy microspheres was estimated to be  $L_{\text{PGMA}} \approx 730$  Da in terms of the content of bromine, with the assumption that each 2-bromopropionyl group was an active site initiating one PGMA chain.

### Preparation of the Macroporous Silica

The previous PGMA-grafted epoxy microspheres were further modified by 3-aminopropyltrimethoxysilane (APTMS) via the

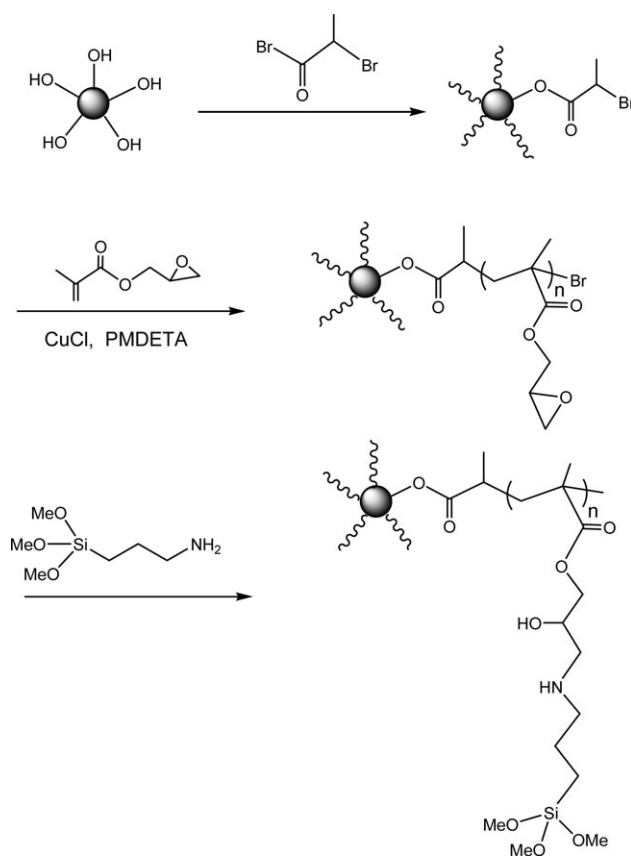


**Figure 2.** FTIR spectra of the (A) control epoxy microspheres, (B) 2-bromopropionyl ester-functionalized epoxy, and (C) PGMA-grafted epoxy.



**Figure 3.**  $^1\text{H-NMR}$  spectrum of the PGMA-grafted epoxy microspheres.

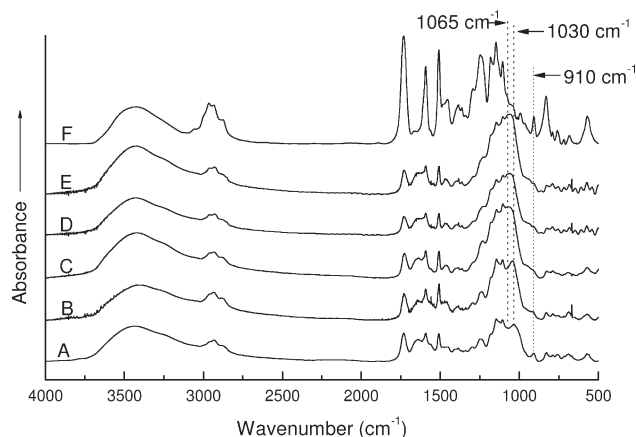
reaction between the epoxide groups of PGMA and the amino groups of APTMS (see Scheme 3) to obtain the APTMS-functionalized epoxy microspheres. Thereafter, TEOS was added to the APTMS-functionalized epoxy microspheres, and the intercomponent sol-gel reactions were carried out to afford organic-inorganic glassy solids, which could be used as precursors to access the macroporous silica. Shown in Figure 4 are the FTIR spectra of the PGMA-grafted epoxy and organic-inorganic glassy solids with various compositions. PGMA-grafted epoxy showed a characteristic at  $910\text{ cm}^{-1}$ , assigned to the stretching vibration of epoxide groups of the PGMA chains. We observed that the bands of epoxide groups in all of the organic-inorganic glassy solids virtually disappeared. The disappearance of epoxide bands indicated that the intercomponent reaction occurring between APTMS and PGMA was achieved; that is, the PGMA-grafted epoxy microspheres were converted into APTMS-functionalized epoxy microspheres. With the occurrence of intercomponent sol-gel reactions, the organic-inorganic glassy solids were obtained; this was evidenced by the appearance of broad bands in the range  $1000\text{--}1200\text{ cm}^{-1}$ , which were characteristic of the Si-O-Si moiety in silicate and polysilsesquioxane (see Figure 4). In this study, the mass ratios of the APTMS-functionalized epoxy microspheres to TEOS were controlled to be 100:0, 90:10, 80:20, 70:30, and 60:40, respectively (see Table I). The purpose of using the APTMS-functionalized epoxy microspheres instead of the control crosslinked epoxy microspheres in the sol-gel process was to form covalent bonds between the epoxy microspheres and silica via their cohydrolysis and copolycondensation reactions with TEOS. In the gel from the APTMS-functionalized epoxy microspheres, an intense band appeared at  $1030\text{ cm}^{-1}$ , which was assigned to the stretching vibrations of Si-O-Si moieties in the networks of polysilsesquioxanes, which were formed via the hydrolysis and condensation of the trifunctional silane moiety (i.e., APTMS). For the gels prepared via the cohydrolysis and copolycondensation of APTMS-functionalized



**Scheme 3.** Functionalization of the epoxy microspheres via the ATRP approach.

epoxy microspheres with TEOS, a new band appeared at  $1065\text{ cm}^{-1}$  in addition to the band at  $1030\text{ cm}^{-1}$ , the intensity of which increased with increasing content of TEOS. This band was attributable to the stretching vibration of Si-O-Si moiety in silica formed via the hydrolysis and condensation of TEOS.

The organic-inorganic glassy solids were used as precursors to prepare the macroporous silica by the removal of the organic components. In this study, the organic portions from the epoxy



**Figure 4.** FTIR spectra of the precursors of macroporous silica: (A) EP10TEOS0, (B) EP9TEOS1, (C) EP8TEOS2, (D) EP7TEOS3, (E) EP6TEOS4, and (F) PGMA-grafted epoxy microspheres.

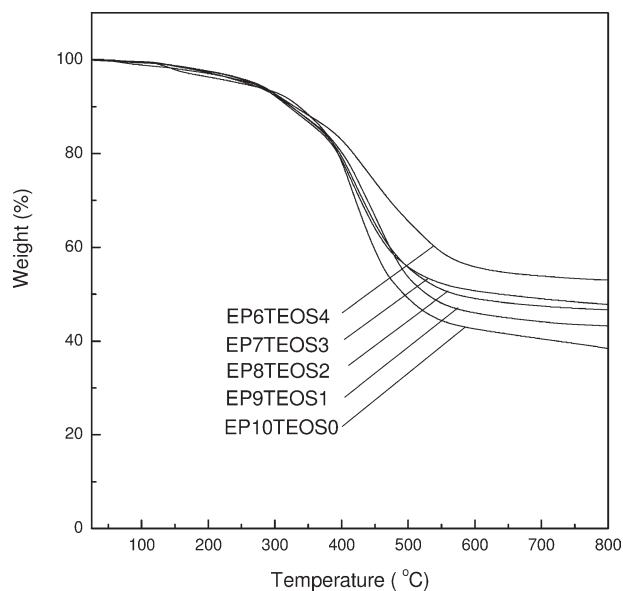


Figure 5. TGA curves of the precursors for the macroporous silica.

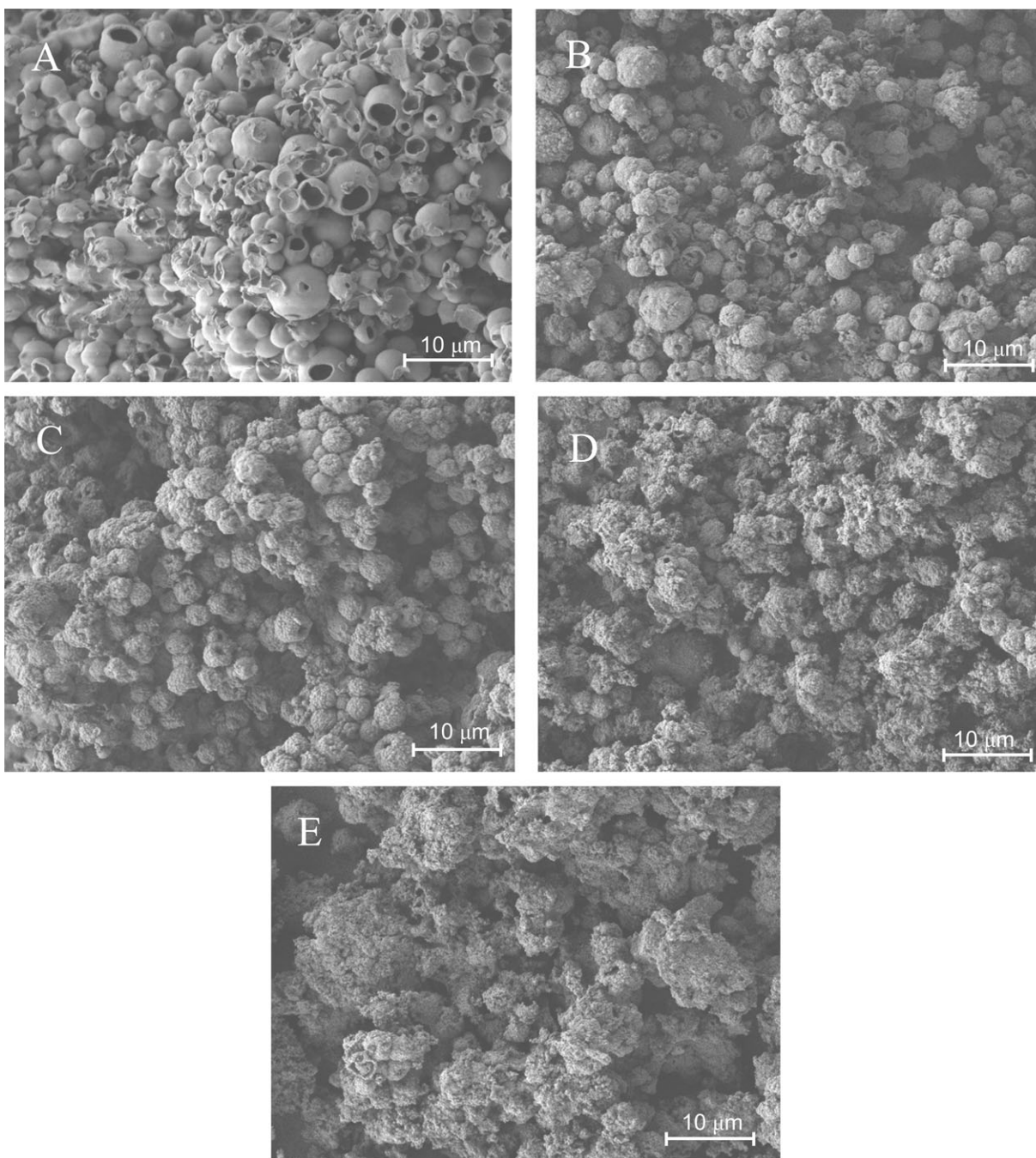
microspheres, PGMA chains, and aminopropyl groups of APTMS were removed via pyrolysis at elevated temperatures. To determine the temperatures degrading the organic portions, the organic–inorganic glassy solids were subjected to TGA, and the TGA curves are presented in Figure 5. All of the hybrid glassy solids displayed initial degradation at about 325°C. The initial mass loss resulted from the thermal degradation of the organic portions. While the temperatures were increased to 500°C or higher, plateaus of degradation appeared; this suggested that all of the organic–inorganic glassy solids were converted into silica. It was observed that the yields of silica increased with increasing content of the silanes, including APTMS and TEOS. The results of TGA were helpful in determining the condition of thermal pyrolysis. It is proposed that the removal of epoxy particles resulted in the formation of the macroscopic pores in the resulting silica with sizes up to 10  $\mu\text{m}$  in diameter, whereas the decomposition of the PGMA main chains, together with the release of gaseous matter from the organic–inorganic glassy solids, resulted in microporosity with sizes lower than 2 nm in the silica matrices.

The formation of macroporosity in the silica was investigated by means of scanning electron microscopy (SEM). Shown in Figure 6 are the SEM micrographs of the as-prepared silica materials. Macroporous structures were observed in all of the cases. For the silica from APTMS-functionalized epoxy (EP10TEOS0), hollow microspheres of silica were obtained with sizes of 2–4  $\mu\text{m}$  in diameter and with a wall thickness of about 20 nm. It is noted that the surface of the hollow microspheres was quite smooth. These hollow microspheres were created via the oxidation and pyrolysis of polysilsesquioxane from the product of the sol–gel process of the APTMS-functionalized epoxy microspheres. It was observed that some silica microspheres were broken, possibly because of the blowing up of some gaseous products formed in the process of calcination. Upon the addition of TEOS to the APTMS-functionalized epoxy micro-

spheres to perform the intercomponent hydrolysis and polycondensation (i.e., co-sol–gel reactions), the surface of these hollow microspheres increasingly became coarse. Careful observation showed that some smaller particles adhered to the surfaces of these hollow microspheres of silica, which resembled the surface structures of a strawberry. The roughness of the surfaces of these hollow silica microspheres increased with increasing content of TEOS. While the content of TEOS was 40 wt %, the surface of the hollow microspheres of silica became irregular. It is proposed that the smaller particles adhering to the surface of the hollow microspheres of silica were created via the intercomponent reactions between APTMS-functionalized epoxy and TEOS. The structures of the hollow microspheres of silica were further investigated by means of TEM, and the TEM micrographs are shown in Figure 7. Hollow spherical structures were observed in all cases. For the macroporous silica resulting from EP10TEOS0, hollow microspheres were obtained with sizes of 2–4  $\mu\text{m}$  in diameter and 20 nm in the thickness of the wall [see Figure 7(A)], and the surfaces of the hollow microspheres of silica were quite smooth. In contrast to those of the hollow microspheres of silica prepared from EP10TEOS0, the surfaces of all of the other hollow microspheres of silica were no longer smooth, and the thickness of the wall significantly increased, as shown in Figure 7B through 7E. The increased thickness of the wall for the hollow microspheres of silica was ascribed to the mutual polycondensation between the APTMS-functionalized epoxy and TEOS. This observation was in good agreement with the SEM results.

The porosity of the silica materials was examined with nitrogen sorption experiments; the nitrogen sorption isotherms are shown in Figure 8. It was noted that the types of the sorption isotherms were quite dependent on the compositions of the precursors (viz., the organic–inorganic glassy solids). For the silica from the APTMS-functionalized epoxy microspheres, a type I sorption isotherm was displayed. This case corresponded to the reversible sorption of a Langmuir single layer. The capacity of adsorption was determined by the volume of the hollow microspheres. According to the sorption isotherm, the BET surface area was measured to be 217.6  $\text{m}^2/\text{g}$ . The silica materials exhibited the sorption isotherms without hysteresis loops, which is typical of the reversible adsorption of multiple layers of nitrogen at the surface of silica. For the macroporous silica derivative from the mixture containing 10 wt % TEOS, sorption isotherms similar to those from APTMS-functionalized epoxy microspheres were exhibited, and the BET surface area was measured to be 217.0  $\text{m}^2/\text{g}$ . It was noted that with increasing content of TEOS, the macroporous silica gradually exhibited type IV sorption isotherms with  $\text{H}_2$ -type hysteresis; this suggested that the materials possessed some caged pores with small windows in the walls. For the macroporous silica derivative from the mixture containing 40 wt % TEOS, the sorption isotherms exhibited two steps at values of relative pressure of 0.1 and 0.9; these values were characteristic of a broad capillary condensation of nitrogen in the sample. The appearance of type IV sorption isotherms with  $\text{H}_2$ -type hysteresis loops suggested that in addition to the macroscopic pores from the removal of epoxy microspheres, some nanoscaled pores were formed in the walls of



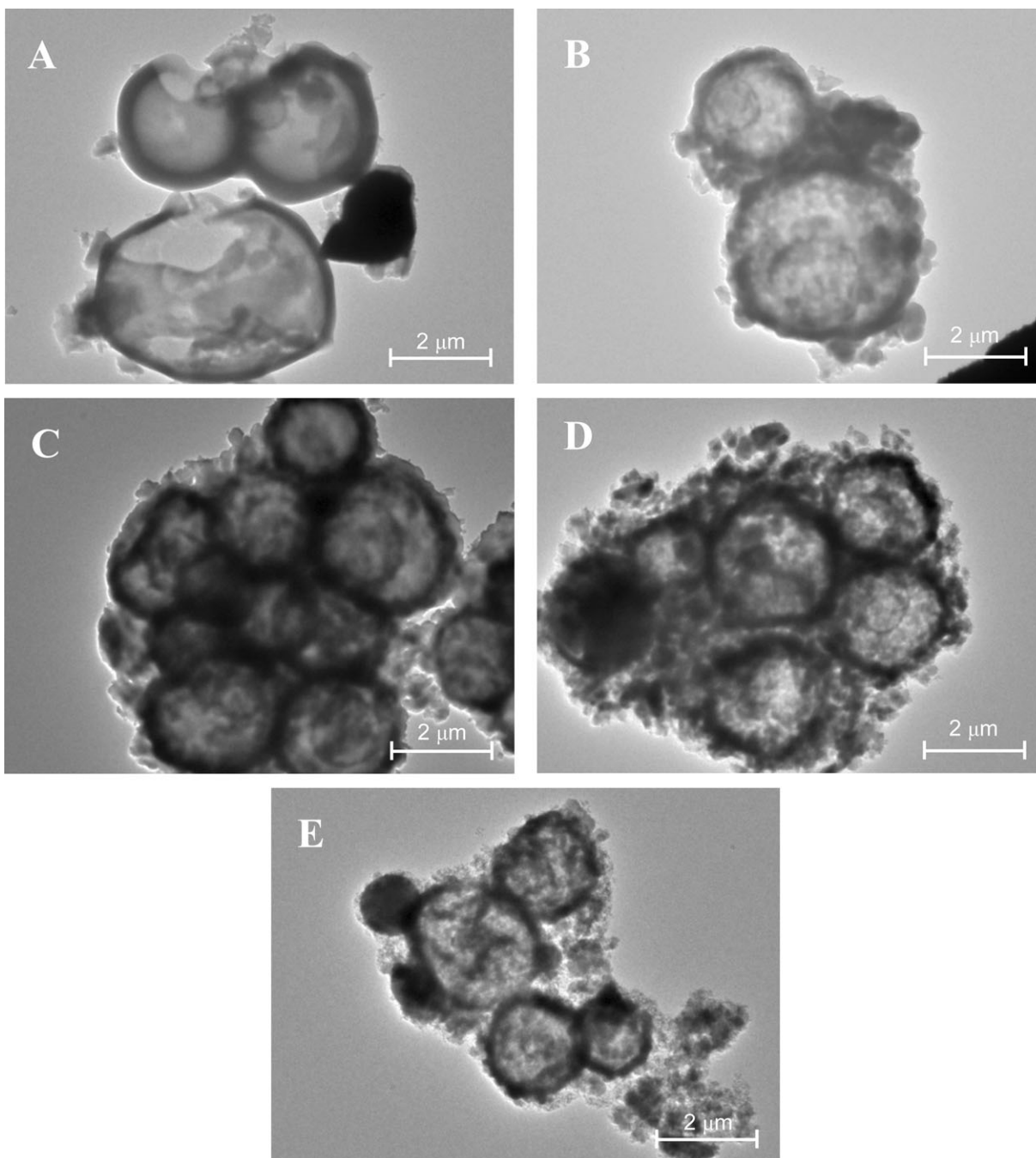


**Figure 6.** FESEM micrographs of the macroporous silica materials: (A) MS1, (B) MS2, (C) M3, (D) M4, and (E) M5. Scale bars = 10  $\mu\text{m}$ .

silica. From the adsorption branches of the nitrogen sorption isotherms, the BET surface areas were calculated to be 227.0, 235.2, 223.7, and 183.9  $\text{m}^2/\text{g}$  for the macroporous silica from the precursors containing 10, 20, 30, and 40 wt % of TEOS, respectively as shown in Figure 8 and Table I. The BET surface areas displayed the maximum while the macroporous silica was prepared with the glassy precursor containing 20 wt % TEOS. It was noted that the values of the BET surface areas did not monotonously decrease with increasing content of TEOS. It is proposed there were two factors that affected the surface area of the macroporous silica: (1) the contents of all of the organic

components and (2) the collapse of pores during the thermal pyrolysis of the glassy precursors. The organic portion in the glassy precursors included the epoxy microspheres and the PGMA chains that were grafted onto the surface of epoxy microspheres. When the glassy precursors were subjected to pyrolysis at elevated temperature, macropores were formed because of the removal of epoxy microspheres, whereas micropores were obtained with the decomposition of other organic components (i.e., PGMA backbones). If all of the porosity survived well in the pyrolysis process, the BET surface area of the resulting macroporous silica would definitely increase with

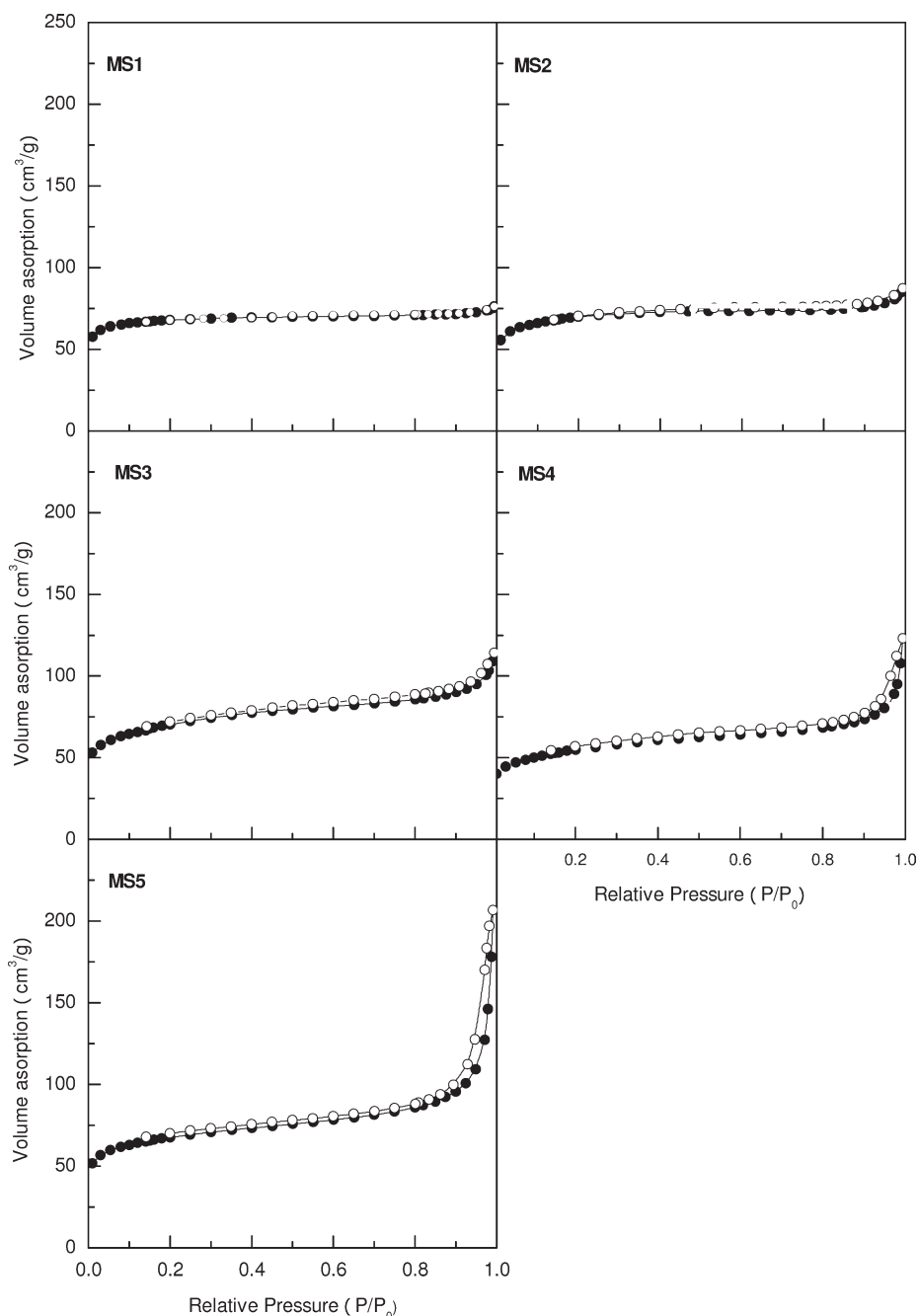




**Figure 7.** TEM micrographs of the macroporous silica materials: (A) MS1, (B) MS2, (C) M3, (D) M4, and (E) M5. Scale bars = 2 μm.

increasing content of APTMS-functionalized epoxy microspheres. However, the results of the BET surface area presented in Table I do not support this speculation. It is plausible that the collapse of the pores was unavoidable, especially for the pyrolysis of polysilsesquioxanes. The collapse of some pores would cause a depression in the BET surface area. For the APTMS-functionalized epoxy microspheres, only the organic–inorganic polysilsesquioxane networks were obtained with the sol–gel process of the trimethoxysilane-bearing epoxy microspheres. The collapse of the pores could have occurred in the process of transformation when the polysilsesquioxane networks were

transformed into the silica networks with oxidation reaction at elevated temperature. It is proposed the collapse in the process of pyrolysis was efficiently suppressed when the tetrafunctional alkoxy silanes (i.e., TEOS) were incorporated to participate in the formation of the crosslinked networks. The higher the content of TEOS was, the fewer pores collapsed with the pyrolysis. In fact, we indeed observed the tendency of the values of the BET surface area to increase with increasing content of TEOS up to 20 wt %. It should be pointed out that the observation that the BET surface areas further decreased with increasing content of TEOS simply accounted for the decrease in the



**Figure 8.** Nitrogen sorption isotherms of the macroporous silica. Solid symbols: adsorption; open symbols: desorption.

content of APTMS-functionalized epoxy microspheres, that is, the porogen.

## CONCLUSIONS

In summary, crosslinked epoxy microspheres with diameters of 5–10  $\mu\text{m}$  were successfully prepared via phase-inverted RIPS with blends of epoxy thermoset with PCL. The surfaces of the crosslinked epoxy microspheres were modified with 2-bromopropionyl groups, and the functionalized epoxy microspheres were used as initiators to perform the surface-initiated ATRP,

and PGMA-grafted epoxy microspheres were successfully obtained. The PGMA-grafted epoxy microspheres were further employed to react with APTMS to obtain epoxy microspheres bearing a great number of trimethoxysilane groups. Co-sol-gel reactions between the APTMS-functionalized epoxy microspheres and tetraethoxysilane (TEOS) were carried out, and organic–inorganic glassy solids were obtained with contents of TEOS up to 40 wt %. The organic–inorganic glassy solids were successfully used as precursors to prepare macroporous silica materials via the pyrolysis at elevated temperature. We found that the macroporous silica possessed BET surface areas in the

range 183.9–235.2 m<sup>2</sup>/g, depending on the mass ratios of APTMS-functionalized epoxy microspheres to TEOS.

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