# Synthesis by a Single-Step Swelling Process and Characterization of Micrometer-Sized Polychloromethylstyrene/Poly(butyl methacrylate) Hemispherical Composite Particles of Narrow Size Distribution

**Sigal Baruch-Sharon, Shlomo Margel**

*Department of Chemistry, Bar-Ilan University, Ramat-Gan 52900, Israel*

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**ABSTRACT:** Polychloromethylstyrene (PCMS) micrometer-sized particles of narrow size distribution were prepared by the dispersion polymerization of chloromethylstyrene in a mixture of ethanol and dimethyl sulfoxide. Micrometer-sized PCMS/poly(butyl methacrylate) hemispherical composite particles of narrow size distribution were prepared by a single-step swelling process of the uniform PCMS template particles with emulsion droplets of butyl methacrylate (BMA) containing benzoyl peroxide, followed by the polymerization of BMA at 73°C within the swollen template particles. The effects of various polymerization parameters, for example, BMA volume, initiator type and concentration, and toluene as the swelling solvent, on the properties (size and size distribution, morphology, polymerization yield, and composition) of the hemispherical composite particles were elucidated. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 108: 3727–3737, 2008

**Key words:** functionalization of polymers; swelling; templates

## INTRODUCTION

Micrometer-sized particles of narrow size distribution have attracted much attention in many applications, including adsorbents for high-pressure liquid chromatography, calibration standards, spacers for liquid crystals, inks, catalysis, and drug delivery.[1–7] Dispersion polymerization is a common method for preparing nonporous, uniform micrometer-sized particles in a single step.[8–12] However, the particles formed by this method possess a relatively small surface area, and their properties, for example, porosity, surface morphology, and functionality, are difficult to manipulate.

Ugelstad and coworkers[13,14] invented a useful multistep swelling and polymerization method for the production of various uniform micrometer-sized particles of controlled desired properties. This basic swelling process was then significantly elaborated by Cheng et al.[15] and Hosoya and coworkers.[16–19] The first step of the multistep swelling method is associated with the activation of template uniform particles [usually polystyrene (PS)] formed by either emulsion polymerization or dispersion polymerization. The activation of the template particles is accomplished by the swelling of the particles dispersed in an aqueous phase with the emulsion of a swelling solvent, for example, dibutyl phthalate or 1-chlorodecane. The first swelling step stimulates the swelling of the template particles in the next steps. When the activation swelling step is completed, the second swelling step takes place by the introduction of the slightly enlarged template particles with monomer(s), an initiator, and a porogen. This can be done in one step or through the sequential addition of each component. The initiator can be added in either the first or second swelling step. The polymerization of the monomers within the uniformly swollen micrometer-sized particles can then be induced by an increase in the temperature. An alternative swelling method, called the *dynamic swelling method*, was developed by Okubo and coworkers.[20–22] According to this method, uniform PS template particles can be swollen enormously, and still maintain their uniformity, by the slow, continuous, dropwise addition of water into an ethanol/water medium containing the template particles and hydrophobic monomer(s) and initiator (e.g., styrene and benzoyl peroxide [BP]). Polymerization can then be performed,

*Correspondence to:* S. Margel (shlomo.margel@mail.biu.ac.il).

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as previously described, by increasing the temperature.

A single-step swelling process for the preparation of micrometer-sized particles of narrow size distribution and controlled properties was recently published by Margel and coworkers.[23–29] According to this process, the swelling of the template particles with the initiator and monomer(s) via a swelling solvent is accomplished in a single step, in contrast to multiple swelling steps where the swelling with these reagents is accomplished in two or more steps. The main differences between the single-step swelling process and the multistep, or Okubo, process are discussed in refs. 23–29.

Particles with a spherical shape are usually produced by the swelling of the PS template particles with monomer(s), which produce polymer(s) miscible with the PS template matrix (e.g., styrene and divinyl styrene), and thus, do not phase separate.[23–26] In contrast, particles with a hemispherical shape are usually produced by the swelling of the template PS particles with monomer(s) [e.g., butyl methacrylate (BMA)], which produce polymer(s) [e.g., poly(butyl methacrylate) (PBMA)] immiscible with the template PS particles.[28,30–33]

This article describes the synthesis and characterization of micrometer-sized polychloromethylstyrene (PCMS)/PBMA, composite particles of hemispherical morphology and narrow size distribution. These composite particles were prepared by a single-step swelling process of uniform PCMS template microspheres with emulsion droplets of BMA containing BP, followed by the polymerization of BMA at 73°C within the swollen template particles. The effects of the various polymerization parameters, such as the BMA volume, initiator type and concentration, and toluene as the swelling solvent, on the properties of the hemispherical composite particles were also elucidated.

## EXPERIMENTAL

### Chemicals

The following analytical-grade chemicals were purchased from Aldrich (Rehovot, Israel) and were used without further purification: BP (98%), styrene, chloromethylstyrene (99%), sodium dodecyl sulfate (SDS), polyvinylpyrrolidone with a molecular weight of 360,000, ethanol, 2-methoxy ethanol, dimethyl sulfoxide, toluene, acetic acid (99.7%), and BMA. Styrene and chloromethylstyrene were passed through activated alumina to remove the inhibitor before use. 2,2′-Azobisisobutyronitrile (AIBN; Aldrich) was recrystallized from ethanol. We purified the water by passing deionized water through an Elgastat Spectrum reverse osmosis system (Elga, Ltd., High Wycombe, United Kingdom).

### Synthesis of the PCMS template particles of narrow size distribution

Uniform PCMS template particles were prepared according to a procedure similar to that described in the literature.[4] In a typical experiment, PCMS particles with an average diameter of 1.6 ± 0.1 μm were formed by the introduction into the reaction flask (0.5 L) of a solution containing polyvinylpyrrolidone (2.3 g) dissolved in a mixture of ethanol (170 mL) and dimethyl sulfoxide (20 mL). The temperature of the mechanically stirred solution (200 rpm) was then preset to 73°C. Nitrogen was bubbled through the solution for about 15 min to exclude air, after which a blanket of nitrogen was maintained over the solution during the polymerization period. A deaerated solution containing the initiator AIBN (0.2 g) and styrene (10 mL) was then added to the reaction flask. The polymerization reaction continued for 24 h and was then stopped by cooling to room temperature. The formed particles were washed by intensive centrifugation cycles with ethanol and then water. The particles were then dried by lyophilization.

### Synthesis of the PS template particles of narrow size distribution

Uniform PS template particles of 1.6 ± 0.3 μm were prepared according to the literature.[9,12]

### Swelling of PCMS and PS template particles with BMA

In a typical experiment, PCMS template particles of 1.6 ± 0.1 μm were swollen with BMA up to approximately 2.3 ± 0.2 μm by the addition to a 20-mL vial of 10 mL of a SDS aqueous solution (1.5% w/v) and 0.5 mL of BMA. BMA emulsion droplets (sizes < 0.4 μm) were then formed by sonication at room temperature (Sonics and Materials, model VCX-750, Tihorn 20KHz) of the former mixture for 1 min. An aqueous suspension (Newtown, Connecticut, USA) (1.75 mL) of the PCMS template particles (7% w/v) was then added to the stirred BMA emulsion. After the swelling was completed and the mixture did not contain any small droplets of the emulsified BMA, as verified by optical microscopy, the diameter of the swollen particles was measured. We prepared PCMS/BMA swollen particles of various properties similarly by changing various swelling parameters, such as the BMA volume.

We swelled PS template particles with BMA by a similar process, substituting the PCMS template particles for the PS.

### Synthesis of uniform micrometer-sized PCMS/PBMA composite particles

In a typical experiment, micrometer-sized PCMS/PBMA composite particles with an average diameter

of 2.3 ± 0.12 μm were prepared by the swelling of the PCMS template particles according to the former procedure with 0.5 mL of BMA containing 5 mg of BP (1% w/v). For polymerization of BMA in the swollen particles, the temperature was raised to 73°C for 20 h. The formed composite particles were washed by intensive centrifugation cycles with water, ethanol, and water again and then dried by lyophilization. We prepared PCMS/PBMA composite particles with various properties (e.g., size and size distribution, morphology, and composition) similarly, by changing the polymerization parameters, for example, BMA concentration, initiator type and concentration, and toluene as the swelling solvent.

### Extraction of the PBMA phase from the PCMS/PBMA composite particles

The dried PCMS/PBMA composite particles were dispersed in acetic acid[34] and then stirred at room temperature for 72 h. The remaining PCMS particles (PCMS phase) were then centrifuged, and the supernatant was then separated from the remaining particles. The PCMS phase particles were then washed by intensive centrifugation cycles with acetic acid and then water and then dried by lyophilization. The supernatant containing the hydrolysis products of PBMA [poly(methacrylic acid) and butanol] in acetic acid was vacuum-dried and left a dried powder of poly(methacrylic acid).

### Posttreatment of the PCMS/PBMA composite particles with toluene

We accomplished the posttreatment of the PCMS/PBMA composite particles with toluene by swelling these PCMS/PBMA composite particles with toluene according to the former described swelling process, substituting the PCMS template particles for the PCMS/PBMA composite particles and BMA for toluene. After completion of the swelling, toluene was removed from the swollen composite particles by evaporation. Briefly, toluene (0.5 mL) was added to 10 mL of a SDS aqueous solution (1.5% w/v). A toluene emulsion was then formed by the sonication of the former mixture at room temperature for 1 h. An aqueous dispersion of the PCMS/PBMA composite particles (1.75 mL, 7% w/v) was then added to the stirred toluene emulsion at room temperature for 2 h. The toluene was then removed by evaporation from the swollen composite particles, and the diameter of the composite particles was measured.

### Characterization of the particles

Optical microscope pictures were obtained with an Olympus microscope (model BX51) (Hicksville, NY, USA). The particles average size and size distribution were determined by the measurement of the diameters of more than 100 particles on optical micrographs with image analysis software from Analysis Auto (Soft Imaging System GmbH, Germany).

Elemental analysis of the various particles was performed with an elemental analysis instrument (model EA1110) from CE Instruments, Thermoquast (Edison, NJ, USA).

Fourier transform infrared (FTIR) analysis was performed with a Bomem FTIR spectrophotometer (model MB100, Hartman & Braun) (Quebec, Canada). The analysis was performed with 13-mm KBr pellets that contained 2 mg of the detected material and 198 mg of KBr. The pellets were scanned over 200 scans at a 4-$cm^{-1}$ resolution.

## RESULTS AND DISCUSSION

### Swelling of the template PCMS particles

PS particles of narrow size distribution are the most common template material used for the preparation of various uniform micrometer-sized particles by different swelling methods.[23–26,28,29] However, PS does not contain functional groups through which simple chemical manipulations, for example, the covalent binding of amino ligands such as proteins, enzymes, and drugs, is possible. In this study, we examined the possibilty of using PCMS instead of PS as template particles for preparing uniform micrometer-sized particles by the single-step swelling process. In contrast to PS, PCMS contains benzylic chlorine groups through which nucleophilic substitution reactions can be achieved for binding appropriate reagents.[35–37] Modified PCMS or related copolymers have been widely used in different processes as bactericide polymers,[38] photosensitizers,[39] solar energy storage units,[40] photoresists,[41] nonlinear optics,[42] and prodrugs for biomedical applications.[43] As a model, we chose to examine the preparation of uniform PCMS/PBMA composite particles by a single-step swelling process of PCMS template particles with BMA, followed by the polymerization of the BMA within the swollen template particles. Figure 1 compares the swelling properties of PS and PCMS particles of similar diameter and size distribution (1.6 ± 0.1 and 1.6 ± 0.3 μm, respectively) as function of BMA concentration. As expected, this figure illustrates that the diameter and size distribution of both PCMS and PS template particles depended significantly on the concentration of BMA. However, Figure 1 shows that in the presence of similar volumes of BMA, the diameter of the swollen PCMS template particles was significantly higher than that of the PS. For example, in the presence of 2.5 mL of BMA, the diameter of the template PCMS and PS particles increased from 1.6

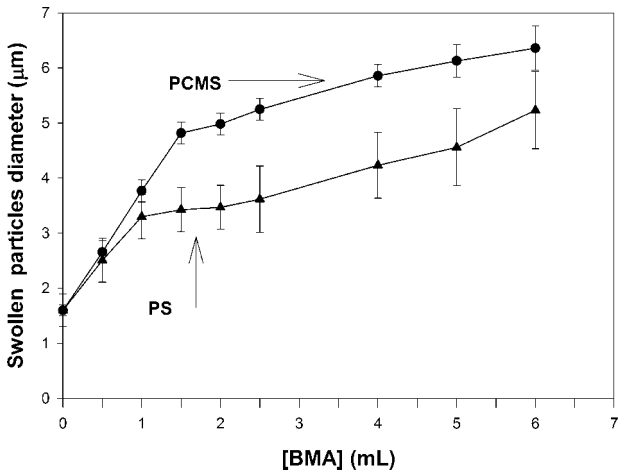


**Figure 1** Effect of the BMA volume on the swelling of the PCMS and PS template particles. The PCMS and PS template particles were swollen with 0.5 mL of BMA, as described in the Experimental section.

± 0.1 to 5.2 ± 0.2 and 3.6 ± 0.6 μm, respectively. This difference in the diameter of the swollen particles was probably due to the higher miscibility of BMA in the PCMS template particles of the PS one. Figure 1 also illustrates that under similar increasing volumes of BMA, the size distribution of the PCMS particles remained narrower than that of the PS. For example, in the presence of 2.0, 4.0, 5.0, and 6.0 mL of BMA, the size distributions of the PCMS particles were ±0.2, ±0.2, ±0.3, and ±0.4 μm, respectively, whereas those of PS were ±0.4, ±0.6, ±0.7, and ±0.7 μm, respectively. When the BMA volume was increased above 6.5 mL, the size and size distribution of both the PCMS and PS template particles increased significantly, and above 9.0 mL of BMA, the particles lost their shape because of their dissolution in the BMA. Similar swelling trials of the template particles with BMA containing 1% BP resulted in similar swelling behavior, as in the absence of BP, which indicated that under the experimental conditions BP did not play any significant role in the swelling of the template particles. Also, as shown in Figure 1, the increase in the diameter (and volume) of the swollen particles was not linearly proportional to the volume of the added BMA. For example, the addition of 1.0 or 4.0 mL of BMA to the PCMS particles led to an increase in the average diameter of the template particles of 231 and 362%, respectively. The first 1.0 mL of BMA increased the diameter of the PCMS particles significantly more than the additional 3.0 mL. This nonlinear behavior was probably due to the packing arrangement of the PCMS chains within the template particles. The degree of entanglement of these chains determined the size (and volume) of the particles. The BMA swelled the template particles by penetrating the PCMS chains of the particles, decreasing their entanglement and, thereby, increasing their counterlength. As a result, the particles were less compact, and their size and volume changed according to their swelling degree.

Figure 2 demonstrates the swelling kinetics of the PCMS template particles by 0.5 mL of BMA. The swelling rate was relatively fast and was completed within about 60 min. Figure 3(A) demonstrates by light microscopy the monodispersity and perfectly round shape of both the PCMS template particles of 1.6 ± 0.1 μm diameter and the BMA swollen particles of 2.6 ± 0.2 μm diameter. The same light microscopy picture was observed for PCMS template particles swollen by 0.5 mL of BMA containing 1% (5 mg) BP.

## PCMS/BMA composite particles

PCMS/PBMA composite particles of narrow size distribution were prepared by the swelling of the PCMS template particles with 0.5 mL of BMA containing 5 mg of BP [Fig. 3(A,B)] followed an increase in the temperature of the swollen particles to 73°C, as described in the Experimental part. The characterization of the formed PCMS/PBMA composite particles was accomplished by light microscopy, FTIR spectroscopy, and elemental analysis, as follows.

## Light microscopy

Figure 3(C) shows by light microscopy the hemispherical morphology of the obtained PCMS/PBMA composite particles, with a dark PCMS phase and a brighter PBMA phase. These composite particles

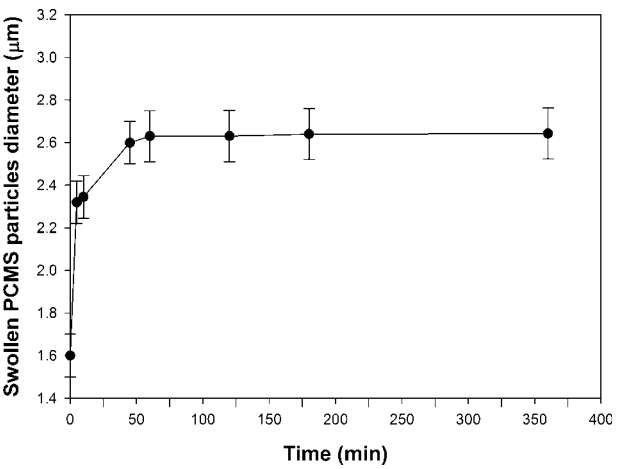


**Figure 2** Swelling kinetics of the PCMS template particles by BMA. The swelling of the template PCMS particles was performed with 0.5 mL of BMA, as described in the Experimental section.

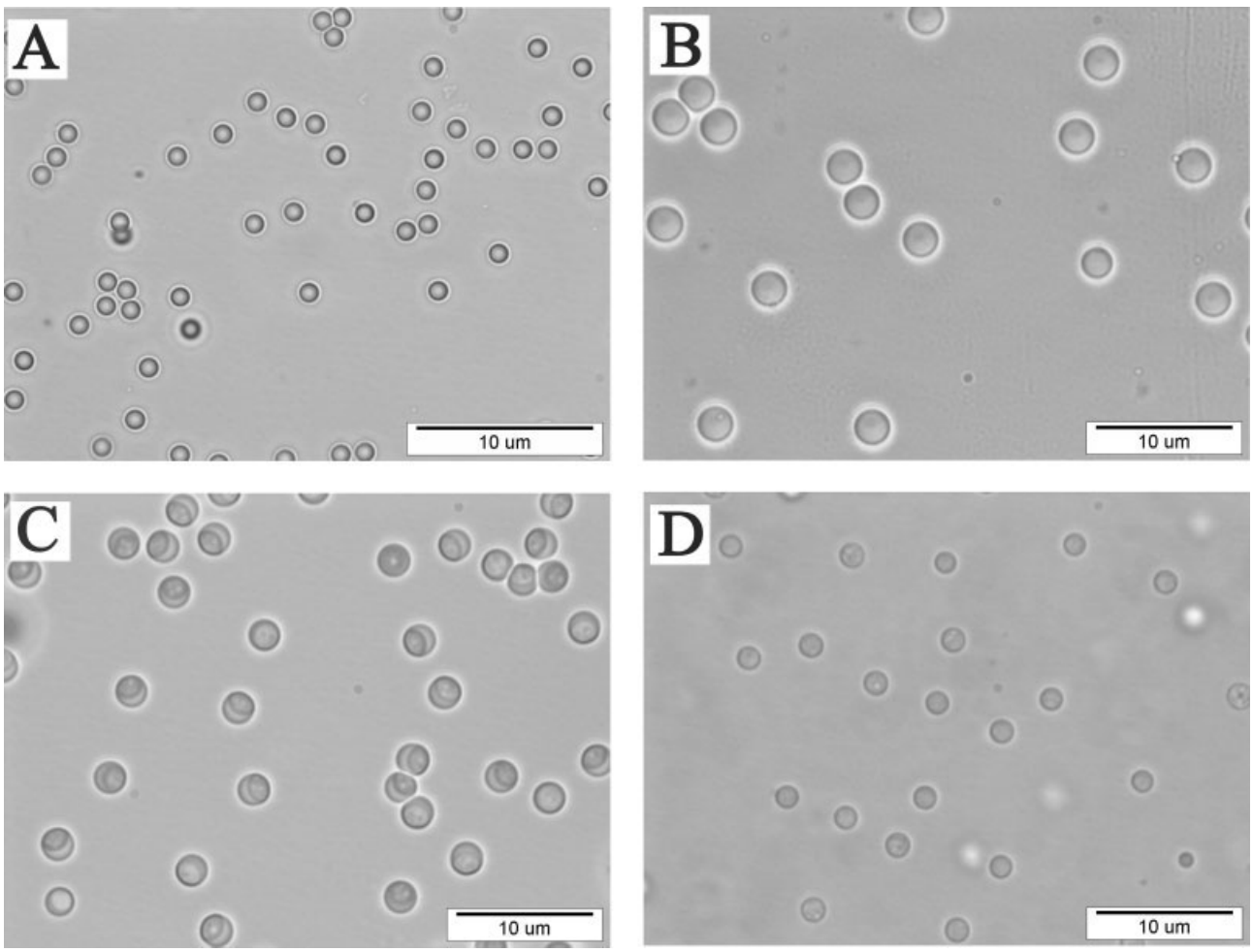


**Figure 3** Light microscopy pictures of the following particles: (A,B) PCMS template particles before and after swelling with BMA, respectively; (C) PCMS/PBMA particles formed by the polymerization of BMA within the swollen PCMS particles; and (D) PCMS phase formed by the dissolution of the PBMA phase of swelling of the PCMS/PBMA composite particles. The swelling of PCMS with 0.5 mL of BMA and the polymerization of BMA within the swollen particles were performed as described in the Experimental section. The dissolution of the PBMA phase of the PCMS/PBMA composite particles with acetic acid was performed as described in the Experimental section.

possessed a diameter and size distribution of 2.3 ± 0.2 μm, a slightly smaller diameter than that of the swollen particles [2.6 ± 0.2 μm; Fig. 3(B)]. Figure 3(D) presents a light microscope picture of the PCMS phase that remained after the dissolution of the PBMA phase belonging to the PCMS/PBMA composite particles with acetic acid, according to the description in the Experimental part. The remaining PCMS phase particles had a spherical shape with a similar size and size distribution as that of the original PCMS template particles, 1.6 ± 0.1 and 1.7 ± 0.2 μm, respectively. We measured the kinetics of formation of the PCMS/PBMA composite particles by following the size increase of the particles as a consequence of the polymerization of BMA within the swollen PCMS template particles, as demonstrated in Figure 4. This figure illustrates the gradual growth of the particles during the first 3 h from 1.6 ± 0.1 to 2.3 ± 0.2 μm, after which the diameter remained constant; this indicated the completion of the BMA polymerization.

## FTIR

Figure 5 depicts the FTIR spectra of the PCMS template particles and the PCMS/PBMA composite particles. Figure 5(A) reveals a typical IR spectrum of PCMS. The absorption peaks at 1494 and 3000–3100 $cm^{-1}$ corresponded to the aromatic —CH stretching bands, those at 2849 and 2922 $cm^{-1}$ corresponded to the —$CH_2$— stretching bands, that at 700 $cm^{-1}$ corresponded to the C—C stretching band, and that at 1266 $cm^{-1}$ corresponded to the C—Cl stretching band. Figure 5(B) shows, in addition to the absorption peaks in Figure 5(A), addi-

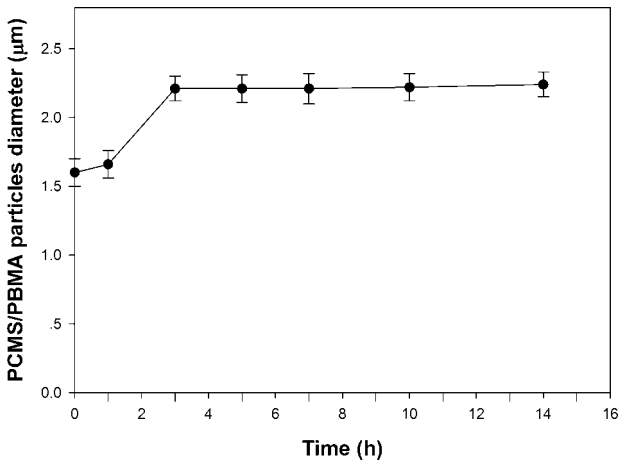


**Figure 4** Kinetics of the BMA polymerization within the swollen PCMS template particles. The swelling of the PCMS template particles with 0.5 mL of BMA and the polymerization of BMA within the swollen particles were performed as described in the Experimental section.

tional peaks at 1100–1300 and 1730 $cm^{-1}$, which corresponded to the carbonyl ester stretching bands belonging to the PBMA part of the PCMS/PBMA composite particles.

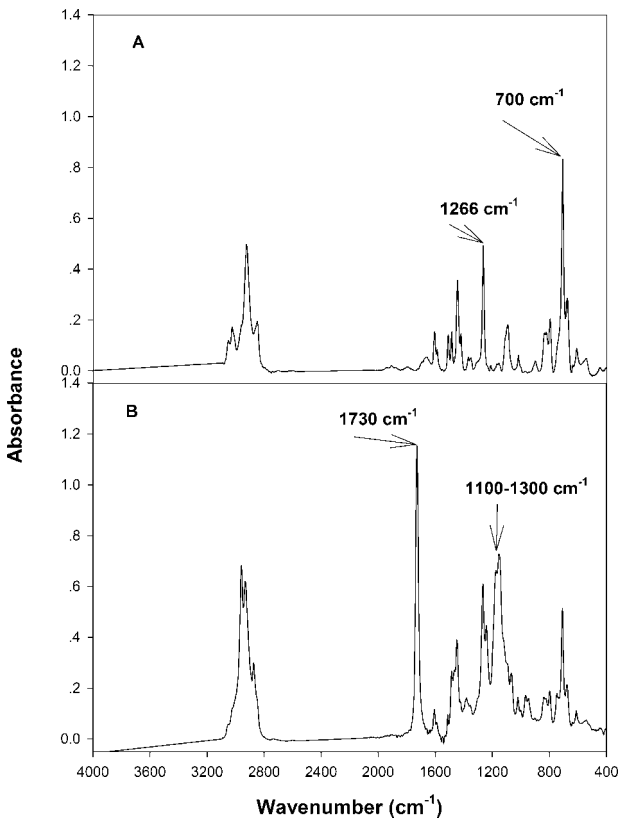


**Figure 5** FTIR spectra of the (A) PCMS template particles and (B) PCMS/PBMA composite particles. The swelling of the PCMS template particles with 0.5 mL of BMA and the polymerization of the BMA within the swollen particles were performed as described in the Experimental section.

### Elemental analysis

The oxygen and chlorine percentages shown in Table I were used to calculated the composition of the PCMS/PBMA composite particles and their phases and the BMA polymerization yield. Cl existed only in PCMS, whereas O existed only in PBMA. Therefore, the ratio between these elements could be used to calculate the composition of the PCMS/PBMA composite particles and the purity of the PCMS phase according to the following equations:

$$\text{PBMA } (\%) = (\%\ \text{O} \times 100)/22.5$$

$$\text{PCMS } (\%) = (\%\ \text{Cl} \times 100)/23.3$$

where 22.5 is the percentage oxygen in pure PBMA and 23.3 is the percentage chlorine in pure PCMS.

Table I indicates that the PCMS/PBMA prepared under the experimental conditions was composed of 36.4% PCMS and 64% PBMA. This relative composition was also used to calculate the BMA polymerization yield, according to the following equation:

$$\text{Polymerization yield } (\%) = W_{\text{PBMA}} \times 100/W_{\text{BMA}}$$

where $W_{\text{PBMA}}$ is the weight of the formed PBMA and $W_{\text{BMA}}$ is the initial weight of the BMA introduced to the polymerization process (0.5 g under the experimental conditions).

$W_{\text{PBMA}}$ could be calculated according to the following equation:

$$W_{\text{PBMA}} = 0.122 \times \%\ \text{PBMA}/\%\ \text{PCMS}$$

where 0.122 is the weight (g) of the PCMS template particles introduced to the swelling process.

**TABLE I**
**Percentages of Oxygen and Chlorine and the Compositions of PCMS/PBMA and Its Phases**

| | wt % | | | |
|---|---|---|---|---|
| Particles | Oxygen | Chlorine | PCMS | PBMA |
| PCMS/PBMA | 14.4 | 8.5 | 36.4 | 64.0 |
| PCMS phase | 5.6 | 17.5 | 75.1 | 24.9 |
| PCMS phase (after toluene treatment) | 5.0 | 18.5 | 79.4 | 22.2 |
| PBMA phase[a] | — | — | — | 100.0 |

The PCMS/PBMA composite particles were prepared as described in the Experimental part. Toluene treatment of the PCMS/PBMA composite particles was performed as described in the Experimental section.

[a] The PBMA phase was extracted from the PCMS/PBMA composite particles with acetic acid, as described in the Experimental section. The purity of the PBMA phase was derived from the oxygen and chlorine analysis of the poly(methacrylic acid) formed by the acetic acid treatment, as described in the Experimental section.

The use of these equations resulted in a BMA polymerization yield of 42.5%.

Table I also indicates that the PCMS phase particles obtained after extraction of the PBMA phase from the composite particles were not pure and were composed of 75.1% PCMS and 24.9% PBMA. On the other hand, this table shows that the PBMA phase was completely pure and did not contain traces of PCMS. The purity of the PBMA phase was derived from the analysis of poly(methacrylic acid) obtained after the evaporation of the supernatant containing the hydrolysis products of PBMA [poly(methacrylic acid) and butanol] in acetic acid, as described in the Experimental part. Elemental analysis of this poly(methacrylic acid) did not indicate the presence of Cl, and the O content was the same as that of pure poly(methacrylic acid) (44%), which indicated that the PBMA phase was completely pure.

### Posttreatment of the PCMS/PBMA composite particles with toluene

A potential way to influence and control the composition of the PCMS phase and to extract some of the PBMA embedded within this phase to the PBMA phase of the composite particles was by the posttreatment of the PCMS/PBMA composite particles with a good solvent (e.g., toluene) for both polymers, as described in the Experimental part.[44] Thereby, it was possible to reconstruct the composite particles from the kinetic state to more thermodynamically stable structures by the posttreatment. When toluene was evaporated gradually from the swollen composite particles, the viscosity of the swollen composite particles increased slowly so that the phase separation proceeded smoothly. The effect of the posttreatment on the composition of the PCMS phase particles is given in Table I, which demonstrates a slight decrease in the percentage of PBMA belonging to the PCMS phase, from 24.9 to 22.2%. This composition change was clearly related to the addition of toluene, as it lowered the viscosity in the polymer particles and enhanced the mobility of both polymer chains, thus enabling the attainment of a more thermodynamically favorable particle composition.[30] However, when the toluene posttreatment was repeated two or three times, no further change in the composition of the PCMS phase was observed, which indicated the strong interaction between the PCMS chains and the remaining PBMA chains embedded within the PCMS. Another possible way to obtain a purer PCMS phase that we tested was by the swelling of the PCMS template particles by a similar way to that described in the Experimental part; we substituted the 0.5 mL of BMA for 0.5 mL of BMA and 0.5 mL of toluene. However, O and Cl analysis of the formed PCMS phase indicated the same composition as obtained by the posttreatment with toluene, that is, 79.4% PCMS and 22.2% PBMA.

### Effects of various polymerization parameters on the properties of the PCMS/PBMA composite particles

#### Effect of the BMA volume

Figure 6(A–C) shows optical micrographs of the PCMS/PBMA composite particles produced by the swelling of the PCMS template particles with increasing volumes of BMA (0.25, 1.0, and 6.0 mL), followed by the polymerization of BMA in the swollen particles according to the description in the Experimental part. Figure 6(A,B) indicates hemispherical composite particle morphology with a dark PCMS phase and a brighter PBMA phase. This figure demonstrate a clear increase in the PBMA phase with an increase in the BMA volume from 0.25 to 1.0 mL. Figure 6(C) indicates that the composite particles prepared in the presence of 6.0 mL of BMA were composed of single and double PCMS domains dispersed in a PBMA continuous phase. This suggests that the percentages of the composite particles having thermodynamically unstable morphologies increased with decreasing viscosity in the polymerizing particles. From the results shown in Figure 6(C), we concluded that PCMS domains deposited homogeneously in the polymerizing particles during polymerization moved and aggregated because the viscosity within the swollen particles was low. However, the particle size of the swollen particles was larger, and the distance through the PCMS domains was so long that the PCMS domains could not aggregate before the viscosity within the polymerizing particle was high in the polymerization process.

Figures 7–9 illustrate the influence of BMA volume on the composition, polymerization yield, and size and size distribution, respectively, of the formed PCMS/PBMA composite particles. Figure 7 indicates that increasing the volume of the BMA from 0.13 to 1.0 mL led to a significant and consistent increase in the PBMA part relative to the PCMS part of the PCMS/PBMA composite particles. For example, increasing the volume of BMA from 0.13 to 0.25, 0.5, and 1 mL increased the weight percentage of PBMA in the composite particles from 31.4 to 54.7, 63.5, and 76.8%, respectively. An additional increase in BMA volume led to a more moderate increase in the weight percentage of PBMA in the composite particles; for example, increasing the volume of BMA from 1 to 2.5 and 6.0 mL increased the weight percentage of PBMA in the composite particles from 76.8 to 83.5 and 94.7%, respectively. Figure 8 shows that when the BMA volume was raised from 0.13 to 0.25

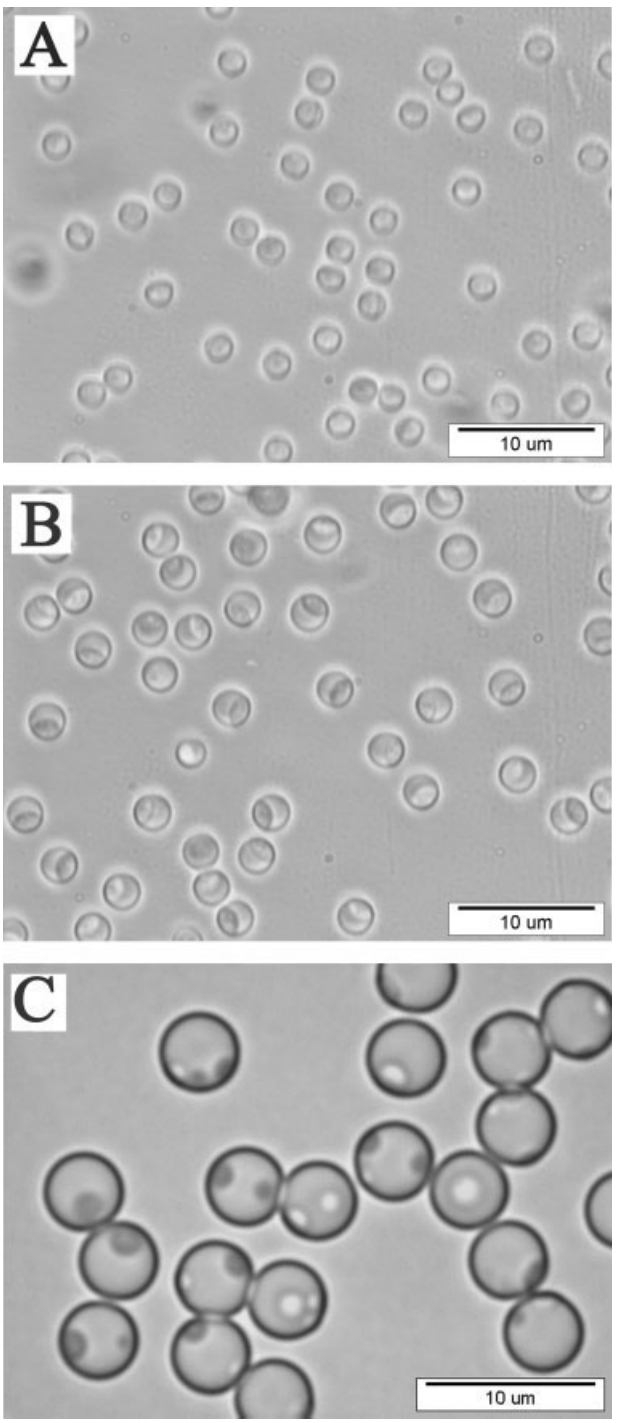


**Figure 6** Light microscopy pictures of the PCMS/PBMA composite particles formed by the swelling of the PCMS template particles with increasing volumes of BMA: (A) 0.25, (B) 1.0, and (C) 6.0 mL. The PCMS/PBMA composite particles were prepared in the presence of different concentrations of BMA, as described in the Experimental section.

mL, the BMA polymerization yield increased to maxima of 43.1 and 59.0%, respectively. A further addition of BMA led to a moderate decrease in the polymerization yield; for example, increasing the BMA volume from 0.25 to 0.5, 1.0, and 6.0 mL decreased

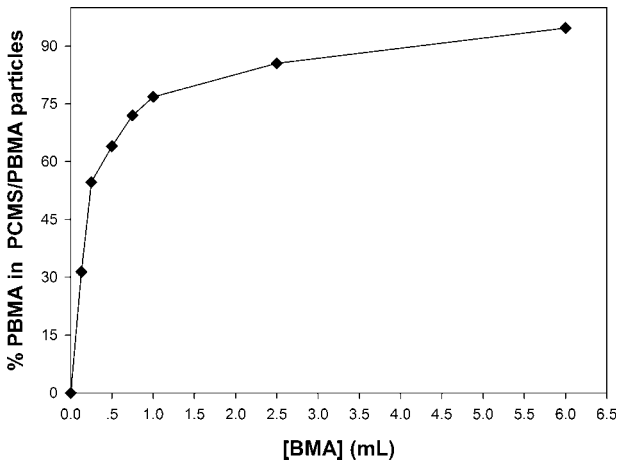


**Figure 7** Effect of the BMA volume on the weight percentage of PBMA in the PCMS/PBMA composite particles. The PCMS/PBMA composite particles were prepared in the presence of different concentrations of BMA, as described in the Experimental section.

the polymerization yield from 59.0 to 42.5, 40.4, and 36.4%, respectively. The gradual decrease in the polymerization yield was probably due to the increasing viscosity within the swollen PCMS particles as the BMA concentration increased. Figure 9 shows the gradual increase in the size distribution and the consistent increase in the diameter of the PCMS/PBMA composite particles as the BMA concentration rose. For example, in the absence and presence of 0.25, 1.5, and 6.0 mL of BMA, the diameter of the composite particles increased from 1.6 ± 0.1 to 2.1 ± 0.2, 2.8 ± 0.2, and 4.9 ± 0.3 μm, respectively. A comparison of Figures 1 and 9 illustrates that for each volume of BMA, the diameter of the PCMS/PBMA composite particles was slightly lower than that of the swollen

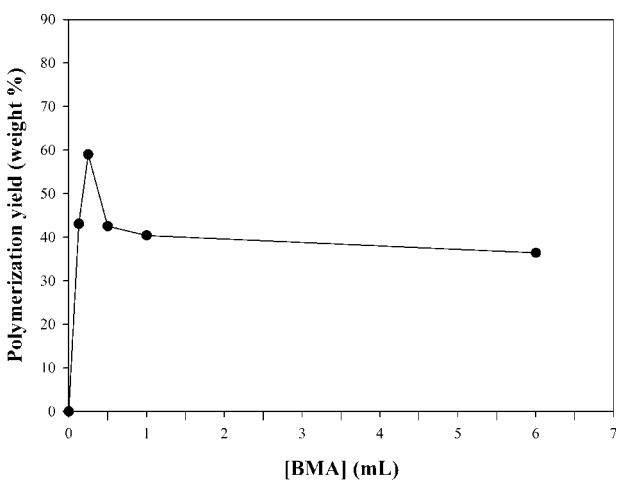


**Figure 8** Effect of the BMA volume on the BMA polymerization yield. The PCMS/PBMA composite particles were prepared in the presence of different concentrations of BMA, as described in the Experimental section.

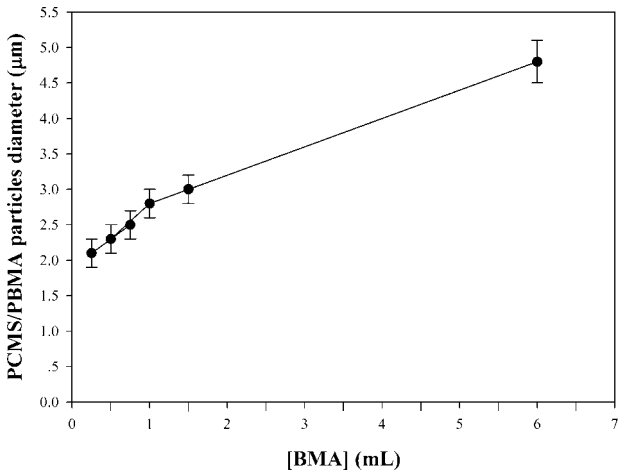


**Figure 9** Effect of the BMA volume on the diameter and size distribution of the PCMS/PBMA composite particles. The PCMS/PBMA composite particles were prepared in the presence of different concentrations of BMA, as described in the Experimental section.

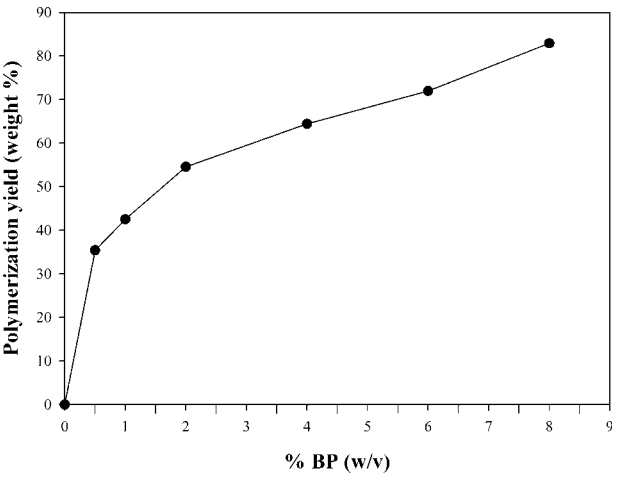


**Figure 11** Effect of the BP concentration on the BMA polymerization yield. The PCMS/PBMA composite particles were prepared in the presence of different concentrations of BP, as described in the Experimental section.

PCMS particles. For example, in the presence of 0.25, 0.5, and 1.5 mL of BMA, the average diameters of the PCMS/PBMA particles were 2.1, 2.3, and 2.8 μm, respectively, whereas those of the swollen particles were 2.4, 2.6, and 4.8 μm, respectively. This difference in the diameters of the swollen and composite particles were probably because the BMA polymerization yield was less than 100%, so that excess BMA was washed off the composite particles, which thus led to a slight shrinking of the particles.

## Effect of the BP concentration

Figures 10–12 illustrate the influence of BP concentration on the composition, polymerization yield, and size and size distribution, respectively, of the formed PCMS/PBMA composite particles. Figure 10 indicates a gradual increase in the PBMA percentage of the PCMS/PBMA composite particles as the BP concentration increased. For example, increasing the BP concentration from 0.5 to 1.0, 2.0, 4.0, and 8.0% led to an increase in the PBMA concentration from 59.2 to 63.5, 69.1, 72.5, and 77.2%, respectively. Figure 11 illustrates similar behavior in the BMA polymerization yield as a function of the BP concentration. For example, increasing the BP concentration from 0.5 to 1.0, 2.0, 4.0, and 8.0% led to an increase in the polymerization yield from 35.4 to 42.5, 54.5, 64.4, and 82.9%, respectively. Figure 12 indicates that an increase in the concentration of the initiator BP

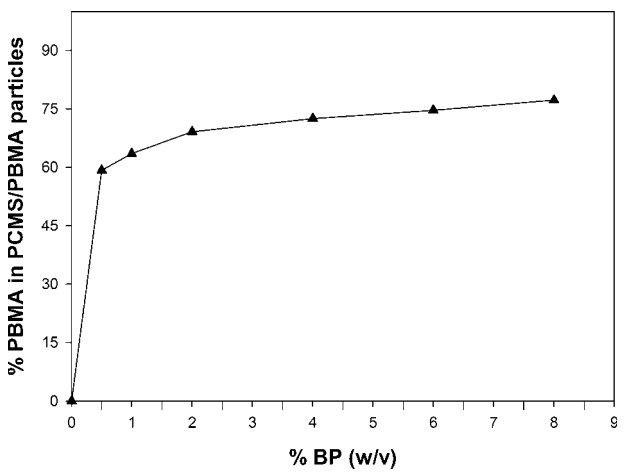


**Figure 10** Effect of the BP concentration on the weight percentage of PBMA in the PCMS/PBMA composite particles. The PCMS/PBMA composite particles were prepared in the presence of different concentrations of BP, as described in the Experimental section.

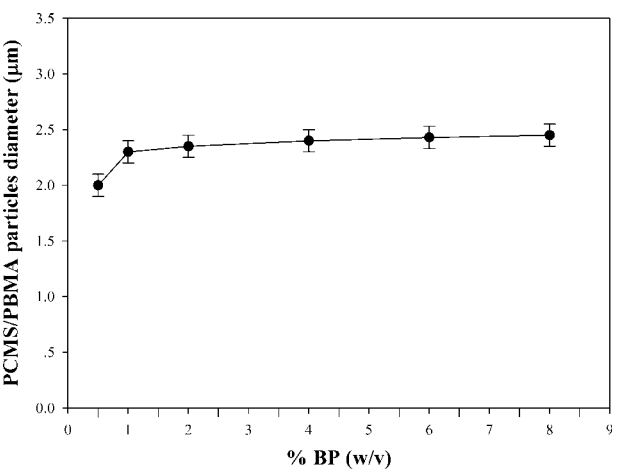


**Figure 12** Effect of the BP concentration on the diameter and size distribution of the PCMS/PBMA composite particles. The PCMS/PBMA composite particles were prepared in the presence of different concentrations of BP, as described in the Experimental section.

**TABLE II**
**Effects of the Initiator Type on the Composition, Polymerization Yield, and Diameter of the PCMS/PBMA Composite Particles**

| | PCMS/PBMA composite particles | | | |
|---|---|---|---|---|
| | wt % | | | |
| Initiator type | PCMS | PBMA | Polymerization yield (wt %) | Diameter (μm) |
| BP | 36.5 | 63.5 | 42.5 | 2.3 ± 0.1 |
| AIBN | 60.2 | 39.8 | 16.1 | 1.8 ± 0.1 |

The PCMS/PBMA composite particles were prepared in the presence of 1% (w/$v_{BMA}$) BP or AIBN, as described in the Experimental section.

from 0.5 to 8.0% did not affect the size distribution of the PCMS/PBMA composite particles. On the other hand, increasing the BP concentration from 0.5 to 1.0% led to an increase in the diameter of the composite particles from 2.0 ± 0.1 to 2.3 ± 0.1 μm, whereas additional increases in the BP concentration, for example, 4.0 and 8.0%, led only to a slight increase in the diameter, for example, 2.4 ± 0.1 and 2.5 ± 0.1 μm, respectively. A similar influence of the initiator concentration was previously reported by Boguslavsky et al.[45] and others.[12,46–49] According to their explanation, increasing the initiator concentration caused an increase in the concentration of the oligomeric radicals and, thus, in the number of PBMA chains. This may have led to an increase in the size, polymerization yield, and the PBMA percentage of the composite particles.

### Effect of the initiator type

Table II illustrates the effect of the initiator type on the composition, polymerization yield, and size and size distribution, respectively, of the formed PCMS/PBMA composite particles. This table illustrates that in the presence of 1% (w/v of BMA) of BP or AIBN, the PBMA percentage, polymerization yield, and size of the PCMS/PBMA were higher than those observed with AIBN, for example, PBMA percentage in the composite particles (63.5 vs 39.8%), BMA polymerization yield (42.5 vs 16.1%), and diameter (2.3 ± 0.1 vs 1.8 ± 0.1 μm). These differences were probably due to the lower initiator efficiency of AIBN compared to BP, as already demonstrated in previous publications.[50,51] Benzoyloxy radicals were seen as much more reactive than cyanopropyl radicals by plucking hydrogens and initiating polymerization with a dodecyl methacrylate radical mechanism.[50]

## CONCLUSIONS

PS particles of narrow size distribution are the most common template material used for the preparation of various uniform micrometer-sized particles by different swelling methods. However, PS does not contain functional groups through which simple chemical manipulations, for example, covalent binding of amino ligands such as proteins, enzymes, and drugs, are possible. In this study, we examined the possibility of using PCMS instead of PS as template particles for preparing uniform micrometer-sized hemispherical particles by the single-step swelling process. For this purpose, uniform PCMS template particles were swollen with emulsion droplets of BMA containing BP, followed by polymerization of the BMA at 73°C within the swollen template particles. The effects of various polymerization parameters, for example, BMA volume, initiator type and concentration, and toluene, on the properties (size and size distribution, morphology, polymerization yield, and composition) of the hemispherical PCMS/PBMA composite particles were elucidated. We plan in future work to continue these studies, especially the preparation of bifunctional PCMS/PBMA composite particles. We will accomplish this by polymerizing BMA within swollen PCMS template particles in the presence of a hydrophilic functional acrylate monomer such as acrylic acid (sodium salt) dissolved in the aqueous continuous phase. Thus, the surface PBMA oligoradicals will copolymerize with the acrylic acid, thereby generating poly(acrylic acid) (PAA) brushes attached to the PBMA phase of the composite particles. The formed PCMS/PBMA–PAA will then be used for various manipulation purposes, for example, the preparation of hydrophilic/hydrophobic particles by attachment of covalently 1-amino dodecane to the PCMS phase of the PCMS/PBMA–PAA composite particles and/or the preparation of particles bearing two different bioactive reagents, by the binding, for example, of an enzyme to the PCMS phase (through the chloromethyl groups) and biotin to the PBMA–PAA phase (via the carbodiimide activation method). In addition to these future plans, efforts to prepare, characterize, and use PCMS/PBMA and PCMS/PBMA–PAA nanosized particles will also be made.

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