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Poly(ethylene glycol)-Coated Monodisperse Micron-Sized Composite Polymer Particles

Hasan Ahmad and Klaus Tauer*

Max Planck Institute of Colloid and Interfaces, Am Mühlenberg, D 14476 Golm, Germany

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ABSTRACT: Polystyrene/poly(styrene−poly(ethylene glycol) monomethacrylate) or PS/P(S−PEGMMA) composite polymer particles in the size range of one to several microns were prepared by seeded copolymerization. Monodisperse micron-sized polystyrene (PS1) particles were first prepared by dispersion polymerization, which were then used as seed particles to carry out seeded copolymerization with styrene and poly(ethylene glycol) monomethacrylate (PEGMMA). Several micron-sized polystyrene (PS2) particles were prepared from monodisperse micron-sized PS1 particles by a modified activated swelling method. These PS2 particles were finally used as seed particles to carry out seeded copolymerization with styrene and PEGMMA. For comparison, some swelling experiments were also carried out in the presence of macromonomer. The size distribution and particle morphology were analyzed by light and scanning electron microscope. The FTIR-ATR technique was used to detect the presence of poly(ethylene glycol) or PEG units on the surface of particles. The results indicate that seeded copolymerization in the final step is the best way to prepare several micron-sized composite polymer particles containing PEG on the surface.

Introduction

Polymer particles with polar functional groups on the surface are widely utilized in biomedical applications, particularly for protein immobilization and cell adhesion studies. Depending on the size and morphology, the particles prepared from polar monomers like 2-hydroxyethyl methacrylate, glycidyl methacrylate, etc., are also considered to be useful for use as size-exclusion HPLC packings.[1−3] Poly(ethylene glycol) (PEG) is another polar unit, which has many interesting properties like high biocompatibility, mechanical and thermal stability, and stealth properties in the reticulo-endothelial system. It has a bizarre solubility pattern, and it is soluble both in water and in many organic solvents.[4−6] PEG attached to an insoluble polymer matrix is considered to be useful as a valuable support for peptide and polynucleotide synthesis.[6−9] For the optimization of continuous flow peptide synthesis and mass transfer in chromatography, the diffusion phenomenon has been considered as important, which is subsequently controlled by the size and monodispersity of the polymer particles. In a previous article,[10] we reported the preparation of several micron-sized polystyrene (PS) particles by seeded polymerization of monodisperse PS seeds with small amount of styrene in the presence of poly(ethylene glycol)-azo initiator. Although we successfully prepared such polymer particles, the concentration of PEG on the surface of particles was too low and could not be detected by FTIR, because it was derived only from the initiator fragments.

The objective of this contribution is to increase the concentration of PEG on the surface of particles by covalently immobilizing PEG derived from macromonomers. For this a series of polystyrene/poly(styrene−poly(ethylene glycol) monomethacrylate) or PS/P(S−PEGMMA) composite polymer particles in the size range of 1−10 μm were prepared. These polymer particles may find application not only for the synthesis of peptide and polynucleotide but also as stationary phase for HPLC and as supports for affinity chromatography and biological catalysts. In this work, styrene and PEGMMA with average molecular weights of PEG chains of 1000 and 4000 g mol^{-1} (PEGMMA1000 and PEGMMA4000) were used during seeded copolymerization in the presence of 1−8 μm sized PS seed particles. Depending on the sizes, the PS seed particles were produced by dispersion polymerization and modified by the activated swelling method. It may be mentioned that symmetrical PEG-azo initiator with PEG of 200 g mol^{-1} (PEGA200) was used during seeded copolymerization.

Experimental Section

Materials and Methods. Styrene from Aldrich was distilled under reduced pressure to remove inhibitors and preserved in a refrigerator. The macromonomers PEGMMA1000 and PEGMMA4000 from ABCR GmbH and Co. (Karlsruhe, Germany) were preserved in the refrigerator and used as received. 2,2′-Azobis(isobutyronitrile) (AIBN) from Fluka and benzoyl peroxide (BPO) from Aldrich were both recrystallyzed from methanol before use. PEGA200 was synthesized as described elsewhere.[11,12] Poly(vinylpyrrolidone) (PVP) from Sigma with molecular weight of 3.6×10^5 g mol^{-1} was used as a polymeric stabilizer. Tricaprylylmethylammonium chloride (aliquate^{336}), a quaternary ammonium salt, from Fluka was used as a costabilizer. 1-Chlorododecane (CD) from Fluka was used as a hydrophobe during swelling experiments. Poly(vinyl alcohol) or PVA type W25/100 (saponification number 100; degree of hydrolysis 90−93%; viscosity at 20 °C of 4% aqueous solution 25 mPa s) from Wacker Polymer Systems, Germany, was used as steric stabilizer to stabilize monomer swollen particles. Deionized water was taken from a Seral Purelab Plus system (18 MΩ cm^{-1}) and degassed before use. Other chemicals were of reagent grade and used without any further purification.

Scanning electron microscopy or SEM (LEO Electron Microscopy Ltd., UK) as well as transmission electron microscopy or TEM (Zeiss EM 912 Omega) was used to characterize polymer particles. A light microscope (Olympus BX50, Japan) was used to see the images of styrene minidroplets and PS seeds swollen with CD and monomers. FTIR-ATR spectra were recorded with a FTS 6000 spectrometer (Biorad) with a horizontal ATR accessory (Zn−Se crystal) form Pike Technologies. Particle size distributions and coefficient of variations

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* Corresponding author. E-mail: ktau@mpikg-golm.mpg.de.

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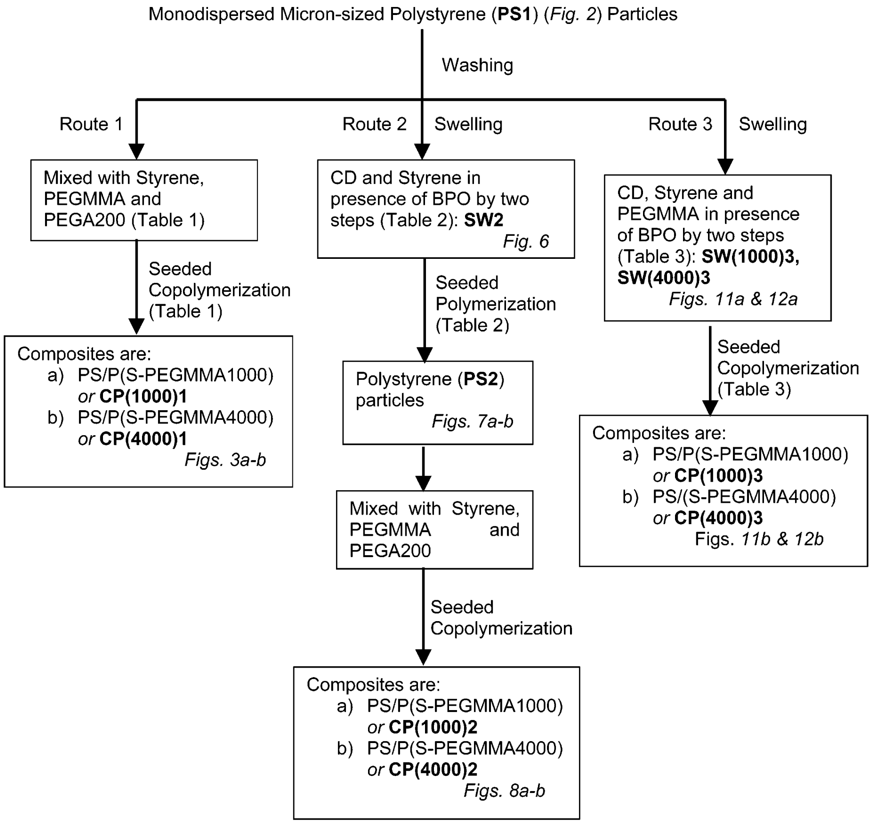

Figure 1. Scheme outlining the production of monodisperse micron-sized composite polymer particles by three different routes. Bold characters represent the abbreviated name of particles.

(CV) were calculated by enumerating at least 600 particles per sample of either electron or light microscopy pictures. It is to note that after seeded polymerizations unwashed samples were examined with electron or light microscopy in order to check whether secondary nucleation took place. Before the application of particles either as seed or before characterization by FT-IR spectroscopy, the samples were washed by repeated centrifugation and redispergation in order to remove any byproducts.

Preparation of Polystyrene (PS1) Particles by Dispersion Polymerization. PS1 particles were prepared batchwise according to standard procedures with a slight modification[13] in a four-necked glass reactor with a heating jacket to control the polymerization temperature. The reactors were equipped with a stirrer, a reflux condenser, and a nitrogen inlet. 20 g of styrene, 0.8 g of PVP, and 0.228 g of aliquate[336] were taken inside the reactor containing 100 g of ethanol and 5 g of water. Polymerization was carried out in the presence of 1% AIBN relative to the amount of monomer at 70 °C for 24 h in a nitrogen atmosphere.

Seeded Copolymerizations/Polymerizations of PS1 Particles. PS1 particles prepared by AIBN were washed several times by replacing the continuous phase with distilled deionized water. Then seeded copolymerizations of PS1 particles were carried out with styrene and PEGMMA in the presence of PEGA200 as initiator. Two different macromonomers represented as PEGMMA1000 and PEGMMA4000 with PEG of molecular weights of 1000 and 4000 g mol^{-1} were used, respectively, during seeded copolymerization. In each case, a mass ratio of seed particles to monomer mixture was 1/0.8. The monomer mixture was composed of styrene: PEGMMA in a molar ratio of 1:1.5. Polymerizations were carried out at 70 °C for 10 h in a nitrogen atmosphere. The conditions are detailed in Table 1, and the process has been summarized in a scheme under route 1 (Figure 1). The produced composite particles are represented as CP(1000)1 and CP(4000)1.

Table 1. Preparation of PS/P(S−PEGMMA) Composite Polymer Particles by Seeded Copolymerization[a]

ingredients[b]	CP(1000)1	CP(4000)1
PS1 emulsion[c]	10.627 g	10.627 g
styrene	0.32 g	0.32 g
PEGMMA1000	4.9267 g	
PEGMMA4000		19.7068
PEGA200	0.168 g	0.168 g
water	50 g	50 g

[a] 70°C, N_2, 100 rpm, 10 h. [b] Abbreviations: PS = polystyrene; PEGMMA1000 and PEGMMA4000 = poly(ethylene glycol) monomethacrylate with PEG of 1000 and 4000 g mol^{-1}; PEGA200 = poly(ethylene glycol)-azo initiator with PEG of 200 g mol^{-1}. [c] Polymer solid, 94.1 g L^{-1}.

The washed micron-sized PS1 particles were used as seed particles to prepare bigger particles in the size range of 2−10 μm. For this, the activated swelling method[14−16] was used with some minor modifications. PS1 seed particles were first swollen with CD minidroplets prepared by magnetic stirring and ultrasonication from a mixture of CD, sodium dodecyl sulfate (SDS), and water. During swelling acetone (2 vol %) was added to facilitate the diffusion of CD through the continuous phase. Before going to the next step, most of the acetone was tried to remove simply by heating at 40 °C for 30 min. PS1 seeds swollen with CD were then swollen with styrene minidroplets prepared by magnetic stirring and ultrasonication from a mixture of styrene, SDS, and BPO. The swelling ratio of styrene/PS1 particles (w/w) was 200/1. Water was used as a continuous phase. The produced PS1 seeds swollen with CD and styrene are named as SW2. Before seeded polymerization Fremy's salt (potassium nitrosodisulfonate), a water-soluble inhibitor, was added to prevent polymerization in the continuous phase. The polymerization conditions are summarized in Table 2, and the process is detailed shortly under route 2 in Figure 1. The produced PS2 particles contained only a small amount of submicron-sized particles which were easily removed during washing by serum replacement before carrying out second-step seeded copolymerization with styrene and macromonomers PEGMMA1000 and PEGMMA4000 in the

Table 2. Preparation of PS2 Particles by Seeded Polymerization Utilizing Modified Activated Swelling Technique[a]

ingredients	
CD Emulsion[b]	
CD	0.08 g
SDS	0.025 g
water	12 g
Seed Emulsion	
PS1 particles	0.04 g
SDS	0.05 g
water	25 g
Monomer Emulsion[c]	
styrene	8.0 g
SDS	0.075 g
BPO	0.12 g
water	30 g

[a] Abbreviations: CD = 1-chlorododecane; SDS = sodium dodecyl sulfate; PS1 = polystyrene; BPO = benzoyl peroxide. [b] CD emulsion was prepared by magnetic stirrer, 900 rpm, 1 h, and then ultrasonication for 2 min, amp 90°. CD and seed emulsions were mixed and stirred at 200 rpm for 24 h at 35°C. 0.25 g of SDS dissolving in 100 mL of water was added collectively to stabilize the system. [c] Monomer emulsion was prepared by magnetic stirrer, 900 rpm, 1 h, and then ultrasonication for 8 min, amp 90°. PS seeds swollen with CD were then mixed with monomer emulsion, stirred at 200 rpm for 24 h at 30°C, 0.3 g of poly(vinyl alcohol) dissolving in 30 mL of water was added collectively. 10^{-4} mol/L of Fremy's salt was added before seeded polymerization at 70 °C, N_2, 100 rpm, 24 h.

Table 3. Preparation of PS/P(S−PEGMMA) Composite Polymer Particles by Seeded Copolymerization Utilizing the Modified Activated Swelling Technique[a]

ingredients	CP(1000)3	CP(4000)3
CD Emulsion[b]		
CD	0.08 g	0.08 g
SDS	0.025 g	0.025 g
water	12 g	12 g
Seed Emulsion		
PS1 particles	0.04 g	0.04 g
SDS	0.05 g	0.05 g
water	25 g	25 g
Monomer Emulsion[c]		
styrene	7.0 g	
PEGMMA1000	10.264 g	
PEGMMA4000		39.068 g
SDS	0.1 g	0.1 g
BPO	0.12 g	0.12 g

[a] Abbreviations: see Tables 1 and 2. [b] CD emulsion was prepared by magnetic stirrer, 900 rpm, 1 h, and then ultrasonication for 2 min, amp 90°. CD and seed emulsions were mixed and stirred at 200 rpm for 24 h at 35°C. 0.25 g of SDS dissolving in 100 mL of water was added collectively to stabilize the system. [c] Monomer emulsion was prepared by magnetic stirrer, 900 rpm, 1 h, and then ultrasonication for 8 min, amp 90°. PS seeds swollen with CD were then mixed with monomer emulsion, stirred at 200 rpm for 24 h at 30°C, 0.3 g of poly(vinyl alcohol) dissolving in 30 mL of water was added collectively. 10^{-4} mol/L of Fremy's salt was added before seeded copolymerization at 70 °C, N_2, 100 rpm, 24 h.

presence of PEGA200. During each seeded copolymerization, a mass ratio of 1/0.5 was maintained between seed particles and monomer mixture where the monomer mixture was composed of styrene and PEGMMA in a molar ratio of 1:1. These copolymerizations were carried out at 60 °C for 10 h in a nitrogen atmosphere. These composite particles are abbreviated as CP(1000)2 and CP(4000)2.

For a comparative study two different swelling experiments of micron-sized PS1 seed particles were carried out according to the scheme detailed in Figure 1. First micron-sized PS1 seed particles were swollen with CD emulsion in the same way as described above. In the second step PS1 seeds preswollen with CD were swollen with a monomer emulsion prepared from a mixture of styrene, PEGMMA, SDS, and BPO. Both macromonomers, PEGMMA1000 and PEMMA4000, were used during swelling experiments. The swelling ratio of (styrene + PEGMMA)/PS1 particles (w/w) was 200/1. Then seeded copolymerizations of the produced SW(1000)3 and SW(4000)3 were carried out under identical conditions. The produced polymer particles are named CP(1000)3 and CP(4000)3, respectively.

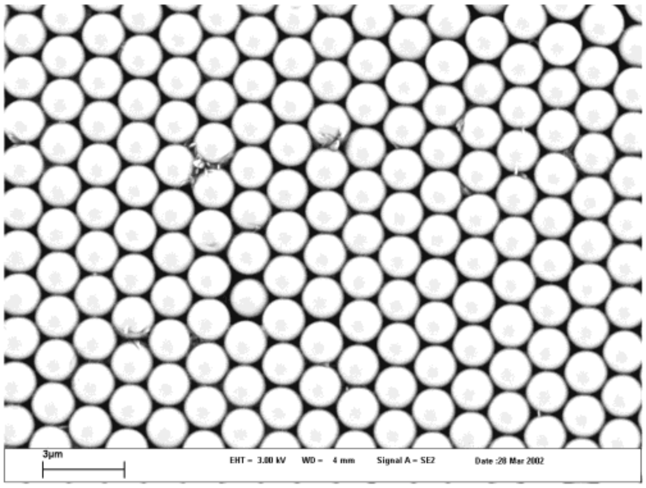

Figure 2. SEM photograph of PS1 particles prepared by dispersion polymerization.

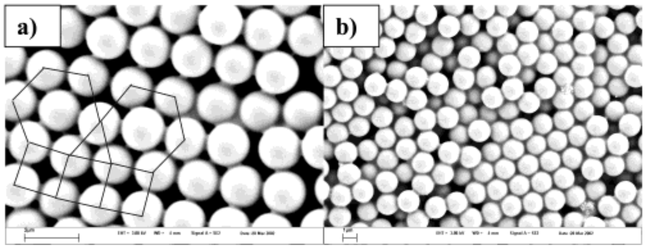

Figure 3. SEM photographs of unwashed (a) CP(1000)1 and (b) CP(4000)1 composite polymer particles prepared by seeded copolymerization in the presence of 1.65 μm sized PS1 seed particles.

Results and Discussion

Figure 2 shows the SEM photograph of PS1 particles prepared by dispersion polymerization. The particles are spherical, have a smooth homogeneous surface, and are arranged in an almost perfectly ordered two-dimensional hexagonal pattern. The size distribution is fairly narrow with average diameter and CV as 1.65 μm and <1%, respectively.

Figure 3 shows the SEM photographs of unwashed CP(1000)1 (Figure 3a) and CP(4000)1 (Figure 3b) composite polymer particles obtained after seeded copolymerization of styrene and macromonomer with 1.65 μm sized PS1 seed particles. Figure 3a shows that the CP(1000)1 composite polymer particles are arranged in an unusual way that is in both hexagonal and cubic patterns as is indicated by the lines in the left part of Figure 3a. This replica also shows the region of hexagonal loose packing, which might indicate a transition to cubic arrangement. Such an arrangement is not common and observed occasionally with monodisperse particles and is referred to as twin formation.[17] In both photographs no submicron-sized (S−PEGMMA) copolymer particles were observed. This indicates that in each case seeded copolymerization proceeds smoothly, that

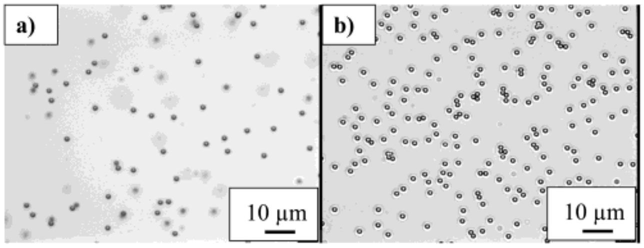

Figure 4. Light microscopic photographs of (a) CP(1000)1 and (b) CP(4000)1 composite polymer particles prepared by seeded copolymerization in the presence of 1.65 μm sized PS1 seed particles.

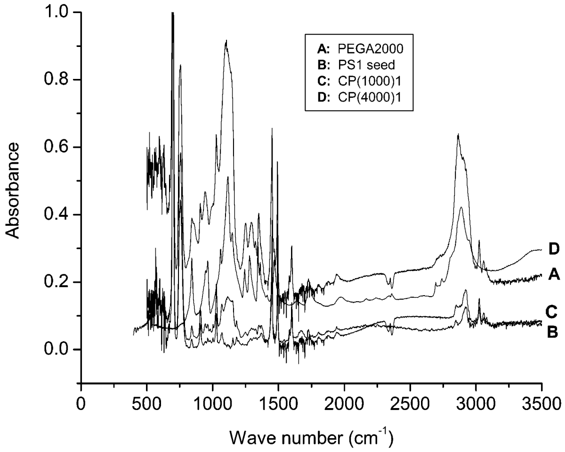

Figure 5. FTIR-ATR spectra of PEGA2000, PS1 seeds, and CP(1000)1 and CP(4000)1 composite polymer particles. In all cases seeds and composite particles were repeatedly washed.

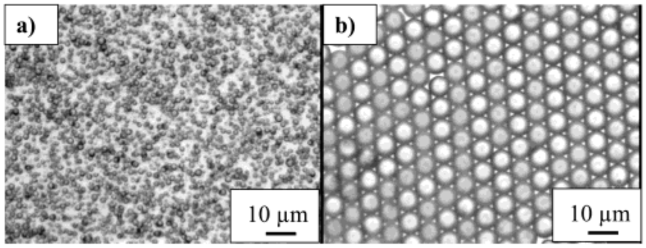

Figure 6. Light microscopic photographs of (a) styrene minidroplets prepared by magnetic stirring and ultrasonication and (b) PS1 seeds swollen with CD and styrene monomer (SW2) prepared under the conditions listed in Table 2.

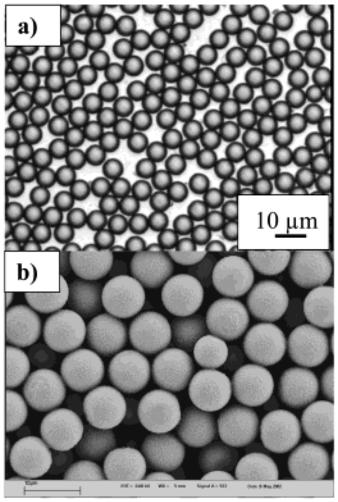

Figure 7. (a) Light microscopic and (b) SEM photographs of PS2 particles prepared by seeded polymerization of SW2.

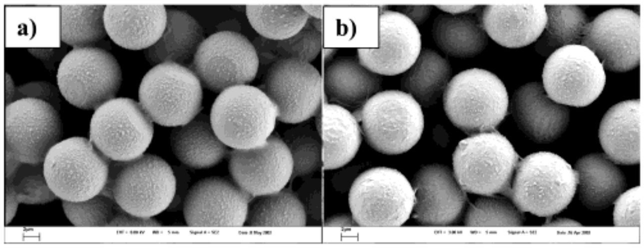

Figure 8. SEM photographs of unwashed (a) CP(1000)2 and (b) CP(4000)2 composite polymer particles prepared by second-step seeded copolymerization in the presence of 8.1 μm sized PS2 seed particles.

is, without any secondary nucleation. The surfaces of composite polymer particles are not smooth, particularly visible at higher magnification, and coagulated as some soluble block copolymers may be deposited during drying of the sample preparation for SEM. In contrast, light microscopic pictures of composite polymer particles shown in Figure 4 show stable colloidal dispersion. The presence of hairy structures derived from the macromonomer is considered to be enough to provide steric stabilization to the colloidal system in the absence of surfactant. Figure 5 shows the FTIR-ATR spectra of PEGA2000 as reference for PEGA initiators, PS1 seeds, and CP(1000)1 and CP(4000)1 composite polymer particles. For all polymer particles, these spectra were recorded after repeated washing to remove any unreacted macromonomer or soluble copolymer. In both composite polymer particles the characteristic peaks due to the PEG unit appeared at around 1100 and 2800 cm^{-1}, respectively. In the case of CP(4000)1 composite particles the magnitude of the peak was comparatively higher. In contrast, no such peak was observed in PS1 seed particles. These results indicate that the prepared composite polymer particles contain PEG unit on the surface of particles.

Figure 6 shows light microscopic pictures of styrene minidroplets and SW2 prepared by modified activated swelling as proposed by Ugelstad and his group.[14−16] A complete absorption of styrene monomer by the PS1 seed particles swollen with CD took place, and the swollen particles were monodisperse with an average diameter and CV of 9.42 μm and <1%, respectively. Light microscopic and SEM photographs of the PS2 particles obtained after seeded polymerization of SW2 are shown in Figure 7. The produced PS2 particles are fairly monodisperse, having an average diameter of about 8.1 μm as measured from the light microscopic pictures. The SEM photograph shows that the surface of the PS2 particles is not smooth and may possibly been damaged during either drying or sample observation. These PS2 particles after repeated washing were then used as seed particles for second-step seeded copolymerization with styrene and PEGMMA in the presence of PEGA200 as initiator.

Figure 8 shows the SEM photographs of unwashed CP(1000)2 (Figure 8a) and CP(4000)2 (Figure 8b) composite polymer particles prepared by second-step seeded copolymerization. In both cases during seeded copolymerization no submicron-sized copolymer particles were produced, which indicates that seeded copolymerization proceeded smoothly without any secondary nucleation. The composite polymer particles are fairly monodisperse and visible bridging occurring during drying possibly due to the entanglement of attached hairy structures of PEG. In contrast, Figure 9 shows light microscopic

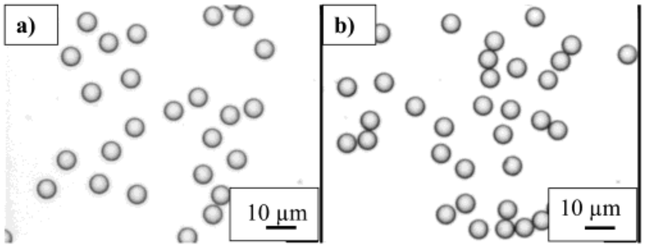

Figure 9. Light microscopic photographs of unwashed (a) CP(1000)2 and (b) CP(4000)2 composite polymer particles prepared by second-step seeded copolymerization in the presence of 8.1 μm sized PS2 seed particles.

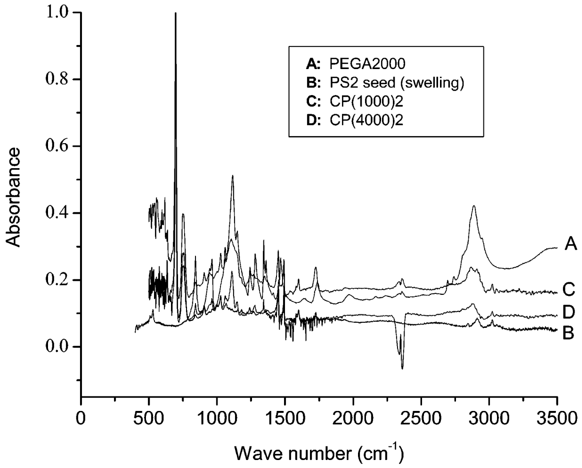

Figure 10. FTIR-ATR spectra of PEGA2000, PS2 seeds, and CP(1000)2 and CP(4000)2 composite polymer particles. In all cases seeds and composite particles were repeatedly washed.

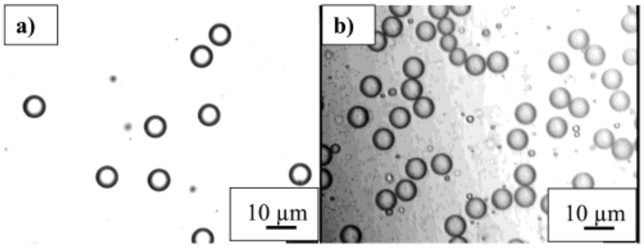

Figure 11. Light microscopic photographs of (a) PS seeds swollen with CD, styrene, and PEGMMA1000 or SW(1000)3 and (b) PS seeds swollen with CD, styrene, and PEGMMA4000 or SW(4000)3, both prepared under the conditions listed in Table 3.

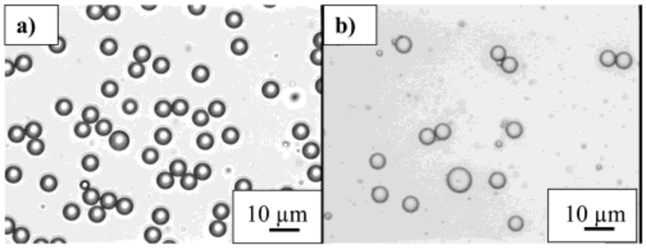

Figure 12. Light microscopic photographs of unwashed (a) CP(1000)3 and (b) CP(4000)3 composite polymer particles prepared by seeded copolymerization of respectively SW(1000)3 and SW(4000)3.

photographs of the same composite polymer particles. In both photographs the composite particles appear colloidally stable and move freely in the aqueous continuous phase. Figure 10 shows the FTIR-ATR spectra of PEGA2000, washed PS2 seeds, and CP(1000)2 and CP(4000)2 composite polymer particles. The characteristic peaks due to PEG unit are clearly visible at around 1100 and 2800 cm^{-1} for both washed composite polymer particles. In the case of PS2 seeds no such peak was observed. These results indicate the presence of PEG chain on the surface of composite polymer particles derived from macromonomer and fragments of macroazo initiator.

Comparatively, Figure 11 shows the light microscopic photographs of SW(1000)3 and SW(4000)3 emulsions prepared by modified activated swelling of monodispersed PS1 particles with CD, styrene, PEGMMA, and BPO. In presence of PEGMMA4000 (cf. Figure 11b), the size of the swollen particles was relatively smaller and the size distribution was broad compared with the emulsions prepared in the presence of PEGMMA1000. But also in the latter case some smaller droplets are visible (cf. Figure 11a). These results clearly show that the activated swelling procedure employed fails in the presence of poly(ethylene glycol) macromonomers. Figure 12 shows the light microscopic photographs of CP(1000)3 and CP(4000)3 polymer particles after seeded copolymerization of SW(1000)3 and SW(4000)3. In both cases submicron-sized particles were produced during seeded copolymerization, which could be expected after failure of the activated swelling process. The particle size distribution of the produced polymer particles was comparatively broader than that observed with particles prepared in absence of PEGMMA (Figure 6a) and increased further in the presence of PEGMMA4000. This is possibly due to the partitioning of PEGMMA between organic and aqueous phases. The presence of macromonomer in the continuous phase possibly enhanced the dissolution of styrene monomer along with BPO from the swollen particles (SW(1000)3 and SW(4000)3) at higher temperature, and thereby copolymerization also took place in the continuous phase. The concentration of Fremy's salt in the continuous phase may not be enough to prevent copolymerization in the continuous phase. At higher concentration of Fremy's salt the conversion of monomer was low as the smell of monomer was observed. The submicron-sized particles produced during seeded copolymerization were removed as far as possible by repeated washing and recorded the FTIR-ATR spectra. In both cases no characteristic peak due to PEG chain was observed. This suggests that during seeded copolymerization macromonomer was either copolymerized with styrene in the continuous phase to form submicron-sized particles or homopolymerized to form water-soluble polymer. These results indicate that seeded copolymerization followed by swelling of monodispersed micron-sized PS particles in the presence of PEGMMA is not viable to design several micron-sized polymer particles containing PEG on the surface of particles.

Conclusions

The results indicate that seeded copolymerization of styrene and PEGMMA in the presence of monodisperse PS particles is the best way to prepare colloidally stable several micron-sized composite polymer particles covered with PEG, without using any surfactant in the final step. The concentration of PEG on the surface of the prepared composite particles was pretty high as detected by FTIR-ATR. Comparatively, in our previous article,[10] it has been reported that PEG derived from the PEG-azo initiator fragments during seeded polymerization was not enough to cover the polymer particles, and because of the very low concentration, its presence could not be detected by FTIR-ATR. These PEG covered monodisperse micron-sized polymer particles, as reported in this article, may be useful as insoluble support for various applications in biomedical fields.

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