

Effect of Supercritical CO₂ on Three-Dimensional Colloid Arrays of PS-MA-EGDMA

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ABSTRACT: Using emulsifier-free emulsion polymerization method, monodispersed crosslinked poly(styrene-co-methacrylic acid-co-ethylene glycol dimethacrylate) colloid microspheres were synthesized. The microspheres were treated in supercritical carbon dioxide (SCCO₂) after they have self-assembled into ordered three-dimensional (3D) colloid arrays. The CO₂ absorbed into the polymer microspheres enhances chain segments mobility and reduces the glass transition temperature (T_g) of polymer, which induce the microspheres coalesce at the relatively low temperature. The coalescence degree of microspheres was studied by varying the experimental temperature, pressure, and exposure time in SCCO₂. The results were shown by scanning electron microscopy (SEM). Further, the lattice spacing of the assembled 3D colloid microspheres was

calculated from the SEM images. It was illustrated that the coalescence degree enhanced with the increase of CO₂ pressure; however, this tendency became weak when CO₂ pressure reached a certain value. Extending exposure time in SCCO₂ or elevating temperature can also increase coalescence degree, and the effect of temperature is more significant. It is believed that these results will make sense when the polymer microspheres are considered to be used as templates in SCCO₂; meanwhile, it raises a new method about tuning the final morphology of the stabilized colloidal crystals and porous materials via controlling the coalescence degree with the assistance of SCCO₂. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 2393–2399, 2011

Key words: microsphere; 3D arrays; supercritical CO₂

INTRODUCTION

In recent years, micrometer and sub-micrometer sized colloid materials have attracted considerable research attentions due to their large applications in chemistry, material science, biotechnology, and electronic engineering. Colloid materials may be used as models for scaffolding templates^{1,2} or as models for condensed matter physics or as building blocks for creating hierarchical nanometer- or micrometer-scale architecture.^{3,4} Monodispersed polymer and silica colloid microspheres were widely used because they can be produced in routine ways and assembled into ordered arrays. The ordered arrays can be

potentially used for the fabrication of the photonic band gap materials^{5,6} and as the sacrificial templates for the preparation of porous films.^{7–10} When the ordered arrays are combined with other functional particles such as nanometer-sized gold, quantum dots, metal, and biofunctional particles, they attract great interests in numerous applications including displays, sensing, electrochemical, and optoelectronic devices, and so on. In these situations, the morphology maintenance of colloid microspheres (especially for the polymer microspheres), which depends on the composition of the polymer and the peripheral effect, is important.

Supercritical fluids (SCFs) are the attractive mediums in the material science because of their special properties: low viscosity, high diffusivity, and near zero surface tension.¹¹ Small changes in temperature and pressure could cause dramatic changes in the dissolvability, diffusivity, and dielectric properties, which make them the effortlessly tunable fluids. Among the SCFs, supercritical CO₂ (SCCO₂) is most frequently used because it is inexpensive, nontoxic, nonflammable, and environmentally benign and has a relatively low-critical temperature and pressure ($T_c = 31^\circ\text{C}$, $P_c = 7.38\text{ MPa}$).^{12–14} Recently, more and more colloid materials have been prepared in SCCO₂. For example, Wakayama and Fukushima and Wakayama et al. have prepared the nanoporous silica, platinum, and titania via nanoscale casting

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process by using activated carbon templates in SCCO_2 .^{15,16} Watkins and coworkers have prepared well-ordered mesoporous silica films by selective condensation silicon alkoxides within microphase-separated block copolymer templates diluted with SCCO_2 .¹⁷ Mokaya and coworkers have prepared hollow silica spheres with large mesopore wall in the presence of block copolymers in SCCO_2 -in-water system.^{18,19} Cabañas et al. have developed a new method to fabricate SiO_2 macroporous film by using polymer colloid as template in SCCO_2 .^{20,21} Recently, in our lab, we use SCCO_2 as the peripheral effect to help polymer epitaxy on carbon nanotubes (CNTs), and the decorated CNTs can be obtained.^{22–24}

As CO_2 can dissolve in polymer and subsequently swell and enhance the mobility of chain segments, it can reduce the glass transition temperature (T_g) and induce the polymer colloid spheres to be coalesced or welded at temperature much lower than at atmospheric pressure. For instance, the sorption of CO_2 in polystyrene (PS) at 40°C and 8.5 MPa is 12–13 wt %.²⁵ The T_g of PS at atmospheric pressure is about 105°C,²⁶ the value decreases about 10°C /MPa up to 6 MPa and reaches 55°C. A further 1 MPa increase of pressure to 7 MPa causes T_g to decrease to 32°C. Above this temperature, T_g becomes pressure independent up to 11 MPa.^{27,28} To make use of CO_2 as a suitable external parameter to aid the polymer colloid spheres array to the practical application, some methods have been applied to improve the polymer's resistant property in SCCO_2 . Crosslinker can be introduced to enhance the strength of the polymer. Additionally, copolymerizing with monomer containing carboxylic acid on the microspheres is equally effective, which is due to the electrostatic repulsion between the OH groups in the carboxylic acid.²⁹

In this study, we have prepared three-dimensional (3D) colloid arrays via the self-assembly of monodispersed crosslinked and surface-modified poly(styrene-*co*-methacrylic acid-*co*-ethylene glycol dimethacrylate) (PS-MA-EGDMA) microspheres. EGDMA is used as the crosslinker, which can enhance the strength of the polymer through the inter-chain links. MA is used as the surface modifying monomer that contains the carboxylic acid group, which prevents the microspheres from aggregation. Then, their 3D arrays structure is treated in SCCO_2 . By varying the different temperature, pressure, and exposure time, the transformation of microspheres has been characterized by scanning electron microscopy (SEM).

EXPERIMENTAL

Materials

Styrene (St) was supplied by Kemiou Chemical Reagents Researching Center in Tianjin, purified by

distillation under reduced pressure. MA was received from Tianjin Chemical Reagent Research Institute. EGDMA was supplied by Alfa Aesar, which was used as crosslinker. Potassium persulfate (KPS) was purchased from Shanghai Aijian Reactant Factory, and it was used after recrystallization. Sodium bicarbonate (NaHCO_3) was obtained from the Tianjin Hongyan Reagent Factory. Deionized water was applied for polymerization and treatment processes. CO_2 with purity of 99.99% was provided by the Zhengzhou Shuangyang Gas Co. and used as received.

Preparation of monodispersed microspheres

Emulsifier-free emulsion copolymerization was carried out by a batch process in a 250 mL, four-necked, round-bottom flask, which was put in a thermostat water bath. The procedure is as follows: First, 10 g of St, 1.2 g of MA, and 0.24 g of NaHCO_3 with 90 mL water were added. Then, the solution was deoxygenated by bubbling nitrogen and stirred mechanically at 250 rpm. When the reaction mixture reached 70°C, solution of 0.08 g KPS dissolved in 10 mL water was added. When the reaction had proceeded for 1 h, 0.3 mL EGDMA was added. The whole polymerization was kept at 70°C for 24 h and the monodispersed crosslinked and surface-modified PS-MA-EGDMA microspheres were fabricated. This obtained emulsion was purified thrice by the centrifugation/redispersion. The detail procedure was described as following: The emulsion was injected into six centrifuge tubes of 30 mL and centrifuged at 9800 rpm for 15 min. After the treatment, the PS particles were separated from the solution and located at the bottom of the centrifuge tubes. Removing the clear liquid on the top and adding 25 mL of deionized water in each tube, then the samples were thoroughly dispersed through sonication under 250 W for 20 min. Repeating the above centrifugation/redispersion procedure for thrice and the final product was dried in vacuum under 40°C for 6 h. Through purification, the obtained dried microspheres could be used for IR measurement and self-assembly procedure.

Formation of ordered 3D colloid arrays

The dried microspheres were dispersed into water to prepare emulsion with the solid content of 3 wt %. The emulsion was directly dropped onto silicon wafer and dried at room temperature to form the 3D colloid arrays.

Treating 3D colloid arrays in SCCO_2

The silicon wafer with the 3D colloid arrays were placed into the bottom of the stainless steel vessel of

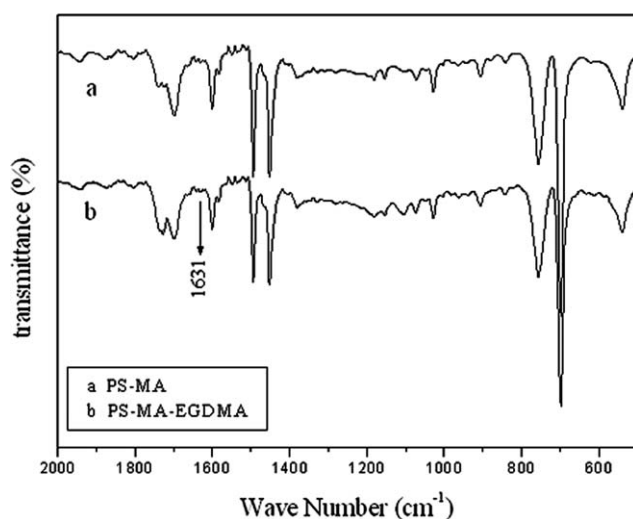


Figure 1 FTIR spectra of PS-MA and PS-MA-EGDMA colloid microspheres.

50 mL. The vessel was placed into a thermostated bath. Then CO₂ was charged into the vessel by a syringe pump (DB-80, Beijing Satellite Manufacturing Factory) until the desire pressure was obtained. After a suitable time, the pressure was released by venting and the sample was kept for analysis.

Characterization

The samples were characterized by a FEI QUANTA-200 scanning electronic microscope at 20 kV acceleration voltages after gold coating. FTIR spectra were measured by using a BRUKER OPTICS TENSOR27 FTIR spectrophotometer in the wavenumber range from 4000 to 400 cm⁻¹ at a resolution of 4 cm⁻¹. Differential scanning calorimetry (DSC) curves were measured by TA DSC Q100 by heating or cooling the sample at the rate of 5°C/min during the range from 20°C to 200°C.

RESULTS AND DISCUSSION

Preparation of monodispersed microspheres

Figure 1 shows the FTIR spectrum of crosslinked and surface-modified PS-MA-EGDMA microspheres. From the figure, we could confirm the presence of St, MA, and EGDMA. In addition, the transmittance peak of the C=C double bonds at 1631 cm⁻¹ is weak due to the low concentration in the microspheres, which indicates that almost all of the double bonds including that of the crosslinker, have reacted completely.³⁰ Other factors such as the diameter of the sphere, the density of carboxylic acid groups bound to the surface of sphere, and the amount of crosslinker, can be finely tuned.^{31,32} Additionally, the DSC curves of PS-MA and crosslinked

PS-MA-EGDMA microspheres show that the T_g of crosslinked microspheres is higher than the uncrosslinked one (Fig. 2), which proves that crosslinker has been incorporated into the PS-MA-EGDMA microspheres.

Three-dimensional colloid arrays

Monodispersed PS-MA-EGDMA microspheres were self-assembled into ordered 3D arrays on silicon wafer. SEM image of the sample is shown in Figure 3(a). The average diameter of these microspheres is 205 nm, and these particles mainly show the face-centered cubic packing. For the spheres in the 3D arrays, each of them contacts with 12 nearest neighbors, except for the microspheres on the top layer which contacts with 9 nearest neighbors. For the microspheres on [111] plane, they appear 2D "hexagon" array.

Effect of SCCO₂ pressure on the 3D colloid arrays

As CO₂ is a small and linear molecule, it diffuses into polymer faster than other swelling agents or plasticizers. The swelling could improve the mobility of the polymer chains and enhance the relaxation rate of polymer. This relaxation is driven by the interfacial tension that exists between polymer and CO₂ as well as Brownian motion of the polymer chains.³³ The 3D colloid arrays were treated in SCCO₂ at 40°C for 3 h under different pressures, and the SEM images of these samples are shown in Figure 3(b-f). In Figure 3(b), we could see that the microspheres pack closer than that of the spheres in Figure 3(a). With the decrease of lattices spacing, the microspheres at the top layer have transformed from sphericity to hexagon. In Figure 3(c-f), with

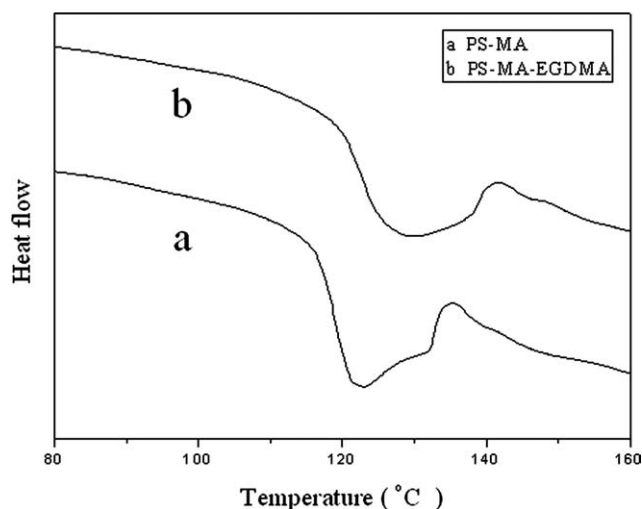


Figure 2 DSC curves of PS-MA and PS-MA-EGDMA colloid microspheres.

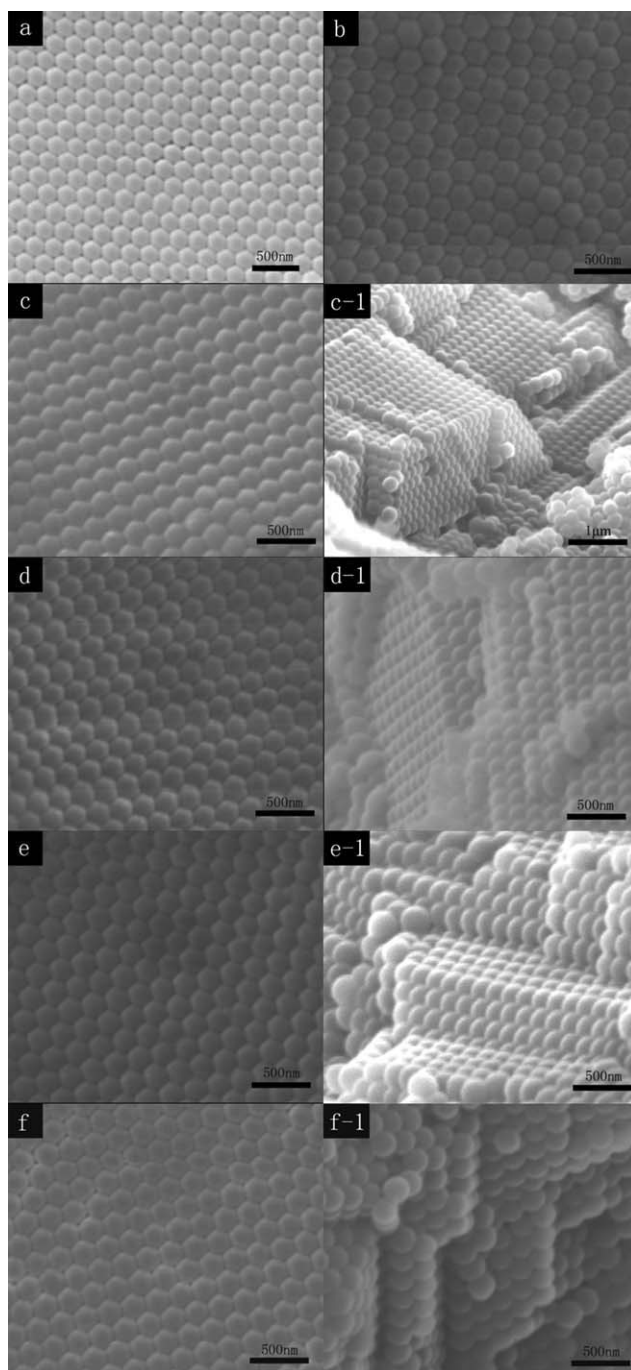


Figure 3 PS-MA-EGDMA 3D colloid arrays before (a) and after treatment in SCCO₂ at 40°C for 3 h under different pressure: (b) 12 MPa, (c) 14 MPa, (d) 16 MPa, (e) 18 MPa, and (f) 20 MPa.

increasing the pressure of CO₂ from 14 to 20 MPa, we find that the morphology of the top layer changes little compared with Figure 3(b). The lattice spacings of the microspheres treated at different condition were calculated from the SEM images and the data are listed in Table I. It can be seen that there is a minimum point for the lattice spacing at 14 MPa. Further increasing CO₂ pressure from 14 to 20 MPa, the lattice spacing became wider again.

Images of the cross sections of 3D arrays are shown in Figure 3(c-1-f-1). Among some spheres with random arrays, the necks between the adjacent ones could prove the existence of the coalescence. The serious coalescence is not observed, which is due to the crosslinker and carboxyl acid in the particles are more resistant to CO₂. Another problem is how to explain the existence of the minimum value of the lattice spacing with the variation of CO₂ pressure? We suggest the following reasons. As CO₂ can be dissolved in polymer and, subsequently, swell and enhance the mobility of chain segments, it can reduce the glass transition temperature (T_g) of the polymer colloid spheres. As we known, the decrease of T_g is attributed to two opposing effects,³⁴ a diluents' effect and a hydrostatic pressure effect. At lower pressure from 12 to 14 MPa, the decrease of T_g is dominated by the diluents' effect. It increases the distance between polymer segments and decreases the strength of the intermolecular interactions between segments. The weakening of these interactions increases the molecular motion, which can lead a transition from a glass state to viscoelastic state. The weld of these particles occurs, and the lattice spacing of the colloidal crystals is decreased. However, if the CO₂ pressure exceeded a certain value, the solubility of CO₂ in polymer reached a certain maximum and the hydrostatic pressure effect is dominant. At these pressures, the solubility does not increase significantly with pressure, but the hydrostatic pressure decreases the molecular distance between polymer segments and inhibits both molecular motion and a glass to viscoelastic state transition. This will cause the T_g increase on the contrary and weaken the weld of the particles. The phenomenon also has been discussed in our previous paper.³⁵ It can be observed that the lattice spacing increased with the pressure increasing from 14 to 20 MPa.

3D colloid arrays were treated in SCCO₂ at 50°C for 3 h under different pressures, and the SEM images of them are shown in Figure 4. The tendency of "sphericity to hexagon" becomes obvious with the increase of pressure. And the lattice spacings were also calculated from the SEM images and the data are listed in Table II. It indicates the lattice spacing decreases with the pressure increasing from 16 to 20 MPa. It can be found that even under the condition in SCCO₂ at 50°C and 20 MPa, the synthesized microspheres still have the excellent resistant property to CO₂.

Effect of exposure time in SCCO₂ on the 3D colloid arrays

The experimental results about the PS-MA-EGDMA 3D colloid arrays treated in SCCO₂ at 40°C and 50°C

TABLE I
Lattice Spacings of PS-MA-EGDMA 3D Colloid,
Calculated from SEM Images, before and After
Treatment in SCCO₂ at 40°C for 3 h under Different
Pressure

Pressure (MPa)	Lattice spacing (nm)
Untreated	205
12	198
14	193
16	196
18	202
20	204

illustrates that different pressures have apparent effect on the micrograph of these colloid arrays. To study the effect of treatment time on the transformation of their microstructure, we adjust the treatment time from 3 h, to 4.5 h and 6 h, respectively, in SCCO₂ at 50°C and 16 MPa.

With the extension of time, the coalescence become more serious and the contacting status among the microspheres transferred from the point contact to compressing each other. The spacing between microspheres becomes smaller and the spheres tend to transform to hexagon [Fig. 5(b,c)].

TABLE II
Lattice Spacings of PS-MA-EGDMA 3D Colloid
Calculated from SEM Images, Treated in SCCO₂ at 50°C
for 3h under Different Pressure

Pressure	Lattice spacing (nm)
16 MPa	202
18 MPa	201
20 MPa	200

The lattice spacings were also calculated from the SEM images and they are listed in Table III. From the table, we find that the lattice spacing decreases with the extension of time when treated in SCCO₂. In Figure 5(c-1), we even can observe a series of microspheres are welded into a string when it was treated in SCCO₂ at 50°C and 16 MPa for 6 h. As the motion of polymer chain segments is a relaxation process, it takes times to transform the chain segments from one equilibrium state to another one via the thermal motion. It can be concluded that a kind of complete relaxation of chain segments can be induced by extending the treatment time in SCCO₂, and similar experimental results also can be found in the literature.³⁶

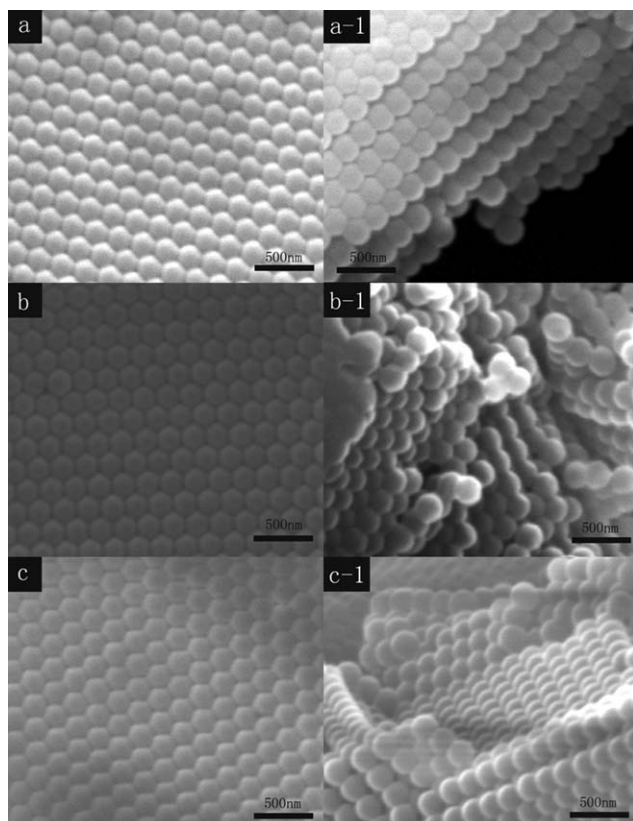


Figure 4 PS-MA-EGDMA 3D colloid arrays treatment in SCCO₂ at 50°C for 3 h under different pressure: (a) 16 MPa, (b) 18 MPa, and (c) 20 MPa.

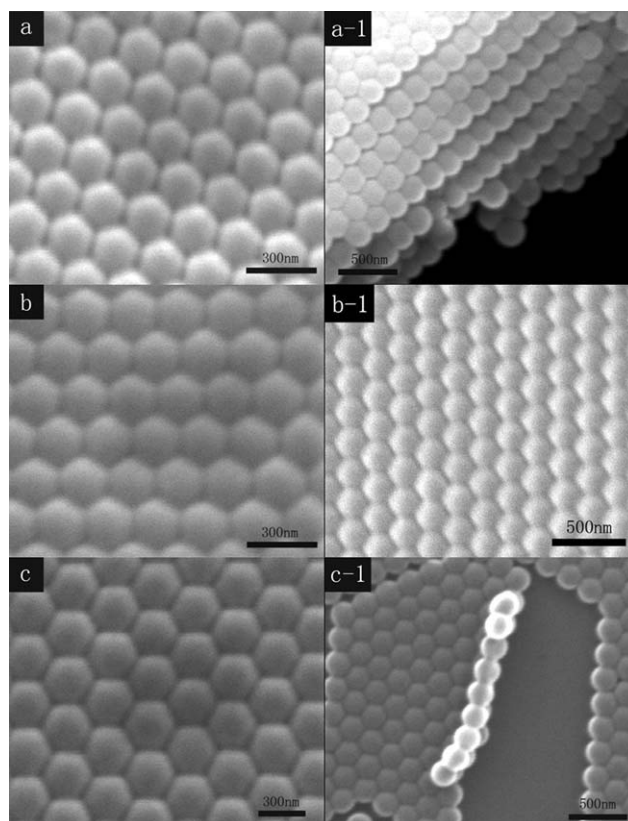


Figure 5 PS-MA-EGDMA 3D colloid arrays treatment in SCCO₂ at 50°C and 16 MPa for different time: (a) 3 h, (b) 4.5 h, and (c) 6 h.

TABLE III
Lattice Spacings of PS-MA-EGDMA 3D Colloid
Calculated from SEM Images, Treated in SCCO₂ at 50°C
and 16 MPa for Different Period of Time

Time	Lattice spacing (nm)
3 h	202
4.5 h	202
6 h	200

Effect of temperature on the 3D colloid arrays

The effect of temperature on the morphology of 3D colloid arrays in SCCO₂ at 20 MPa were shown in Figure 6. In the SEM images of Figure 6(a,b), it can be found that both the top layer microspheres were closer packed than the untreated sample. The cross section in SEM image [Fig. 6(b-1)] reveals that the coalescence degree is more dramatic at 60°C. When the temperature reaches 70°C [Fig. 6(c)], we can scarcely find the microspheres, only the ordered unapparent spots are detected, which indicates that the 3D colloid arrays almost transform to a flat film. Extending the treatment time to 6 h at 60°C (Fig. 7), sections of the 3D arrays also tend to transform to a bulk film, which indicates that effect of extending time have the same function with increasing temperature. As mentioned before, the solubility of CO₂ in polymer and the swelling degree will keep constant when the pressure has increased to a certain value. However, in this case, the effect of temperature is still significant. This can be attributed to the following reasons. On the one hand, with the increase of the temperature, the polymer chain segments become highly active; on the other hand, increased free volume with higher temperature enlarges the intermolecular free

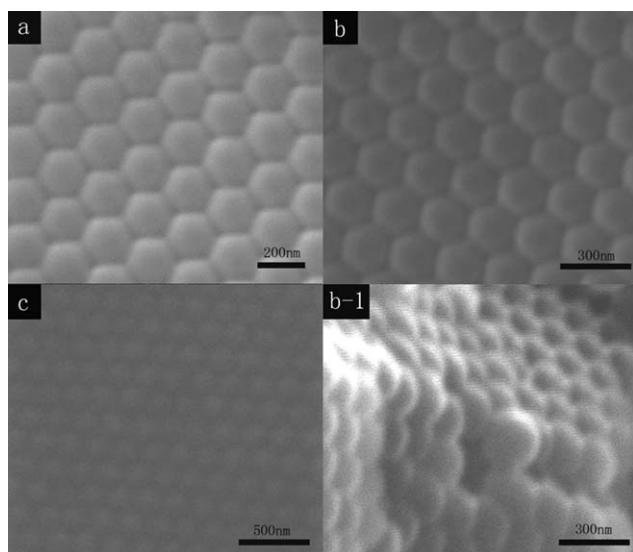


Figure 6 PS-MA-EGDMA 3D colloid arrays treatment in SCCO₂ at 20 MPa and different temperature (a) 50°C, (b) 60°C, and (c) 70°C for 3 h.

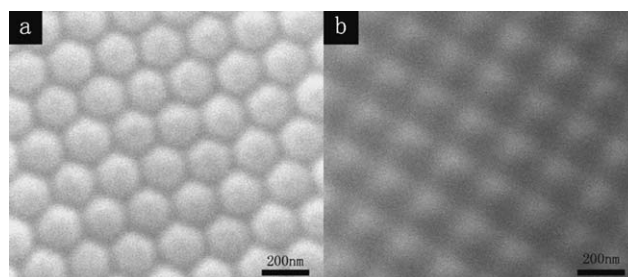


Figure 7 PS-MA-EGDMA 3D colloid arrays treatment in SCCO₂ at 60°C and 20 MPa for 6 h.

space, which could result in the further interdiffusion and entanglement of the polymer chains between microspheres and induce the transformation of 3D colloid arrays to a bulk film, just as the explanation of Abramowitz et al.³⁶ When compared with the report in the literature,³⁷ it shows that the morphology of our microspheres can maintain in SCCO₂ for longer time, which may suggest that our samples can be used in a wider range of applications.

CONCLUSIONS

In summary, 3D ordered colloid arrays of monodispersed crosslinked PS-MA-EGDMA microspheres were treated in SCCO₂ to adjust their final micro morphology. By varying a series of temperature, pressure, and exposure time, the coalescence degrees of these microspheres were finely tuned. At 40°C and 12 MPa, the particles have slightly coalesced, but the coalescence degree does not grow with the increasing pressure. Further extending the exposure time or increasing the temperature in SCCO₂ can improve the relaxation of chain segments, thus increase the coalescence degree. It is found that suitable treatment of the 3D colloid array, a series of microspheres can be welded into a string. This, in effect, supplies a new platform to tune the final morphology of the stabilized colloidal crystals in a controlled manner. It also supplies wider space to apply the SCCO₂ as the peripheral effect to control the final morphology of the template colloid. These results are important for the polymer microspheres when they were used in SCCO₂ as templates, such as preparing unsymmetrical particles³⁵ or macroporous films^{20,21} with different morphologies and components. In addition, considering the special properties of SCCO₂ and its green character, there is no solvent residual in the product, so it is more benign to the environment.

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