

Effect of Supercritical Carbon Dioxide on the Ordering and Aggregation of Polystyrene Latex Particles

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Monodisperse latex particles microspheres of controlled size and variable composition have been produced in three-dimensional ordered arrays.[1] These materials can be used as templates for structured porous material including inorganic oxides, carbons, metals and polymers. Structure of the polymeric template can be altered by compressed gases and supercritical fluids. In this communication, we study the effect of supercritical CO₂ (scCO₂) on polystyrene (PS) latex particles decorated with different polar groups. Crossed-linked PS particles have been also studied. SEM pictures of the materials after CO₂ treatment unravel a delicate balance between particle aggregation and electrostatic interactions.

INTRODUCTION

There is a great interest in producing periodic porous materials to be used as membranes, catalytic surfaces, supports, ion exchangers, chemical sensors, dielectrics in microelectronics, photonic crystals, etc... [2] 3D-latex arrays have been used as templates for structured porous inorganic oxides.[1,3] Morphological control of the template is required.

Ordering and aggregation of polymeric templates is affected by supercritical fluids. Supercritical fluids or compressed gases such as CO₂ are effective plasticizers for polymers. Sorption data of CO₂ into PS have been recently reviewed.[4] At 40°C and 96.5 bar solubility of CO₂ is ca. 13.4 % wt. and T_g depression is close to 1 °C/bar up to 60 bar of CO₂. Sorption of CO₂ into the polymer makes polymer swell, polymer chain mobility increases and particles tend to aggregate. Template morphology can be changed using supercritical fluids.

Different stabilizers can be used to prevent particle aggregation. This idea has been applied in dispersion and emulsion polymerisation in scCO₂ which employs surfactants during polymerisation.[5] The surfactants attach to the polymer particle either by physical adsorption or chemical grafting and prevent particles from aggregating by electrostatic, electrosteric or steric stabilization. Both homopolymers and block copolymers have been used for this purpose. On the other hand cross-linked PS microspheres were produced by unstabilized suspension polymerisation in scCO₂ without surfactants. Particles were stabilized against coagulation by their rigid, cross-linked surfaces.[6]

In this communication we investigate both approaches to control morphology and particle aggregation of pre-made 3D-latex arrays. Particle aggregation in scCO₂ has been suppressed by attaching stabilizing moieties to the PS latex surface during synthesis. Swelling of PS with solvents can be also decreased by cross-linking.

MATERIALS AND METHODS

PS particles decorated with different hydrophilic groups on their surface: 2-hydroxyethyl methacrylate (HEMA), methacrylic acid (MA), acrylic acid (AA) and itaconic acid (IA) were prepared by emulsion copolymerisation of styrene (S) and the corresponding monomers (Figure 1) in water following a procedure previously described.[1] The molar ratio hydrophilic monomer to styrene was 1:15 in every case. Cross-linked PS emulsions produced by copolymerisation of styrene (S) and divinylbenzene (DVB) were also studied. The emulsion was filtered through glass wool and dialysed for four weeks against water. 3D-Latex arrays were prepared either by evaporation of the solvent or by membrane filtration. The materials were dried at room temperature under air or at 45 °C in an oven.

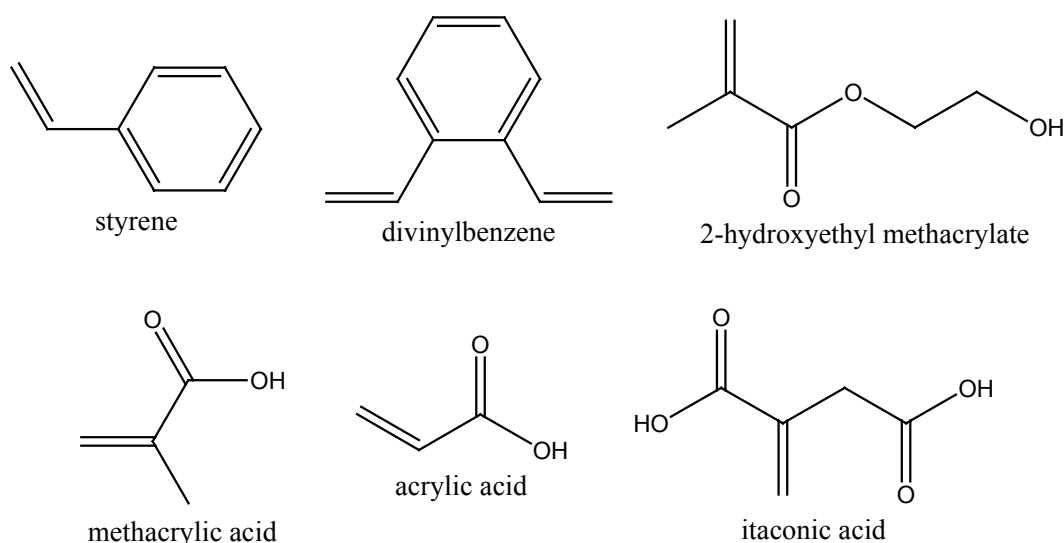


Figure 1. Monomers employed in the polymerization of PS latex particles.

Pieces of 3D-latex arrays of variable thickness (1-3 mm) were treated in scCO₂ at 50 °C and a pressure between 80-105 bars. Starting material had low mechanical consistency. Experiments were performed in a *ca.* 30 ml high-pressure reactor from HIP. The reactor containing a small amount of solid sample was immersed in a thermostated bath at 50 °C and filled with CO₂ using a high-pressure syringe pump (Isco, Inc. Model 260D) at 50 °C up to the required pressure. Vessel contents were kept at these conditions for a period between 15 and 90 minutes depending on the material. After CO₂ treatment, the vessel was quickly depressurised and material was kept for analysis.

Scanning electron microscopy (SEM) of the samples was carried out on a JEOL 2000FX electron microscope operating a 20 kV. Samples were gold coated prior to analysis.

RESULTS

A SEM picture of a PS-HEMA array is shown in Fig. 2a. Mono-sized round particles self-organize in 3-D ordered arrays of particles. The sample shows a fcc packing of particles together with some less ordered regions. The presence of hydrophilic segments at the surface of the particle assists in ordering the spheres.

PS-HEMA samples were treated in scCO₂ at 50 °C and 85 and 105 bar (ρ_{CO_2} =0.249 and 0.446 g cm⁻³, respectively)[7] for periods of 90, 15 and 10 minutes. After only 10 minutes,

CO₂ treatment at 50 °C and 85 bar caused contraction and hardening of the sample. SEM picture of this sample (Fig. 2b) revealed coalescence of particles due to the plasticization and swelling of the polymer in scCO₂. HEMA groups at the particle surface do not stabilize particle in CO₂.

A piece of the same sample was also treated in N₂ at the same P and T ($\rho=0.089\text{ g cm}^{-3}$)[7] for 1 hour without noticeable effect on ordering and aggregation. This was expected because of the lower solubility of N₂ in the polymer at these conditions.

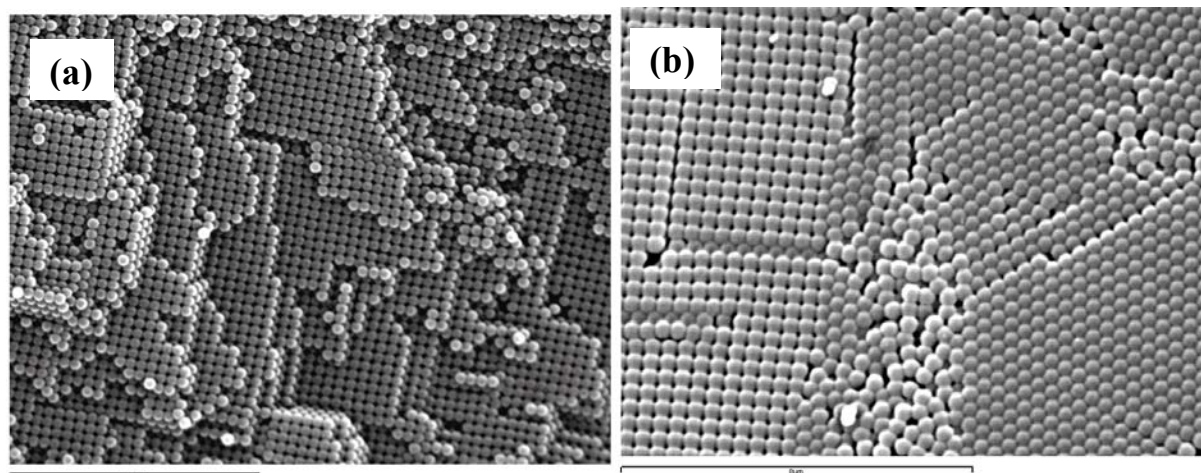


Figure 2. SEM of PS-HEMA: (a) before and (b) after treatment with CO₂ at 50 °C and 85 bar for 10 minutes (scale bars 10 and 8 μm).

PS-AA membranes synthesized at different pH were also treated in scCO₂ at 50 °C and 85 bar for 15 minutes. Visual inspection of the sample after treatment showed no apparent change in the material. SEM analysis however revealed partial aggregation of the particles. Aggregation was less important for the samples synthesized at pH=8 and pH=10 (Fig. 3a and 3b, respectively). Figure 3a displays ordered particles with hexagonal shape. Change from round to hexagonal particles is a consequence of the swelling and partial aggregation of the particles. 3-D ordering of the array is preserved.

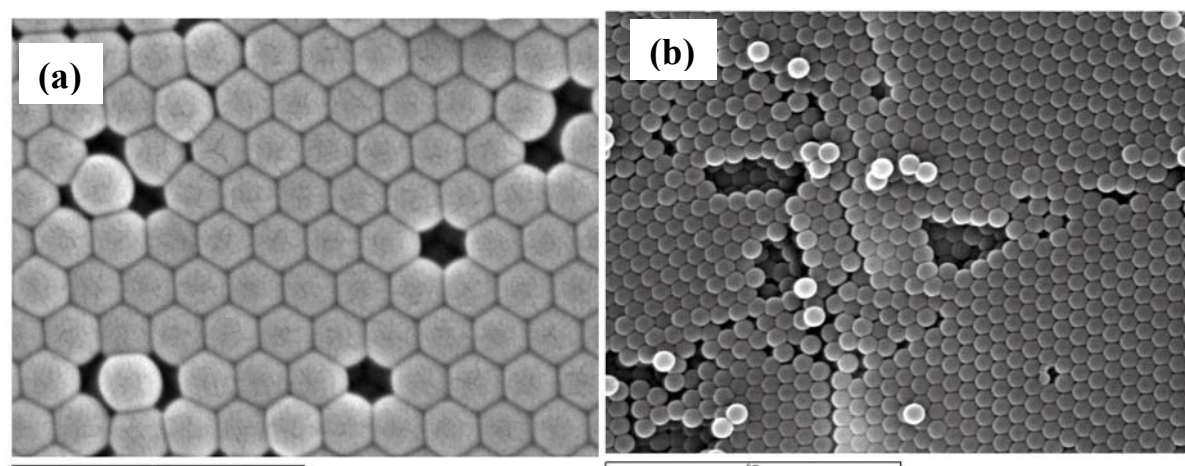


Figure 3. SEM of PS-AA: (a) pH=8 and (b) pH=10.5 after treatment with CO₂ at 50 °C and 85 bar for 15 min (scale bars 2 μm and 6 μm, respectively).

When AA groups were changed by the slightly more hydrophobic MA groups, aggregation of the material was almost suppressed. SEM pictures of a PS-MA latex array before and after treatment are shown in Fig. 4a and 4b, respectively. Sample treated in CO₂ showed almost no particle aggregation and order was preserved.

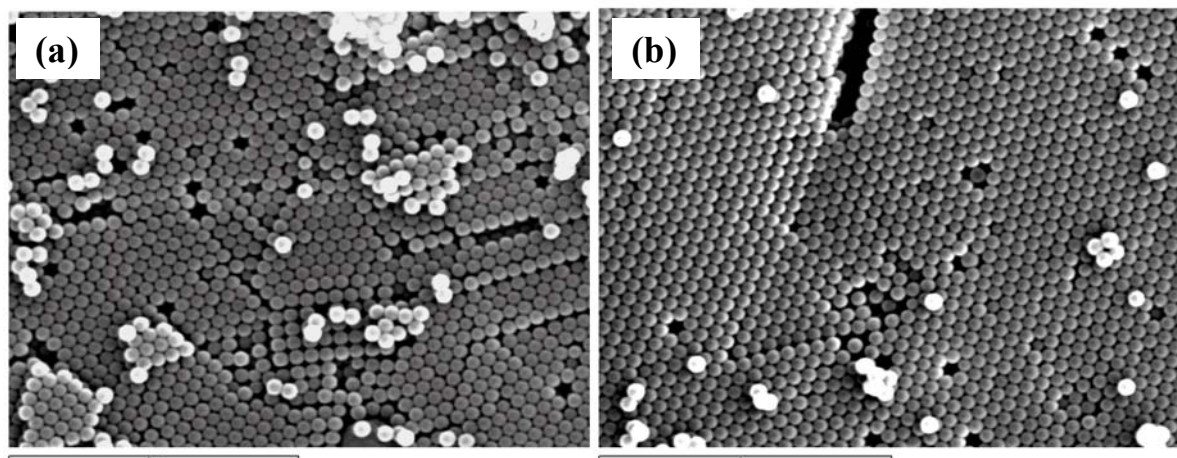


Figure 4 SEM of PS-MA: (a) before (b) after treatment with CO₂ at 50 °C and 85 bar for 15 min (scale bars 6 μm).

PS-IA sample contains a higher concentration of carboxylic acid groups on the surface according to the IA monomer introduced in the copolymerisation. SEM pictures of a PS-IA membrane treated in CO₂ at 50 °C and 85 bar show that the material is composed of discrete polymer particles (Fig. 5a and 5b). Swelling of the polymer particles with CO₂ is very important, but repulsive interactions between surface groups seem to prevent interpenetration of spheres and aggregation. Swollen particles, however, reorganize to minimize the structural tensions and as a result 3-D order is lost. In Fig 5b partial deformation of the originally round particles with SEM beam can be observed, nevertheless it is clear that particles do not aggregate.

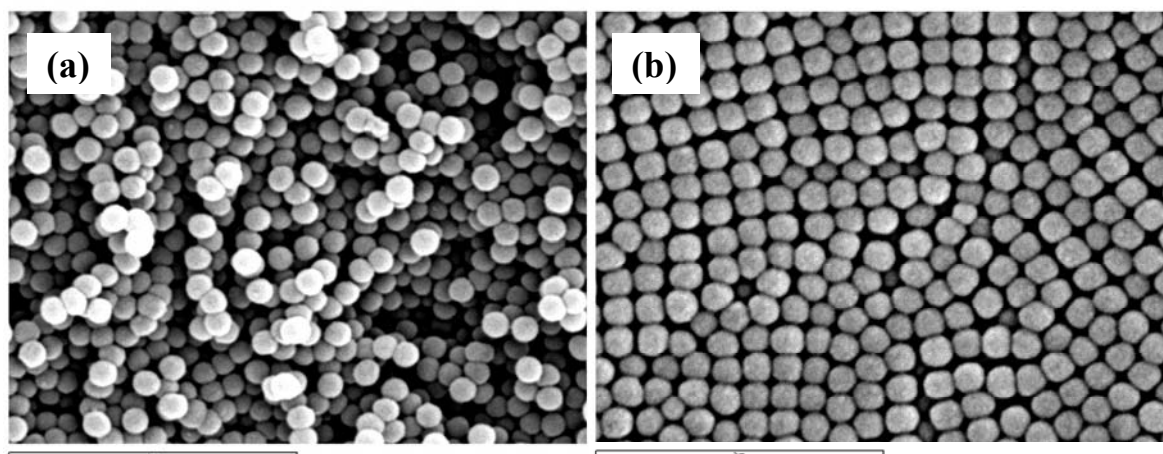


Figure 5 SEM of PS-IA after treatment with CO₂ at 50 °C and 85 bar for 15 min (scale bars 3 and 4 μm).

Cross-linked PS-DVB membranes were also treated in CO₂. Particle aggregation depends on the amount of DVB employed in the synthesis. Latex particles with a higher degree of cross-linking, up to 15% wt. of DVB, were more resistant to scCO₂ because of their larger rigidity and the lower CO₂ sorption into them. Effect of CO₂ on sample PS-DVB (molar ratio PS to DVB 1:15) is illustrated in Fig. 6. Latex particles do not aggregate but 3-D order is lost. Since forces keeping particles together in the membrane are rather weak, the structural tensions produced by the small swelling of the cross-linked particles are enough to disrupt 3D-order of the latex array.

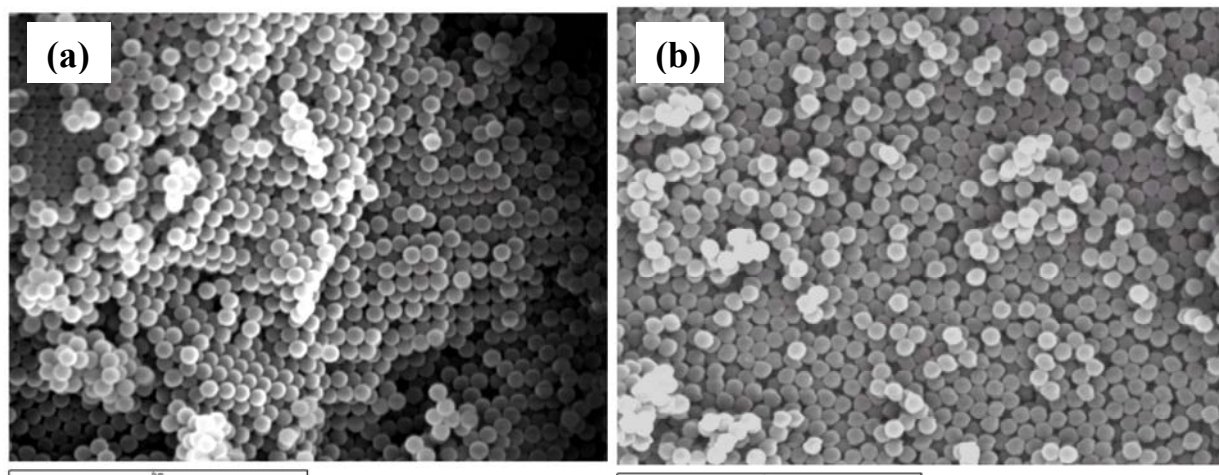


Figure 6. PS-DVB: (a) before and (b) after treatment with CO₂ at 50 °C and 85 bar for 90 minutes.

CONCLUSIONS

ScCO₂ affects the ordering and aggregation of latex particles. Preliminary experiments studying the effect of CO₂ on PS latex particles are presented. We have varied the chemical composition of PS latex arrays in an attempt of control aggregation in CO₂. All the materials were treated in CO₂ at 50 °C and 85 bar. PS-HEMA particles aggregated readily in scCO₂. Changing HEMA by AA and MA groups, particle aggregation decreased preserving 3D-order of the latex array. PS-IA particles did not aggregate but 3D-order and packing was lost. A similar effect was found when cross-linked PS particles were treated in CO₂.

Experiments show a direct relation between particle aggregation and chemical composition. When electrostatic repulsion between particles is overcome, PS particles aggregate after swelling. With some of the moieties studied (MA and AA), repulsion between groups is larger and aggregation can be controlled keeping 3-D order. If repulsion increases further (IA) structural tensions are created and 3D-order is lost. Additional experiments treating these materials at different conditions will be conducted. A fine control of the different variables is necessary to tune the morphology of these polymeric templates.

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