

Microsphere Pattern Prepared by a “Reverse” Breath Figure Method

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ABSTRACT: We have reported an interesting method, named *reverse breath figure*, for the preparation of polymeric microsphere patterns. By the same procedure as breath figure, instead of under a humid atmosphere, linear and star-shaped poly(styrene-*block*-butadiene) copolymers dissolved in solvents such as toluene, trichloroform, and dichloromethane were cast onto the surface of a glass substrate in methanol or ethanol vapor. After the complete evaporation of the solvent, microspheres with the diameters ranging from hundreds of nanometers to several micrometers were prepared. The microsphere patterns are the reverse of the honeycomb porous structure of breath figure. The mechanism of the microsphere formation has been studied to show that when the surface tension of the polymer solution is 1.5 mN/m higher than that of the condensed liquid, microsphere patterns can be prepared, whereas a honeycomb porous film of breath figure can be obtained when the surface tension of the polymer solution is lower than that of the condensed liquid. The viscosity of the polymer solution is also an important factor to influence the fabrication of the microsphere patterns.

1. Introduction

The self-assembly of polymer is of critical importance for the fabrication of nanostructured and microstructured devices such as membranes, films, spheres, and monoliths,^{1–5} which have great potential application in the fields of separation,⁶ tissue engineering,⁷ drug delivery,⁸ photonic band gap,⁹ electronic,¹⁰ catalysis,¹¹ and lithography.¹² Among the many methods,^{13–16} the water-droplet templating method, namely the breath figure method, is mostly used for the preparation periodic array porous films.^{1,17–23} During the preparation, a polymer solution is cast on a substrate under a humid atmosphere. The cooling surface caused by rapid solvent evaporation results in the water vapor condensation, and then the condensed water droplets are trapped into the solution. After complete evaporation of the solvent, honeycomb structures are formed with the pore sizes ranging from hundreds of nanometers to several micrometers. Further post-treatment will lead to special characteristics of the obtained porous film.^{24,25} However, literature search indicates that all the honeycomb porous polymeric films have been fabricated under water vapor.^{1,26} This might make people wonder: what would the structure of the materials be if a polymer solution was cast in an organic nonsolvent vapor atmosphere? Therefore, linear and star-shaped poly(styrene-*block*-butadiene) copolymers dissolved in solvents such as toluene, trichloroform, and dichloromethane were cast onto the surface of glass substrate in methanol or ethanol vapor atmosphere. After the evaporation of the solvent, microsphere patterns other than honeycomb porous structure have been obtained. This was the reverse of the breath figure if the spheres were looked as the pores in a honeycomb porous film. The mechanism of the microsphere pattern formation has been investigated.

2. Experimental Section

Materials. Poly(styrene-*block*-butadiene) copolymers of different molecular architectures were polymerized anionically

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according to the literature.²⁷ The linear triblock copolymer with polybutadiene the inner block ((SB)2), and the star-shaped four-arm copolymer with polybutadiene as the inner blocks ((SB)4), were fractionated by using the continuous spin fractionation (CSF) method²⁷ to increase the molecular uniformity. The weight-average molecular weights of (SB)2 and (SB)4 were 85.5 and 220 kg/mol from light scattering measurement, polydispersity indices ($d = M_w/M_n$) were 1.12 and 1.11 from GPC, butadiene contents were 74.2 and 74.4% from ¹H NMR measurements, respectively.²⁷ Analytical grade toluene (TL), chloroform (CHCl₃), dichloromethane (DCM), cyclohexane (CH), ethanol (EtOH), and methanol (MeOH) were purchased from commercial resources in China and were used as received without further purification.

Sample Preparation. The glass substrates (1 × 1 cm²) were cleaned by a detergent and acetone successively and then air-dried before positioning them in a glass vessel. A saturated vapor in the cap-sealed glass vessel was obtained beforehand by adding 2 mL of nonsolvents such as distilled water, MeOH, or EtOH into the bottle. The substrate was at least 1 cm higher than the liquid level. The polymers dissolved in solvents such as TL, DCM, CHCl₃, and CH with the desired concentrations were cast onto the surface of the glass substrate with a microsyringe. With the evaporation of the solvent, the transparent solution became turbid. After the complete evaporation of solvent (taking about 1 h at room temperature), a thin layer of polymer material on the substrate was obtained.

Analysis. The thus-obtained material was coated with a thin layer of gold (about 2 nm) to observe its microstructure by using an electron probe microanalyzer instrument (JXA-8100, JEOL, Japan). The surface tensions (σ) of the liquids used to prepare the material were measured on a DSA100 surface tension instrument (Krüss, Germany) by the hanging-drop method.

3. Results and Discussion

Formation of Microsphere. Poly(styrene-*block*-butadiene) copolymers with linear or star-shaped molecular architecture were dissolved in TL, with a typical concentration in solution of 1 wt %. Upon casting a drop of the polymer solution onto a glass slide in a static MeOH vapor atmosphere, the solution

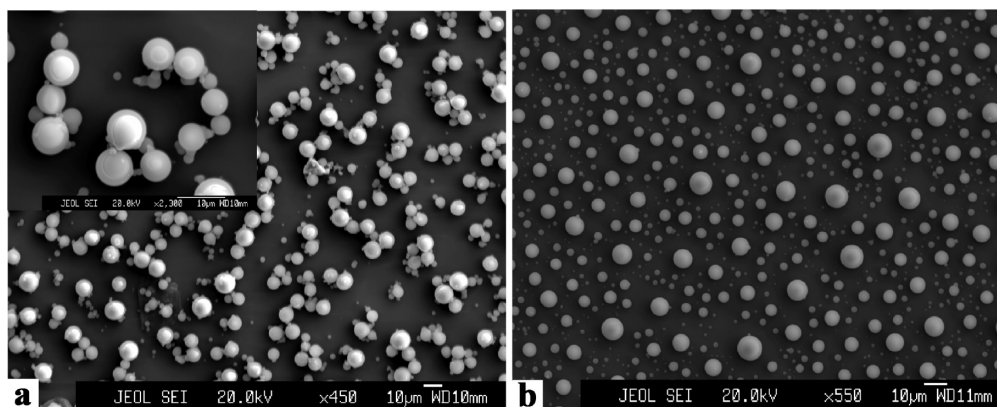


Figure 1. SEM images of the microsphere patterns prepared from 1 wt % polymer/TL solution in MeOH vapor at room temperature by the RBF method. The polymers were (SB)4 (a) and (SB)2 (b). The inset is a magnification by a factor of 2300.

surface turned turbid like the usual breath figure process.^{1,21} This observation can be easily understood by the rapid evaporation of the volatile solvent resulting in the cooling of the solution surface and the condensation of MeOH vapor into tiny droplets, which disperses in the polymer solution thereafter. After the complete evaporation of the solvent, microsphere patterns (Figure 1) were observed on the glass substrate, which were totally different from the porous honeycomb structure of the films prepared in the atmosphere of pure water vapor (breath figure process). The microspheres prepared from either linear or star-shaped poly(styrene-*block*-butadiene) copolymers range from several hundred nanometers to several micrometers in diameter, which is the same level as the pore sizes of breath figure patterns. The graphs suggest that the casting polymer solution is separated by the condensed MeOH liquid into microdroplets during the evaporation of TL. After the complete evaporation of the solvent and the nonsolvent, the microdroplets of polymer solution turned into microspheres. Therefore, the microdroplets of polymer solution could be looked as the templates dispersed in the continuous nonsolvent phase; this is just a reverse of breath figure pattern, in which the condensed water droplets have been proved to template a continuous polymer solution to form honeycomb patterned pores.¹ Literature search did not yield reports on this phenomenon, so it is named as *reverse breath figure* (RBF) by the authors.

When casting the (SB)4 solution in MeOH vapor at different environmental temperatures, all the resulting materials reveal microsphere pattern structure as shown in Figure 2, which further confirms the RBF method. With the increase of temperature, the scattered spheres join together (Figures 1a and 2) gradually. The effects of the molecular architecture of the polymer and of the temperature on the microsphere patterns are analyzed to be caused by the surface tension difference between the polymer solution and the condensed liquid, as discussed in the next section.

Mechanism of the Microsphere Formation. Why is there so much difference between the microsphere pattern for the RBF and the honeycomb porous pattern for the breath figure? The vapor pressure of the liquids was first considered. Below 50 °C, the vapor pressure of TL is higher than that of water, while it is lower than water when over 50 °C. However, at below (room temperature) and above 50 °C (80 and 90 °C), only porous honeycomb patterns were prepared when using TL as the solvent and pure water as the vapor, showing typical breath figure processes. However, the vapor pressure

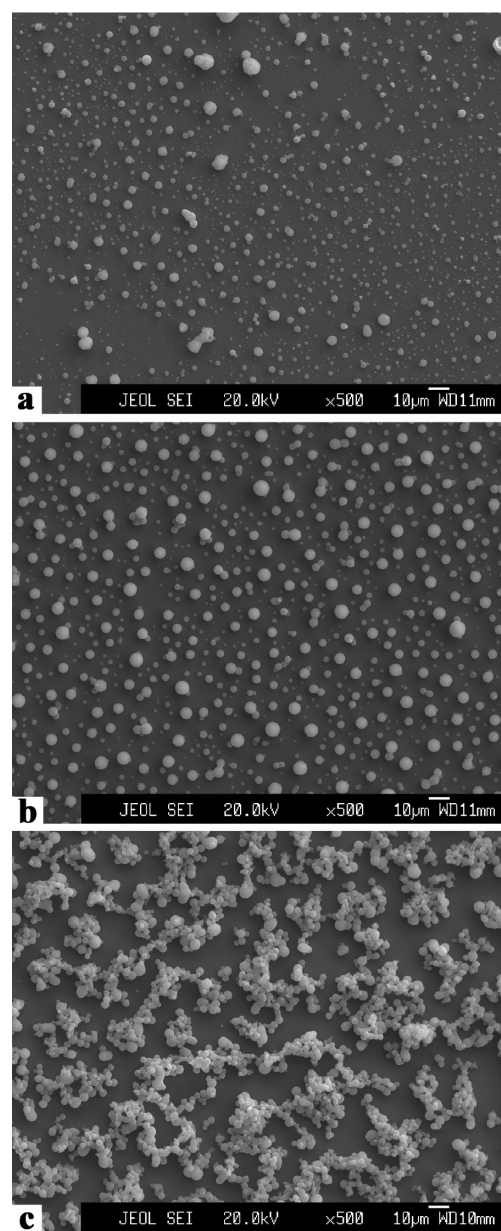


Figure 2. Microsphere patterns prepared from the 1 wt % (SB)4/TL solution in MeOH vapor at different temperatures: (a) -18, (b) 4, and (c) 50 °C.

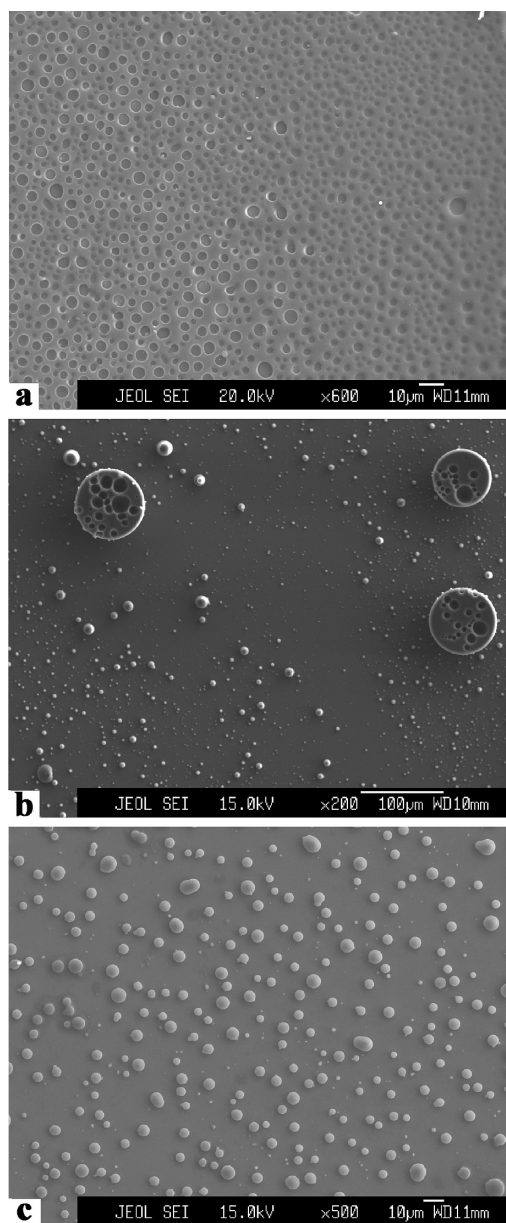


Figure 3. Microstructure evolution of the materials prepared under water/MeOH mixture vapor at room temperature. The molar percentage of MeOH (MPM, %) in the vapor was 90, 95, and 98 respectively for (a), (b), and (c). TL was used as the solvent, and the polymer was (SB)4 with the concentration of 1 wt %.

of MeOH is always higher than that of TL in the experimental temperature range (-18 to 50 $^{\circ}\text{C}$), and microsphere patterns were always obtained by using TL as the solvent and pure MeOH as the vapor. This indicates that the vapor pressure of the liquid is not the key factor to controlling the formation of the microsphere patterns or the porous honeycomb patterns. Then, the effect of composition of the vapor on the structure has been studied, with the results shown in Figure 3. According to Henry's law and Dalton's law, a mixed vapor with the designed molar percentage of MeOH content (MPM) can be produced by mixing stoichiometric water and MeOH. When the MPM was less than 90% (such as 80% and 90%), only honeycomb porous patterns could be obtained, exhibiting typical breath figure processes. When the MPM reached 98%, only microsphere structure existed to suggest a typical RBF process. However, a structure with both the above-mentioned breath figure patterns

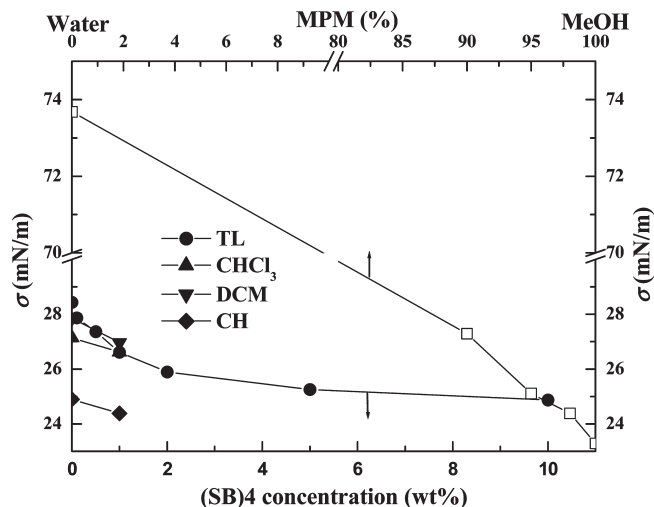


Figure 4. Surface tensions of the (SB)4 solutions in different solvents at room temperature (23 $^{\circ}\text{C}$) and of the liquid water/MeOH mixture to produce the designed the MPM. The data points for each system are connected independently for easier discrimination.

and RBF patterns, namely mixtures of microsphere and porous materials, has been prepared when the MPM was 95%. To understand this, one could hypothesize that the evaporation of the solvent would lead to the cooling of the polymer solution surface, resulting in the condensation of both water and MeOH vapor to form mixture liquid droplets; the composition of the mixture liquid droplets should be close to that of the liquid mixture to produce the vapor with the designed MPM, though quasi-equilibrium of the preparation process. According to the experimental results, the condensed mixture liquid droplets coalesce, while the polymer solution shrinks to form dispersed microdroplets, yielding the final microsphere pattern. In comparison, the condensed water droplets do not coalesce due to thermo-capillary effects and to the encapsulation effects of the surrounding polymer solution layer and form the pores of breath figure.¹ It is thus concluded that the surface tension (σ) of the liquids (the polymer solution and the condensed liquid) might play an important role to influence the morphology of the material.

The surface tensions of the liquids in air are presented in Figure 4. The surface tension of TL was measured to be 28.43 mN/m, and that of the solution decreased to 26.61 mN/m upon the addition of (SB)4 (1 wt %), while those for mixture of MeOH and water to produce the vapor with the designed MPM were 27.29 (MPM = 90%), 25.11 (MPM = 95%), and 24.38 mN/m (MPM = 98%). So it is easy to find that, when the surface tension of the condensed liquid (MPM = 90%) is higher than that of the polymer solution, honeycomb porous film of breath figure can be prepared; contrarily, when the surface tension of the condensed liquid (MPM = 98%) is lower than that of the polymer solution, microsphere pattern of RBF can be obtained; if the surface tension of the condensed liquid is close to that of the polymer solution (MPM = 95%), mixed structures have been observed. In other words, when the surface tension of the condensed liquid is higher than that of the polymer solution, the condensed liquid forms stable microdroplets to disperse in the polymer solution, and then honeycomb porous film can be obtained eventually (breath figure process); whereas, the condensed liquid spreads out, and the polymer solution shrinks to form microdroplets due to its higher surface tension and to form microsphere pattern at last (RBF process). These results indicate that the difference in surface

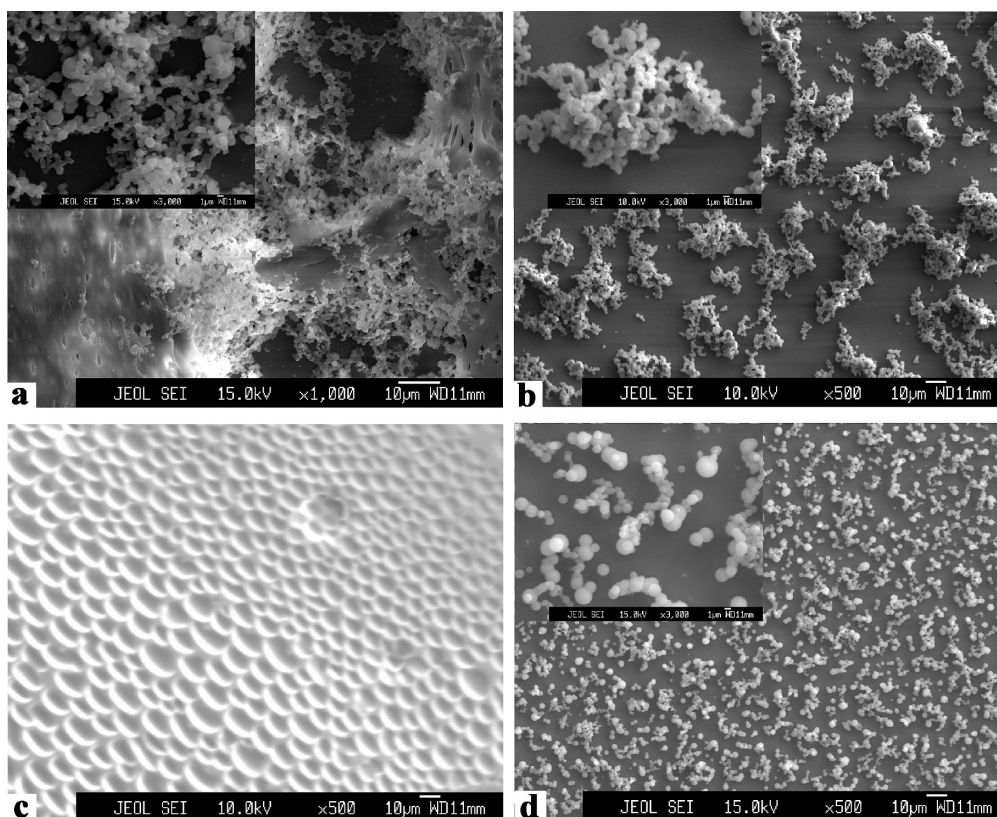


Figure 5. Microstructure of the materials prepared from 1 wt % (SB)4 solution at room temperature but using different solvents and vapors: (a) CHCl_3 was used as the solvent and MeOH was the vapor; (b) DCM was used as the solvent and MeOH was the vapor; (c) CH was used as the solvent and MeOH was the vapor; (d) TL was used as the solvent and EtOH was the vapor. The insets are magnifications by a factor of 3000.

tension between the polymer solution and the condensed liquid is the key factor to control the morphology of the material. In order to obtain a monotonous microsphere pattern, the surface tension of the starting polymer solution should be at least 1.5 mN/m (26.61–25.11) higher than that of the condensed liquid. This finding is also helpful to understand the effect of the molecular architecture of the polymer and of the temperature on the microsphere patterns (Figures 1 and 2): a higher surface tension of the linear (SB)2 solution or of the star-shaped (SB)4 solution at low temperatures would certainly result in a larger shrinkage of the polymer solution microdroplets to form dispersed microspheres (Figures 1b and 2a,b), while relative low surface tensions would cause the connection of the polymer solution microdroplets and of the subsequent microspheres (Figures 1a and 2c).

When the polymer was dissolved in other solvents such as CHCl_3 and DCM, the surface tension of the solutions were also 1.5 mN/m higher than that of MeOH (Figure 4). So the materials prepared by the RBF method were still microsphere patterns, as shown in Figure 5a,b. The connection of the spheres might be caused by the high vapor pressure of the solvents, namely, the high evaporation rates resulting in the very fast shrinkage of the polymer solution microdroplets. The image shown in Figure 5c is the imbricate structured film prepared by casting (SB)4/CH solution in the MeOH vapor. This could be explained by the fact that the surface tension of the polymer solution (24.38 mN/m) is just slightly higher than that of MeOH ($\Delta\sigma = 1.1$ mN/m), leading to the shrinkage of the polymer solution or the outspreading of the condensed MeOH not proceeding efficiently. At the same time, a similar density between the polymer solution and the MeOH resulted in eventually shallow and big pores. The

microsphere pattern shown in Figure 5d was prepared by using the vapor of EtOH, whose surface tension is slightly lower than that of MeOH. These results are consistent with that shown in Figure 3b, suggesting that a minimum of 1.5 mN/m for the surface tension of the starting polymer solution higher than that of the condensed liquid is required for the preparation of microsphere pattern.

The influence of the polymer concentration on the microstructure of the material is shown in Figure 6. It is found that purebred microsphere pattern can be obtained when the polymer concentration ranges from 0.5 to 2 wt %. This can also be explained by the difference of the surface tension between the polymer solution and MeOH, which is shown in Figure 4. However, microsphere patterns surrounded by polymer layer of giant pore structure have been found at polymer concentration of 5 wt %. This is strange because the surface tension of the polymer solution at 5 wt % is still 1.5 mN/m higher than that of MeOH, which would lead to microsphere pattern as discussed above. This can be understood in the following manner: the concentration at the edge of the casting polymer solution drop would increase quicker due to faster solvent evaporation when compared with that of the inner part of the drop; as a result of the increase in concentration, the viscosity of the polymer solution at the edge would rise while its surface tension would decrease, both leading to the decrease in flow ability of the polymer solution, so that the condensed MeOH microdroplets would coalesce in these area and spread out a little but would be encapsulated by the viscous polymer solution layer to eventually template the above-mentioned giant pores; whereas, a microsphere pattern could be formed by the process of RBF due to much slower increase in concentration of the inner part of the casting solution drop. Moreover, a purebred

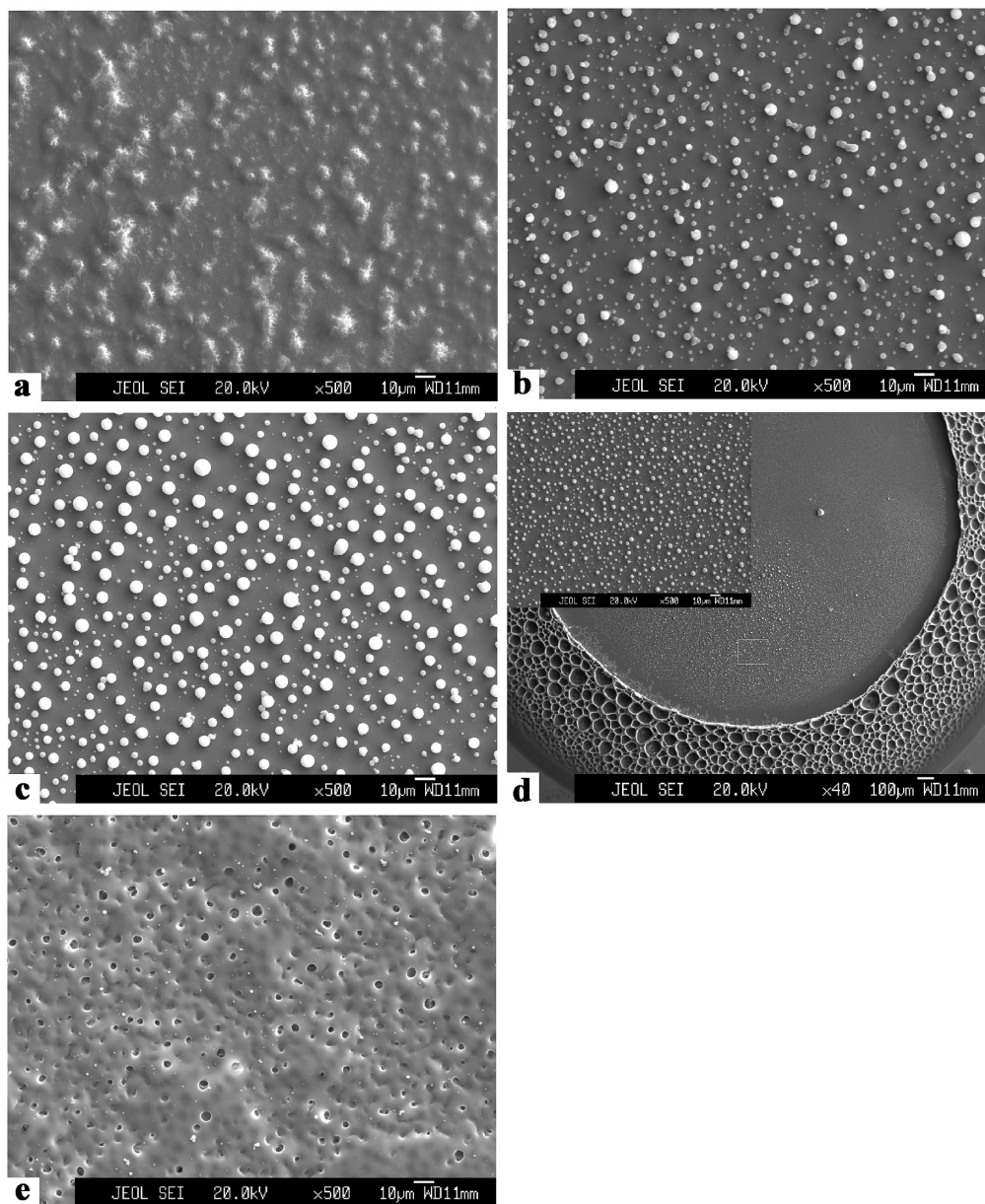


Figure 6. Microstructure evolution of the materials prepared in MeOH vapor at room temperature from different polymer concentrations: (a) 0.1, (b) 0.5, (c) 2.0, (d) 5.0, and (e) 10 wt %. The polymer was (SB)4, and the solvent was TL. The inset is a magnification by a factor of 500.

porous structure of the material was prepared from 10 wt % solution as a result of its high viscosity. On the other hand, when the polymer concentration is too low, such as 0.1 wt %, there might be not enough polymer in the shrinking droplets of polymer solution to form microspheres; in this case a thin layer of sparking-star structure would be formed. These results indicate that an appropriate viscosity of the polymer solution is also required for the preparation of microsphere pattern by the method of RBF.

4. Conclusions

We have shown a facile way, namely reverse breath figure method, to prepare a microsphere pattern. The beauty of this approach is its simplicity: a microsphere pattern can be obtained by simply casting a polymer solution onto a glass substrate in the vapor of an organic solvent up to the complete evaporation of the solvent. The results indicate that the surface tension of the polymer solution should be 1.5 mN/m higher than that of the condensation liquid in order to obtain pure microsphere pattern

and that an appropriate viscosity of the polymer solution is required at the same time. We believe that this method is promising for applications such as drug delivery, biondiagnostics, separation, coating, catalysis carriers, microfabrication, and so on.⁵

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