

Macroporous Polymer Thin Film Prepared from Temporarily Stabilized Water-in-Oil Emulsion

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We report a simple and convenient method for fabricating ordered porous structure in a polymeric thin film. A temporarily stabilized water-in-oil emulsion, where aqueous droplets were dispersed in the medium of polymer–organic solvent solution, was utilized for the preparation of porous structure. The water-in-oil emulsion was simply prepared by sonicating the mixture of water and polymer–organic solvent solution without any colloid stabilizer. The growth of aqueous droplets was profoundly retarded by dissolving a small amount of sucrose, selectively soluble in the dispersed phase. The prepared emulsion was recovered onto a substrate through dip-coating and subsequently air-dried to get a well-ordered porous polymer film. The polymer content in the polymer solution phase and the compositional ratio of the aqueous phase to the polymer solution phase was optimized to fabricate well-ordered structures.

Introduction

Porous materials are generally divided into several categories according to their pore size. Microporous materials have the pores with the diameters below 2 nm, mesoporous ones have pores from 2 to 50 nm, and macroporous ones have pores above 50 nm.¹ Among various types of porous materials, porous polymers have gathered a lot of attention, mainly due to the easy fabrication process and the variety of functionalities based on the diversity of polymeric materials.^{2–4} They can be used as template materials easily removable without severe calcinations. They have the advantages of low cost and light weight. The applications of porous polymers include selective adsorbents,⁵ catalytic supports,⁶ membranes,⁷ lightweight structural materials,⁸ chromatographic materials,⁹ and cell growth matrix.¹⁰

To now, various methods have been developed for the synthesis of the porous polymeric materials. Polymerized high internal phase emulsion (HIPE) is one of the widely used methods.^{11–13} It is a very simple process based on emulsion templating and is appropriate for mass production of porous polymeric material. However, well-ordered porous structure was rarely obtained and harmful reagents for polymerization were frequently involved in the fabrication process. This method has been applied for the preparation of monolithic porous polymer materials rather than polymer thin film.

“Breath figures” is another well-known method. Two or three dimensionally ordered porous structure can be fabricated in a

polymeric thin film. This approach utilizes the condensation of water vapor on the surface of a polymer–organic solvent solution.^{14–21} The droplets of the condensed water self-assemble into a hexagonally ordered array at the air–solution interface.²¹ Upon the evaporation of solvents, well-ordered porous polymer structures are obtained, replicating the ordered structure of the aqueous droplets. However, this method is known to require precise control over the processing environment during the fabrication process. Any gradient of humidity or solvent evaporation rate in the film plane direction leads to a large distribution of pore size. Besides, self-assembly of block copolymers or swelling and evaporation with a solvent/nonsolvent mixture has been utilized to prepare porous polymeric materials.^{22,23}

Here we introduce a new fabrication method for porous polymeric thin films without using any template material or complicated chemistry. A water-in-oil emulsion where aqueous droplets were dispersed in a polymer–organic solvent solution was temporarily stabilized by dissolving a small amount of solute, selectively soluble to water phase. The dip-coating of the emulsion on a substrate and the subsequent air-drying simply led to hexagonally ordered porous structure in polymer thin films. The present approach does not require any template material. Neither the complicated polymer synthetic technique nor the particular functionalization of chemical structure is required. Various porous polymeric materials consisting of pure polymeric component can be prepared by a simple process. The influence from various processing parameters was investigated for a well-ordered porous structure.

Experimental Section

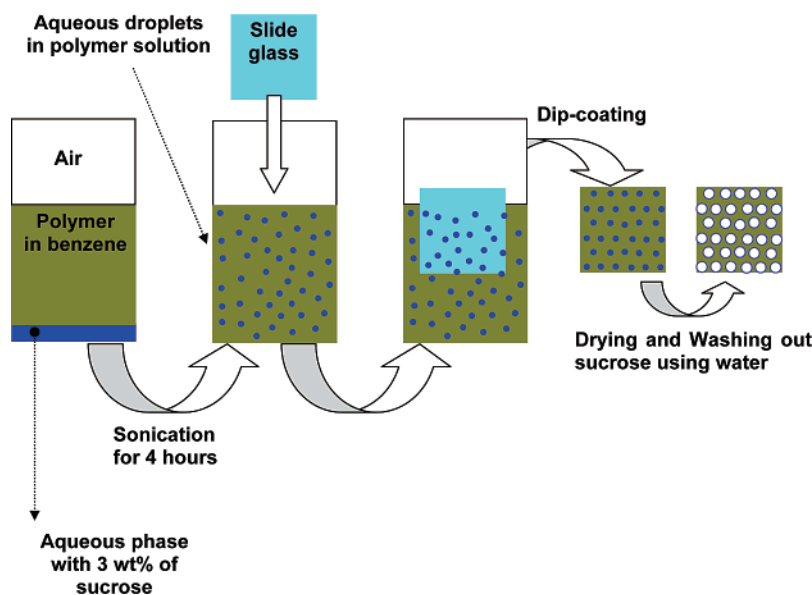
Materials. Two kinds of poly(methyl methacrylate)s (PMMA, M_w : 350 and 120 kg mol⁻¹), polystyrene (PS, M_w : 350 kg mol⁻¹), and sucrose (formula weight: 342.3 g mol⁻¹) were purchased from Aldrich and used without further purification.

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SCHEME 1: Schematic Procedure for a Porous Polymeric Film

Benzene was purchased from Merck and used as received. Dichlorodimethylsilane was purchased from Aldrich and used as received.

Methods. Ten weight percent solution of polymer (PMMA or PS) in benzene was prepared and diluted to get various concentrations from 0.1 to 7 wt %. Three weight percent aqueous solution of sucrose was prepared from deionized water. The predetermined amounts of the two solutions were mixed and sonicated at room temperature (Branson 3510 sonicator at 42 kHz and 100 W for 4 h) to prepare an emulsion, where aqueous droplets (water phase) were dispersed in the medium of polymer–benzene solution (oil phase). The average size of the dispersed droplets in the emulsion was measured using light scattering (Brookhaven 90 Plus Particle Size Analyzer operated at a constant scattering angle of 90° and 25°). The emulsion was recovered onto a glass slide by dip-coating. For the fabrication of porous film of PMMA, a bare glass slide was used as a substrate. It was washed with acetone and deionized water several times prior to dip-coating. For PS film a silanized slide glass was used as a hydrophobic substrate. After dip-coating, the emulsion on the substrate was dried under a strong stream of air to get a porous polymer film. The obtained film was subsequently air-dried in ambient conditions for 12 h and soaked in deionized water for 24 h to remove any residual sucrose. The porous structure was examined using a scanning electron microscope (SEM) (JEOL JSM 5610). The samples for SEM observation were gold-coated to prevent beam damage and to enhance image contrast.

Results and Discussion

The procedure for the fabrication of a porous polymer film is schematically illustrated in Scheme 1. The oil phase was the dilute solution of a polymer in benzene and the water phase was pure water or the dilute aqueous solution of sucrose. The predetermined amounts of the oil phase and the aqueous phase were sealed in a bottle. Because the two phases were immiscible and the density of the aqueous phase was higher, the aqueous phase precipitated to the bottom. Upon sonication, emulsion droplets were produced at the water–oil interface and diffused into the polymer solution phase. It usually took about 30 min for the entire mass of 50–100 g to become turbid. Note that when the aqueous phase was pure water, the breakdown of

emulsion occurred so fast that further processing for film preparation was not allowed. However, the stability of dispersion was remarkably promoted by dissolving a small amount of sucrose (3 wt %) in the water phase. The temporarily stabilized emulsion was recovered on a substrate by dip-coating. Air-drying of the emulsion on a substrate resulted in a well-ordered porous polymer film. Note that the wetting property of the emulsion to a substrate influenced the quality of the final structure. When the wetting was poor, well-ordered porous structure was hardly obtained.

Figures 1a and 1b show SEM images of the porous films of PMMA (M_w : 120 kg mol⁻¹) and PS (M_w : 350 kg mol⁻¹), respectively. Benzene was used as a common solvent in the oil phases. Well-ordered hexagonal porous structures were fabricated for both polymers. The pore size distribution in the PMMA film is summarized in Table 1. The average value was about 710 nm. The average center-to-center distance between neighboring pores was 970 nm. The defect density in ordering was quantized by counting the number of neighboring pores for each pore (Table 2). About 72% of the pores had six neighbors forming hexagonally ordered structure. For a porous PMMA film a bare glass was used as a substrate. However, a glass surface hydrophobically modified by silanization was used for a PS film to promote the wetting. A cross-sectional SEM observation revealed that the fabricated pores penetrated through the film thickness. The large increase of pore size upon the air-drying of emulsion resulted in the membrane-like structure.

Figures 1c and 1d show high-magnification SEM images of the ordered porous films made from the PMMAs with different molecular weights ($M_w = 120$ kg mol⁻¹ for (c) and $M_w = 350$ kg mol⁻¹ for (d) for each). Well-ordered porous structures were fabricated for both molecular weights. The weight fraction of the aqueous phase in the emulsion was fixed (2 wt %) but the polymer content in the oil phase was optimized for the best quality of ordered structure. The polymer content in the polymer solution phase was 3 wt % for the low molecular weight PMMA and 2 wt % for the high molecular weight PMMA. The center-to-center distance between neighboring pores was about 930 nm for the high molecular weight PMMA film. Because the center-to-center distance of cylinders was mainly determined by the fraction of the dispersed phase in the emulsion, the measured value was very close to that of the low molecular

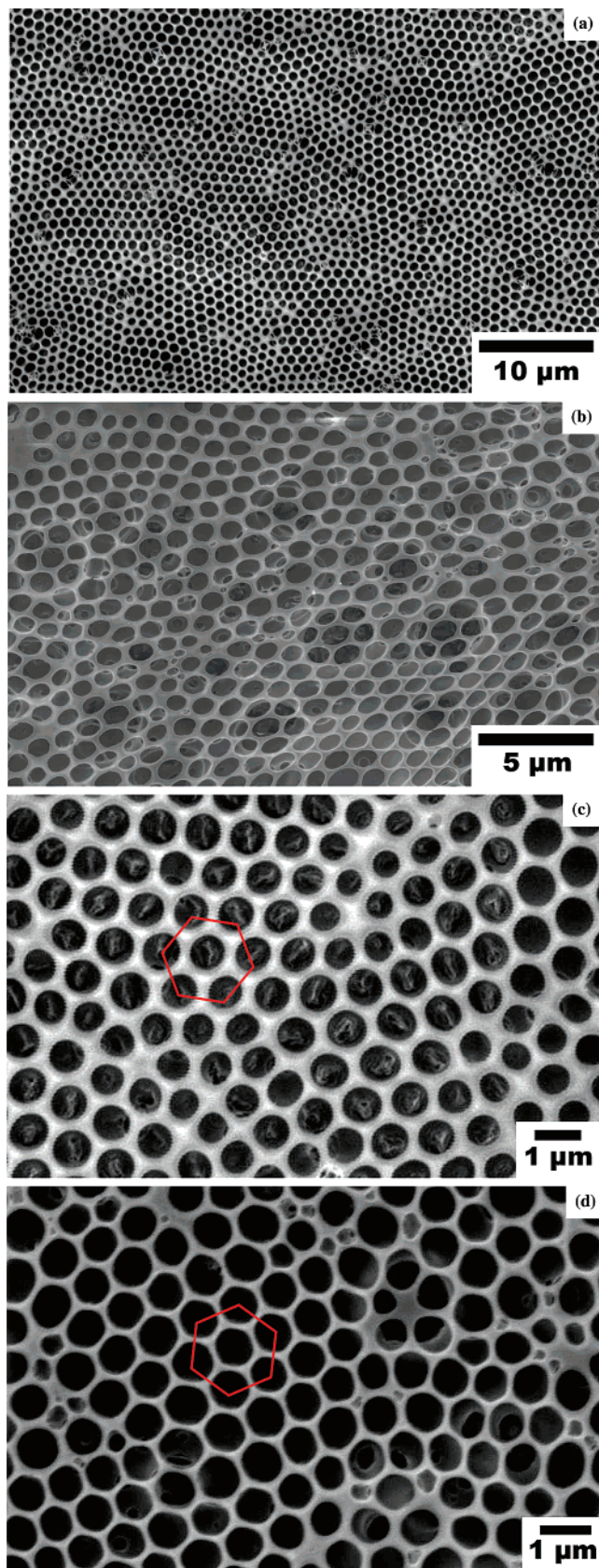


Figure 1. Low-magnification SEM images of (a) a porous PMMA ($M_w = 120 \text{ kg mol}^{-1}$) film, and (b) a PS ($M_w = 350 \text{ kg mol}^{-1}$) film. High-magnification SEM images of (c) a high molecular weight PMMA ($M_w = 120 \text{ kg mol}^{-1}$) film and (d) a low molecular weight PMMA ($M_w = 350 \text{ kg mol}^{-1}$) film.

weight PMMA film (Figure 1a). Meanwhile, the pore diameter was determined by the polymer content in oil phase. The pore

TABLE 1: Statistical Distribution of Pore Diameter

pore size range (nm)	number density of pores per unit area ($\times 10^{-1} \mu\text{m}^{-2}$) ^a
490–580	0.79 (7%)
580–670	3.22 (27%)
670–760	4.60 (38%)
760–850	2.74 (23%)
850–940	0.61 (5%)

^a Obtained from a SEM image in Figure 1a.

TABLE 2: Number Densities of Pores Having Various Numbers of Neighbors

number of neighboring pores	number density of pores per unit area (μm^{-2}) ^a
4	4.4 (4%)
5	18.1 (18%)
6	73.1 (72%)
7	5.4 (5%)
8	0.2 (<1%)

^a Obtained from a SEM image in Figure 1a.

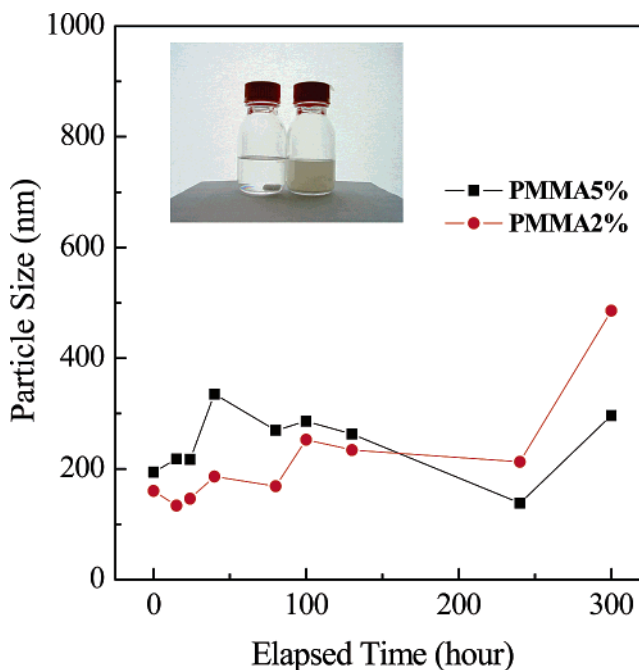


Figure 2. Time-resolved variation of the size of dispersed droplet after sonication. PMMA concentration in oil phase was 2 or 5 wt % for each. Inset shows the status of the mixtures of 2 wt % PMMA solution and 3 wt % sucrose solution before (left) and after (right) sonication.

diameter in the film made from the emulsion with 3 wt % of polymer in the oil phase was about 710 nm but that with 2 wt % of polymer was about 760 nm for each.

In our approach the concentration of polymer in the continuous phase was very low such that a large value of volume reduction occurred during the air-drying of the emulsion. The pore size in the porous polymer film was largely different from the droplet size in emulsion. The exact size of the aqueous droplets dispersed in emulsion was measured by light scattering. The droplet size in the emulsion containing pure water as a dispersed phase could not be measured because the emulsion destabilized as soon as sonication was ceased. The stability of emulsion, however, could be profoundly promoted by dissolving a small amount of sucrose in the aqueous phase.

Figure 2 shows the variation of the droplet size as a function of time. For the emulsion with 2 wt % PMMA solution, the average diameter of 160 nm was obtained immediately after

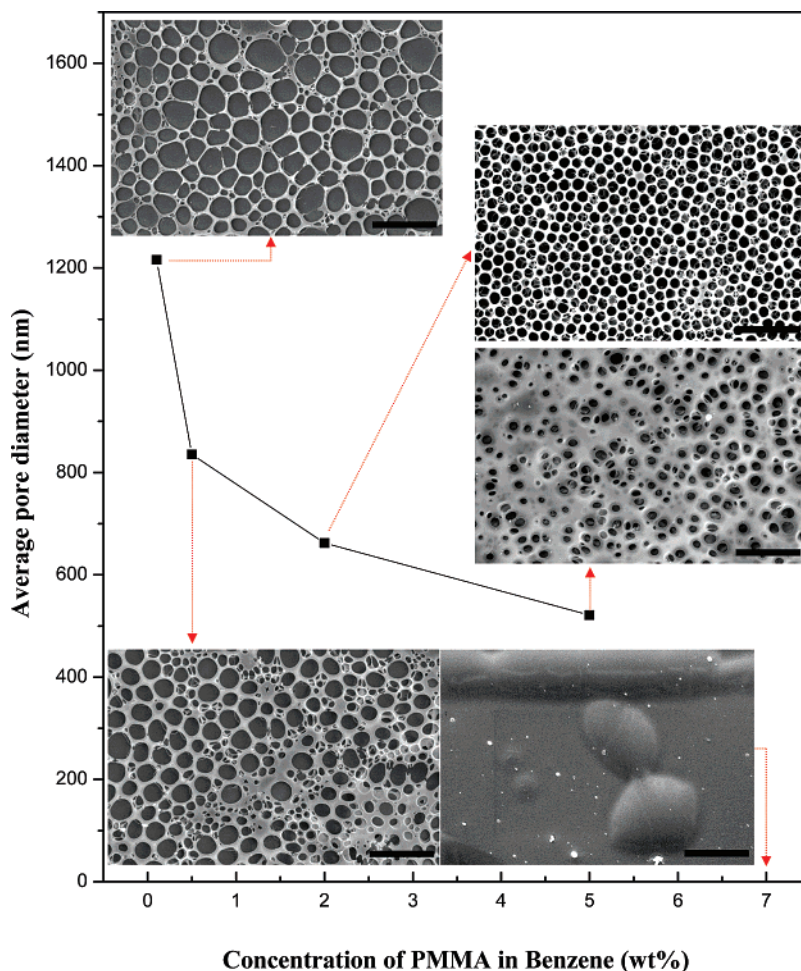


Figure 3. Average pore sizes in the porous PMMA films prepared from the emulsions consisting of various concentrations of PMMA in benzene. Sucrose concentration was fixed at 3 wt % in the aqueous phase. The weight fraction of the aqueous phase in emulsion was fixed at 2 wt %. Inset shows the SEM image of the obtained PMMA film. Scale bar in each figure corresponds to 5 μm .

sonication. The size increased slowly with time and it reached 260 nm at 40 h of elapsed time. After that, the size decreased monotonically, mainly attributed to the precipitation of the large coalesced droplets. The droplet size in the emulsion with a 5 wt % polymer solution evolved in a similar way. The initial droplet size was about 200 nm and reached a maximum at 40 h.

The droplet growth in an emulsion may occur through either collision and coalescence or diffusive coarsening of dispersed molecule (Ostwald ripening).^{24,25} In the present research dissolving a small amount of sucrose retarded the growth of dispersed droplets, suggesting that the main mechanism for domain growth should be Ostwald ripening. Sucrose is not soluble in any solvent except water due to its strong intermolecular hydrogen bonding of eight hydroxyl groups. Ostwald ripening, where the large size droplets increase at the expense of the small droplets, can be suppressed by the addition of a third component selectively soluble to the dispersed phase. The diffusion of dispersed molecules from small droplets to large droplets can be reduced because it would cause an increase in the concentration of the third component in the small droplets and a decrease in the large droplets.^{25,26} The content of the dispersed phase of 2 wt % was sufficiently low enough to exclude effective numbers of the collision for coalescence in the experimental time scale.

After the preparation of the emulsion, it was dip-coated on a substrate and it underwent an air-drying process. Because benzene evaporates much more rapidly than water at an ambient

temperature, the compositional ratio of the aqueous phase to the polymer solution phase increases during the drying process. The coalescence of droplets in the drying process is known to be prevented by thermo-capillary convection.²¹ Due to the difference in the evaporation rate of water and benzene, a temperature gradient is built up between aqueous droplets and the continuous polymer solution.^{27–29} The temperature gradient induces the convective motion in and between the droplets and suppresses the coalescence of the droplets, as long as a finite temperature gradient exists.

We subsequently investigated various processing conditions to understand the relationship between processing parameters and the quality of the finally produced porous structure. The composition of PMMA in oil phase and the compositional ratio of aqueous phase to oil phase were varied for the optimization of the processing conditions. Figure 3 presents the evolution of the average pore diameter in the porous film of a PMMA (M_w : 120 kg mol^{-1}) as a function of the polymer content in the oil phase. The typical morphologies of the porous polymer films obtained at various polymer contents in the organic phase are inserted as insets. The average pore diameter varied in the range from 1200 to 520 nm, as the polymer content was changed from 0.1 to 5 wt %. When the polymer content was very low (0.1 or 0.5 wt %), the polymer film did not cover up the entire substrate after drying. (Bare substrate surfaces were exposed in places.) Additionally the pore size was very large in the covered region due to the coalescence of droplets. For the polymer content of 2 wt %, the pore size distribution was very narrow and the pores

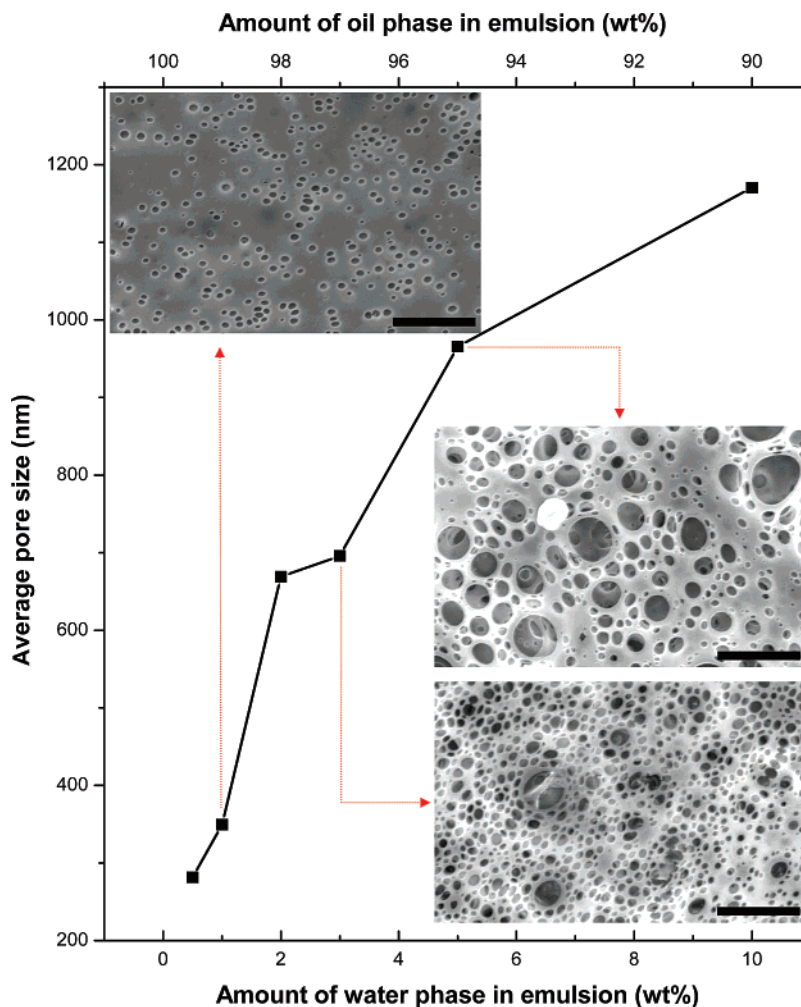


Figure 4. Average pore sizes in the porous PMMA films prepared from the emulsions having various weight fractions of aqueous phases. The contents of PMMA in oil phase and sucrose in the aqueous phase were 2 and 3 wt %, respectively. Scale bar in each figure corresponds to 5 μm .

were hexagonally packed to form an ordered structure. Above 2 wt %, the quality of the porous structure became worse with the polymer content. The SEM image of a porous film obtained from an emulsion with 5 wt % of polymer content in oil phase shows randomly distributed pores with a broad distribution of pore size. When the polymer concentration in the oil phase approached 7 wt %, porous structure appeared no longer. The high viscosity of polymer solution prevented the formation of the aqueous droplets with narrow size distribution. The viscosity of the polymer solution containing 7 wt % of solute was measured to be 32 cP, approximately 8 times the value of a 2 wt % solution.

To investigate the evolution of porous structure with the amount of the dispersed phase, the porous films of a PMMA (M_w : 120 kg mol⁻¹) were prepared from a series of emulsions consisting of various amounts of aqueous phase (0.5–10 wt %). The concentration of sucrose in the aqueous phase was fixed at 3 wt % and the polymer content in the oil phase was 2 wt %, respectively. The average pore diameter is plotted against the amount of aqueous phase in Figure 4. Insets are the typical morphologies of the porous films obtained from the emulsions with the various amounts of aqueous phases. The SEM image of the film prepared from an emulsion containing less than 1 wt % of dispersed phase shows that the number density of pores was too low for regular packing. Pores were randomly distributed without any positional ordering. In contrast, when the amount of the dispersed phase was above 2 wt %, very large pores whose diameters were greater than 1 μm appeared. The

pore size of the film obtained from the emulsion with 3 wt % of aqueous phase showed a large distribution. Very large pores with diameters of several micrometers were observed along with small ones. The large pores should have been produced by the coalescence of several small pores. Such a large distribution of pore size diminished the ordering of pores.

Conclusion

We developed a new fabrication process for polymeric thin films with ordered porous structure. Aqueous droplets (water phase) were dispersed in a polymer solution (oil phase) simply by a sonication process. No emulsifier was applied. However, dissolving a small amount of sucrose in the water phase retarded the coalescence of the dispersed droplets such that further processing for porous film preparation was allowed. Dip-coating of the prepared emulsion onto a substrate and subsequent air-drying enabled the formation of a porous polymer film. Hexagonally packed pores with diameters around 700–750 nm were fabricated in the thin films of PMMA and PS. This simple and universal approach is expected to be applied to other polymers also. Because no colloid stabilizer was used, the fabricated porous material was made of pure polymeric component. The pore diameter in the porous polymer film could be controlled by changing the polymer content in oil phase without influencing the center-to-center distance between neighboring pores. The analysis presented here shows that the quality of the porous structures was critically influenced by the processing

parameters such as polymer concentration in oil phase and the compositional ratio of water phase to oil phase.

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