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Preparation of a Unique Microporous Structure via Two Step Phase Separation in the Course of Drying a Ternary Polymer Solution

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A unique porous polymeric film was prepared by drying a ternary polymer solution: a polystyrene (PS), polyethylene glycol (PEG), and toluene solution. Highly ordered micropores, ranging from 5 to 12 μm in diameter, were formed on the film surface, and the rim of each micropore was surrounded by a ring of PEG. The effects of the weight ratio of the polymer blend and molecular weight of the polymer (PEG) on the porous structure were investigated. Based on in situ visual observation and light scattering measurements, the formation mechanism of the porous structure was speculated to be a two step phase separation: the phase separation into PEG-rich and PEG-poor (i.e., PS-rich) phases occurred first at the surface area of the ternary solutions, where polymers were condensed due to solvent evaporation. The PEG-rich phase became droplets and had an ordered structure on the surface. The PEG-poor phase became a matrix where PS and solvent coexisted as a single phase solution. Secondary phase separation then followed in the PEG droplets, which was induced by further solvent evaporation, and formed into solvent-rich and PEG-rich domains within the droplets. Solvent evaporation and secondary phase separation created a cavity structure in each PEG droplet structured on the film surface.

Introduction

Microporous polymeric thin films attract much attention for their potential use as templating materials,¹ membrane filters,² optical devices,³ catalytic scaffolds,⁴ and scaffolds for biological cells.^{5–7} There are several methods for preparing porous polymer films, such as sintering, stretching, track etching, lithography,⁸ and phase separation. Among them, phase separation is a useful method by which a majority of porous materials are prepared. Recently, phase separation of immiscible polymers has been extensively studied for fabricating highly ordered porous films. Matsuyama et al.⁹ prepared microporous membranes of polypropylene and polybutene from diphenyl ether solution via thermally induced phase separation (TIPS). Won et al.¹⁰ prepared an asymmetric membrane of polysulfone from 1-methyl-2-pyrrolidinone from an ethyl acetate–polymer solution via phase inversion. Cui and Han¹¹ developed a porous film of polystyrene/poly(2-vinylpyridine) via dry casting of an ethylbenzene–polymer solution. Walheim et al.¹² prepared a porous thin film of polystyrene (PS) and poly(methyl methacrylate) (PMMA) by spin-coating of polymer–solvent solutions. Although phase separation has been applied by several researchers to prepare porous materials, the formation mechanism of a porous structure is not yet fully understood. The major difficulty in understanding

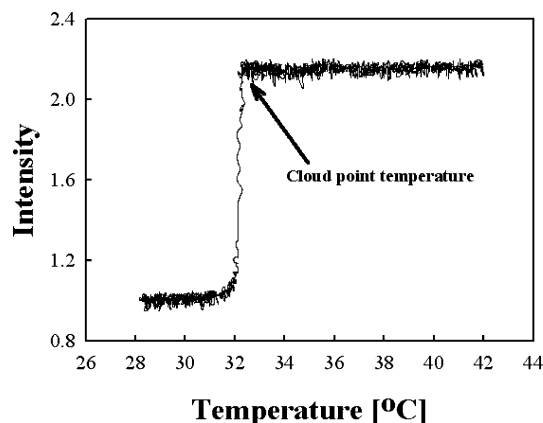


Figure 1. Determination of the cloud point temperature for PS/PEG200 (70/30) (w/w) at 78 wt % toluene.

Table 1. Characteristics of PEG, PS, and Toluene Used in This Work

materials	\bar{M}_w	\bar{M}_n	\bar{M}_w/\bar{M}_n	δ (MPa) ^{0.5}	$\chi_{\text{polymer/solvent}}$
PEG200	280	260	1.07	26.1 ¹⁵	2.68
PEG400	610	540	1.12	23.1 ¹⁵	1.03
PEG600	1100	870	1.31	22.5 ¹⁵	0.79
PS	222 000	99 000	2.24	18.6 ¹⁴	0.34
toluene				18.2 ¹⁴	

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the formation mechanism was attributed to the fact that the mechanism was not unique and it would be different by various factors such as the interaction between polymer and solvent, polymer properties, drying conditions, and film thickness. Cui and Han¹¹ reported that the difference in the surface tension of the two polymers in solvent determined their porous structure. A convection flow was induced by the difference in surface tension of the ternary mixture of polystyrene/poly(2-vinylpyridine)/ethylbenzene blends, and the polymers were transported from the spots of low surface tension to those of high surface tension by convection flow. The pore structure was then formed at the domains of low surface tension by solvent evaporation. Walheim et al.¹² showed a different formation mechanism of the

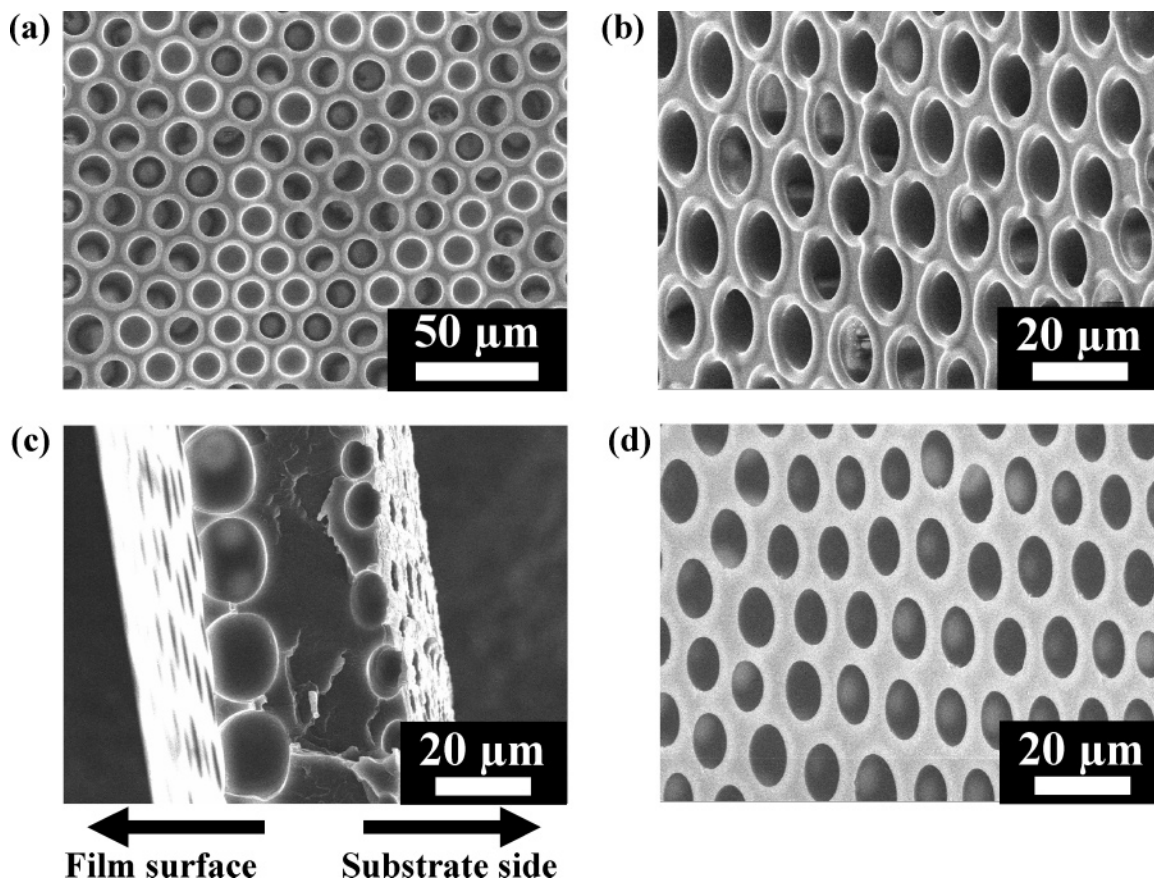


Figure 2. SEM micrographs of PS/PEG200 (70/30) (w/w) cast from 90 wt % toluene solution under 3 L/min N_2 flow: (a) surface micrograph; (b) surface micrograph tilted at 60°; (c) cross-sectional micrograph; and (d) surface micrograph tilted at 60° after rinsing PEG by water.

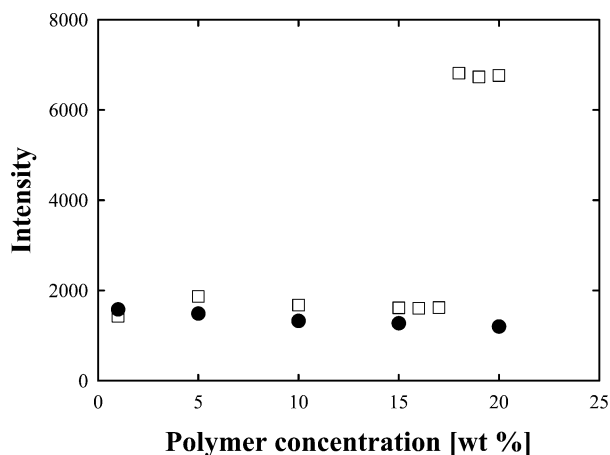


Figure 3. Intensity versus polymer concentration: PS/toluene solution (●) and PS/PEG200/toluene solution (□).

porous structure where the pore structure was formed due to a difference in the relative solubility of the two polymers in a PS/PMMA/toluene system. As the solvent evaporated, due to the lower solubility of PMMA in toluene, the PMMA phase solidified first and then was depleted from toluene, while the PS phase was still swollen with toluene. Further solvent evaporation reduced the size of the swollen PS domain and created cavities in the PMMA domain. As can be seen from previous research, various porous structures could be created because a wide variety of phase transitions existed and they could induce different formations of stable structures in solution.

In this paper, a porous polymeric film, which possesses a highly ordered unique porous structure on its surface, was prepared from a PS, PEG, and toluene solution. Highly ordered micropores,

5–12 μm in pore size, were formed on the film surface, and the rim of each micropore was surrounded by a ring of PEG. The effects of the molecular weight of PEG and the weight ratio of PS to PEG in ternary solution on the uniformity of pore size and the number density of pores were investigated. The formation mechanism of the porous structure in PEG/PS blended films, which was different from the mechanism proposed by Cui and Han¹¹ and Walheim *et al.*,¹² was discussed based on observations of phase separation by light scattering measurements and by using an optical microscope.

Experimental Section

Materials. Polystyrene (PS) was purchased from Aldrich Chemical Co. Three polyethylene glycols with different molecular weights (PEG200, PEG400, and PEG600) were obtained from Wako Pure Chemicals Ind. Ltd., Japan and used as received. The weight average molecular weight, M_w , the number average molecular weight, M_n , and polydispersity, M_w/M_n , of the polymers were measured by gel permeation chromatography (GPC) (Shimadzu, model DGU-20A3; column, Shodex GPC KF-806L; eluent, chloroform). The retention time and molecular weight were calibrated using PS standards. Toluene-dehydrate (Wako Pure Chemicals Ind. Ltd., Japan; purity, 99.5%) was used as solvent without further purification. The material properties including molecular weights are listed in Table 1.

Film Preparation. PS and PEG200 were blended at a weight ratio of 70/30 and dissolved into toluene with 10 wt % initial polymer concentration. The solution was cast by a microinjector onto an aluminum Petri dish, which was 2.1 cm in radius and 0.5 cm in depth. The film thickness was controlled by changing the amount of injected solution. The volume of solution to be injected was 100 μL in the nominal case. The initial thickness of solution was about 300 μm . The cast samples were then dried under a nitrogen purge in a temperature-controlled incubator. Humidity and temperature in

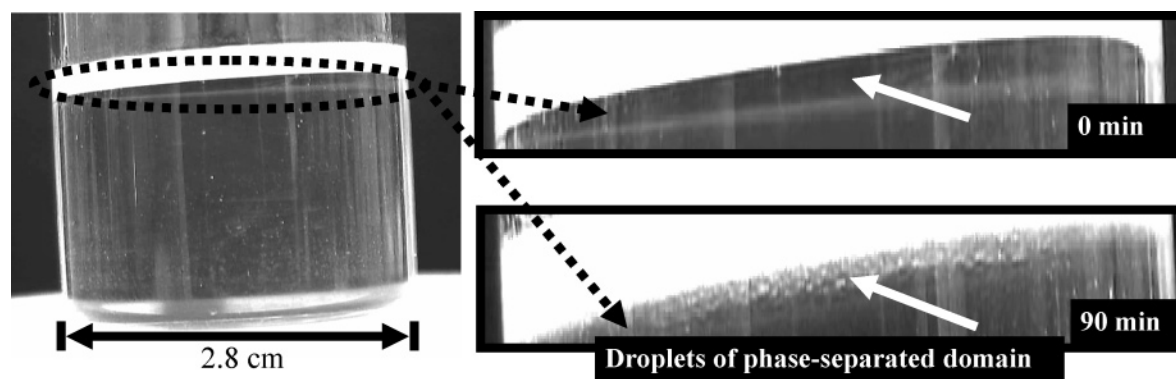


Figure 4. Formation of phase-separated PEG domains on the solution surface (digital video camera observation). The solution of PS/PEG200 (70/30) (w/w) at 90 wt % in toluene was used.

the incubator were measured by a hygro-thermograph (SK-L200T II, SATO KEIRYOKI MFG. Co. Ltd.). All experiments were carried out under 3 L/min nitrogen (purity 99.9%) flow at 30 °C.

Observation of Film Morphology. The surface morphology of dried films was observed by a scanning electron microscope (SEM; Tiny-SEM 1540, Technex Lab Co. Ltd.). The dried film was placed on the SEM stage, coated with gold-palladium under a vacuum atmosphere, and observed with the SEM.

Visual Observation. Visual observation of phase separation was also conducted. The phase separation of the PS/PEG200/toluene ternary solution, of which the initial polymer concentration was 10 wt % in solution, was observed in situ using a digital video camera (Sony, DCR-HC1000) at room temperature. In addition, a microscope (Keyence, VH-Z450) with a digital camera (Keyence, VH-6300) was used at room temperature to observe the formation of a porous structure on the film surface.

Cloud Point Measurement. Cloud point measurements were carried out to confirm that phase separation into PEG-rich and PEG-poor phases occurred prior to phase separation into PS-rich and PS-poor phases and that the secondary phase separation occurred in the PEG-rich phase. PS/toluene binary solutions and PS/PEG200/toluene ternary solutions with different initial polymer concentrations were prepared for light scattering measurements to observe demixing phenomena of the ternary solution. The solutions were filtered before measurement with a 0.45 μm Millipore membrane (Whatman Puradisc 13 mm syringe filters) to remove dust from the solution for accurate light scattering measurement. The scattered light intensities were measured by using an ALV-5000E (ALV-GmbH) instrument equipped with a YAG laser operated at 532.0 nm. The scattering angle was 90°. All measurements were taken at 20 °C.

The effects of polymer concentration and PS/PEG weight ratio on the cloud point temperature were investigated by applying a simple laser scattering scheme (Keyence, LV-H62) to solutions with different initial polymer concentrations and weight ratios in solution. The detail of the scheme was described elsewhere.¹³ A cell containing a sample solution was immersed in a temperature-controlled water bath. The temperature was increased until the solution became homogeneous, and then it was decreased at the rate of 0.1 °C/min until the solution became turbid due to phase separation under continuous stirring. The intensity of the laser beam transmission through the solution was monitored as a function of temperature. As shown in Figure 1, the cloud point temperature was determined by the temperature at which the light intensity changed drastically.

Static Light Scattering Measurements. The mechanism of phase separation was investigated by using a static light scattering analyzer (Otsuka Electronics Co., DYNA-100) with a He–Ne laser ($\lambda = 633$ nm) as the light source. The solution was cast on a glass plate and dried on the temperature-controlled stage in the analyzer to achieve the isotherm. The scattered light intensity was detected by using a photomultiplier charge-coupled device (CCD) at an angle ranging from

0 to 40°. The time interval for the measurement was 0.5 s, and the measuring temperature was 30 °C.

Results and Discussion

Resulting Porous Structure. A mixture of polystyrene/polyethylene glycol 200 (70/30) blend and toluene solution (90 wt % solvent concentration) was prepared and cast on an aluminum Petri dish. It was then dried under nitrogen purging in a temperature-controlled incubator. Figure 2 shows SEM micrographs of surface and cross-sectional areas of the resulting PS/PEG films. As shown in Figure 2a, an ordered porous structure of about 12 μm in pore size was formed on the surface. The porous structure is unique in the view that the rim of each pore is surrounded by a ring of PEG. The rim structure could be confirmed clearly by a SEM micrograph taken by tilting the SEM stage at 60° (Figure 2b). Figure 2c shows a SEM image of the cross-sectional area of the film, which is about 40 μm in thickness. The porous structure was exclusively formed on both the surface and interface between the substrate and solution. No porous structure was observed inside the film as illustrated in Figure 2c. Figure 2d shows a SEM micrograph taken by tilting the SEM stage at 60° after the film was rinsed by water to remove the PEG. Comparison of Figure 2d with Figure 2b clearly shows that the rings surrounding the pores were completely removed by water rinsing. This indicates that the rings were made of PEG.

Formation Mechanism of Porous Structures. In the course of drying the ternary solution, solvent evaporation induces phase separation. Since the solubilities of PS and PEG in toluene are different,^{14,15} PEG, for which toluene is a poor solvent, precipitates from the solution and forms PEG-rich and PEG-poor domains. To confirm that the phase separation of PEG occurred first, cloud point measurements of a binary PS/toluene solution and ternary PS/PEG200/toluene solution were conducted. Results of the cloud point measurements by the laser scattering method are illustrated in Figure 3. The scattered light intensity of the ternary PS/PEG200/toluene solution increased when the polymer concentration became 18 wt %, while that of the binary PS/toluene solution did not change in the range of polymer concentration from 0 to 20 wt %. These results indicate that the ternary solution demixed while the PS/toluene binary solution did not. Figure 4 shows a snapshot picture taken by visual observation experiments in the course of drying the PS/PEG200 (70/30) from the 90 wt % toluene solution. The droplets precipitated from the solution at the surface layer, where the polymer concentration was increased by solvent evaporation. The polymer composition analysis of the droplets

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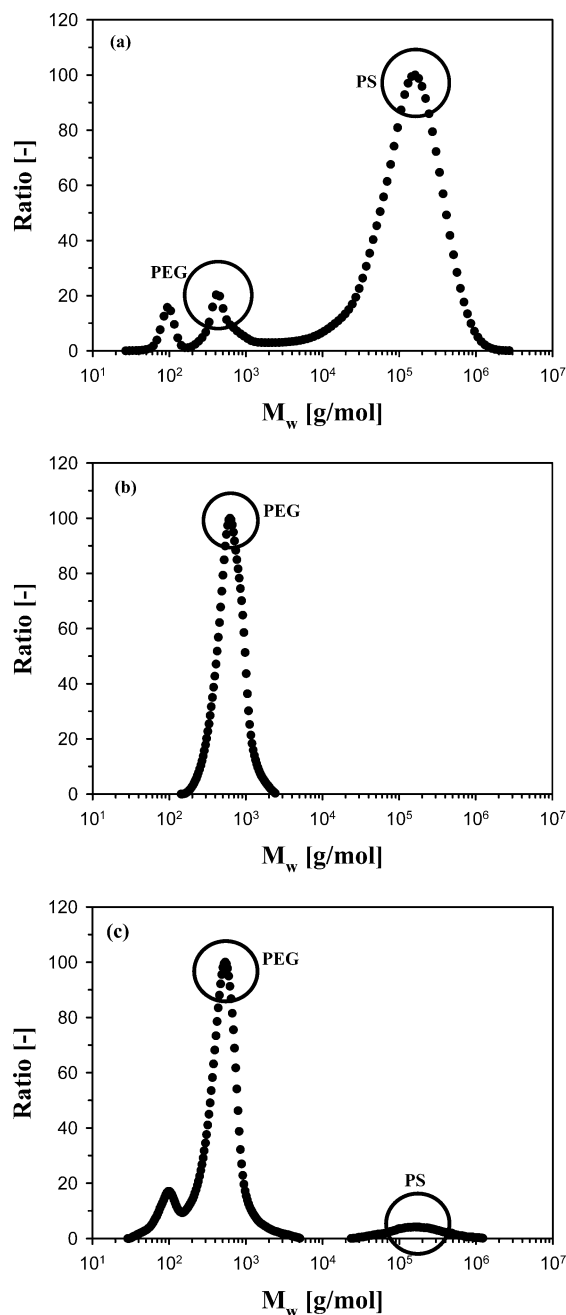


Figure 5. GPC peak profiles for PEG-rich domains and PEG-rich rings: (a) PS/PEG reference sample with a weight ratio of 1 to 1; (b) PEG-rich domain precipitated by primary phase separation; and (c) PEG-ring surrounding the rim of pores.

was conducted by GPC: the droplets were retrieved from the solution by a syringe, and the polymer composition was measured after rinsing the droplets on a $0.1 \mu\text{m}$ Millipore membrane filter with pure toluene. The measured GPC peak profile of the droplets is illustrated in Figure 5b. It clearly shows the major polymer in the droplets was PEG. The polymer composition of the ring was also analyzed by GPC: the resulting porous film was rinsed, the rings were removed by distilled water, and then the composition of the polymers dissolved in the water was analyzed. PEG and a small amount of PS were detected as illustrated in Figure 5c. The PS/PEG weight ratio in the ring was calculated to be 1–99. From these experimental results, it could be considered that the primary phase separation forms PEG-rich and PEG-poor (PS/toluene-rich) domains.

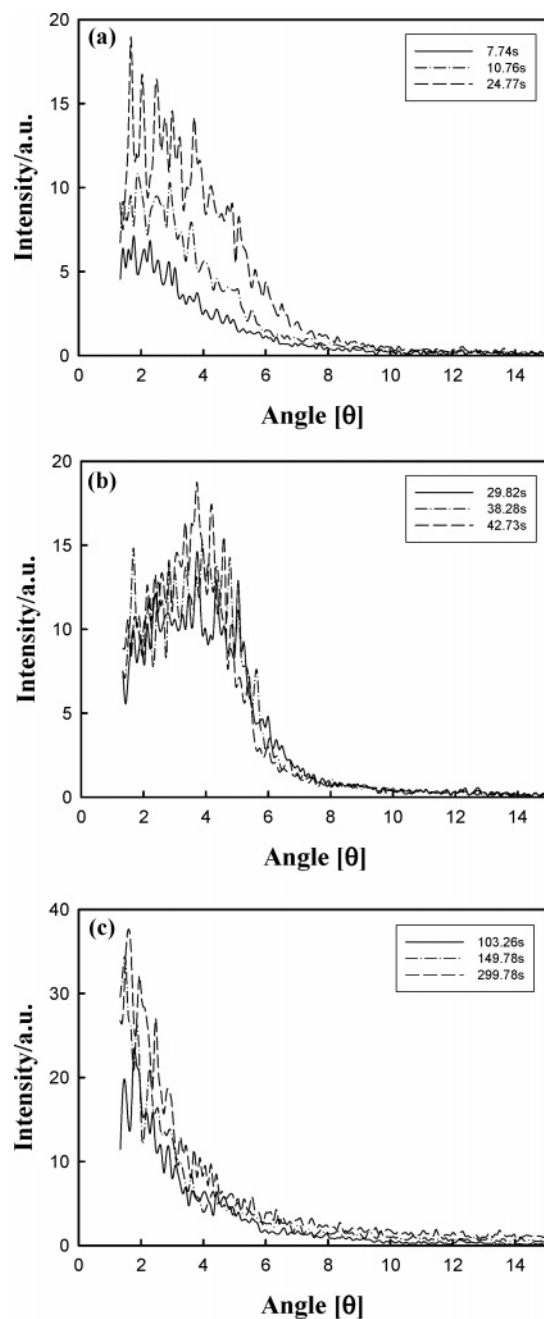


Figure 6. Light scattering patterns recorded for PS/PEG/toluene systems as a function of the angle at different times: (a) initial stage (7.74–24.77 s); (b) middle stage (29.82–42.73 s); and (c) later stage (103.26–299.78 s).

To characterize the primary phase separation, time-resolved light scattering measurements were conducted.^{16–19} The results are illustrated in Figure 6a. Figure 6a shows a monotonic decrease in scattered light intensity with increasing angle and a monotonic increase with time. This light scattering pattern indicates that the phase separation of the PEG-rich phase from PS/PEG/toluene solution was nucleation and growth (NG).¹⁹

The precipitated PEG took droplet shapes, and the droplets created an ordered structure on the surface. Figure 7 shows top view pictures of the solution in a Petri dish taken by the microscope camera in the course of the drying process. In the pictures on the right-hand side, several droplet shape domains were observed,

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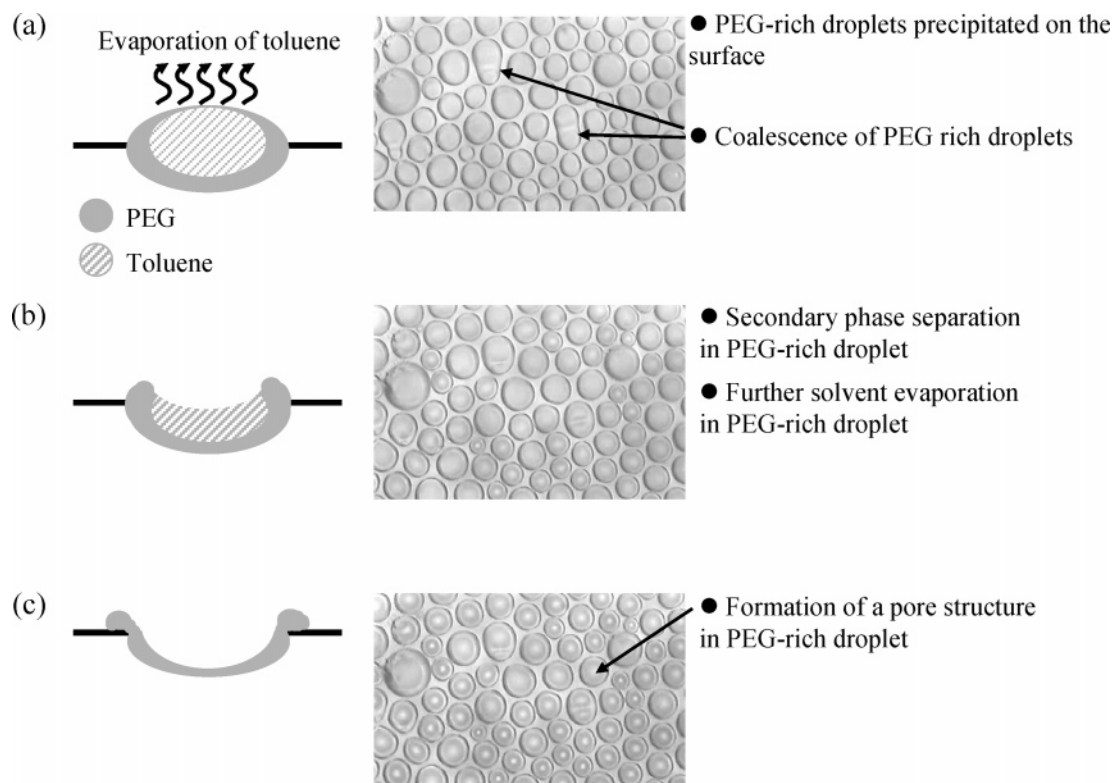


Figure 7. Schematics and pictures taken with a microscope in the visual observation mode to explain the formation of the pore structure.

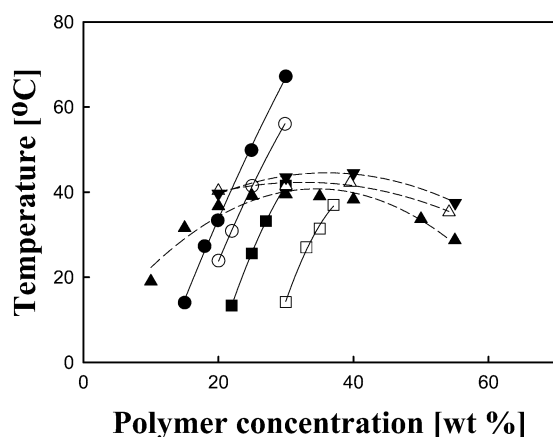


Figure 8. Cloud point temperature of PS/PEG200/toluene solution versus polymer concentration in solutions of PS/PEG with different blend ratios: (▲) 0/100; (△) 0.02/99.98; (▼) 0.04/99.96; (●) 60/40; (○) 70/30; (■) 80/20; and (□) 90/10 wt % of PS/PEG200.

where the PEG-rich domain precipitated on the surface as illustrated in Figure 7a. As time proceeded, the droplets coalesced and the droplet size became larger. At a certain time after the primary phase separation, the secondary phase separation occurred in the droplet as can be seen in Figure 7b and c, where the center of the PEG droplets became bright and a spherical shape phase appeared in the center of each droplet. The new domain could be considered to be a toluene-rich domain, and it created a cavity in each PEG droplet by further solvent evaporation as illustrated in the pictures on the left-hand side of Figure 7.

To confirm the occurrence of the secondary phase separation in the PEG-rich domain, cloud point measurements of PEG200/toluene solution with a small amount of PS were conducted. Figure 8 shows the cloud point temperature–polymer concentration curves for ternary solutions with different PS/PEG weight ratios. As shown in Figure 8, the miscibility of polymer to toluene increases with temperature and the PS/PEG/toluene mixture has

upper critical solution temperature (UCST) behavior. It is also found that binodal lines (cloud point temperature–polymer concentration curve) changed with the PS content. When the PS content is very small, as is the case with the 99.98/0.02 and 99.96/0.04 PEG/PS weight ratios, the binodal lines represented by the dotted line show a convex shape in the polymer concentration range from 0 to 60 wt %. The PEG-rich domain was formed by the primary phase separation. The PEG-rich domain contained a small amount of PS as shown by the GPC peak profile (Figure 5c). For the PEG-rich domain, the convex shape binodal line can be applied. In the drying experiments, solvent evaporation continued in the PEG-rich domain after the primary phase separation. The polymer concentration in the PEG-rich domain was increased by drying even under the isotherm condition. The domain would be thrust into the two-phase regime given by the dotted line to form solvent-rich and PEG-rich domains in the droplet.

Time-resolved light scattering measurements were also conducted in the course of drying the ternary system. At the initial stage of the scattering measurements, the scattered light intensity change was associated with nucleation and growth of the primary phase separation as illustrated in Figure 6a. At the middle stage, the scattered light intensity was not stable. This instability is probably due to droplet coalescence. At the later stage of the measurements, the scattered light intensity decreased monotonically with increasing angle and increased with time as illustrated in Figure 6c. This is a typical pattern of nucleation and growth. Thus, the kinetics of the secondary phase separation could be regarded as nucleation and growth.

Periodicity of the Surface Structure. The aforementioned formation mechanism of the PEG-rich domain in the solution does not explain the formation of the ordered pattern at the surface. Since the light scattering measurements suggested a nucleation and growth mechanism of the phase separation, we could not expect any periodic domain distribution generated by spinodal decomposition in a critical or near-critical two-component

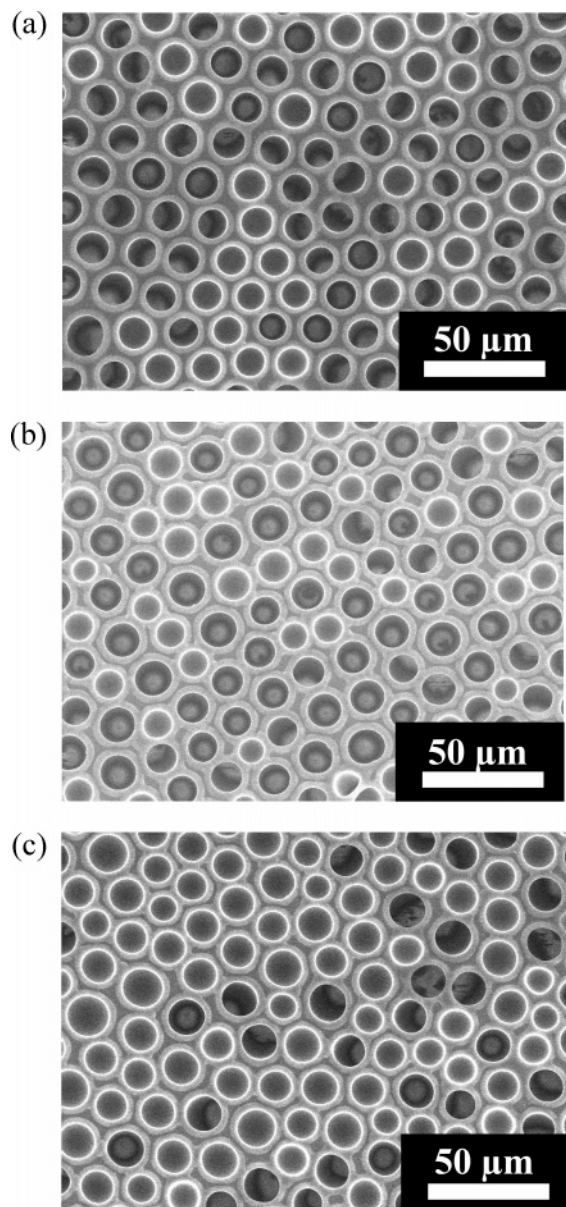


Figure 9. SEM micrographs of PS/PEG200 (70/30) (w/w) films cast from toluene solution at 10 wt % polymer with different initial solution thicknesses: (a) 300 μm ; (b) 500 μm ; and (c) 700 μm .

polymer system.²⁰ Thus, the ordered structure of the droplets observed in this study can be attributed to either capillary interaction^{21–23} or Marangoni convection.^{24–26} Preliminary experiments were conducted by varying the solution thickness to investigate the Marangoni convection effect. Since the Marangoni number is function of thickness, the formation of films with different thicknesses should lead to a strong change in the surface pattern. Figure 9 shows the surface patterns observed for three films with different thicknesses. The film thickness was changed by varying the amount of injected

solution. As can be seen in Figure 9, the surface pattern did not change drastically with film thickness. Therefore, it is highly possible that the periodicity of the surface structure of PS/PEG/toluene was determined by the capillary interactions.

Formation Mechanism of the PEG Ring at the Rim of the Pore. The formation mechanism was also speculated as follows: by the primary phase separation, the PEG-rich droplets were formed and floated at the surface of the solution in a balance of surface tensions.²⁷ Further solvent evaporation was considered to induce the secondary phase separation in the PEG-rich droplets and form solvent-rich and PEG-rich domains within the droplets. Because of the low density of toluene (0.87 g/cm³) and the low viscosity of PEG200 (45–65 mPa·s), the phase separated solvent-rich domain coalesced easily and moved toward the surface. The cavity was created by further solvent evaporation as a footprint of the solvent-rich domain in the droplet as illustrated by the left-hand side of Figure 7. It is probably because the interior of the micropore was coated with PEG and an amount of PEG was pushed into the air by the surface tension balance at the rim of pore. It was considered that this mechanism created the ring of PEG at each micropore.

Formation of Pores at the Substrate Side. As illustrated in Figure 2c, some pores were observed at the substrate side of the film. This is due to the higher density of PEG than those of PS and the solvents (the densities of PEG, PS, and toluene are 1.11, 1.04, and 0.87 g/cm³, respectively). The PEG-rich droplets precipitated at the air–solution surface floated on the surfaces of solutions by a balance of surface tensions.²⁷ However, the droplets sunk down to the bottom due to gravity when the balance was broken. During drying, some of the precipitated droplets sunk and then created pores at the substrate side; however, they did not show any higher ordered structures.

Effect of the Weight Ratio of PS to PEG in the Polymer Blend on the Formation of Pore Structure. The effect of the weight ratios of PS and PEG200 in the polymer blend on the uniformity of pore size and the number density of pores on the film surface was investigated. Four PS/PEG/toluene solutions, of which the weight ratios of PS/PEG in the blend were 90/10, 80/20, 70/30, and 60/40, were prepared, while the initial polymer concentration in the solution was set at 10 wt %. Figure 10 shows SEM micrographs of film surfaces with different PS and PEG weight ratios. As shown in Figure 10, both the pore size and the number density of pores were changed by the weight ratio of PS/PEG. The average pore size, its variance, and the number density of pores on each film were measured from the SEM micrographs. The results are illustrated in Figure 11. The average pore size increased from 3.9 to 12.6 μm , and the number of pores in a unit surface area decreased from 7×10^{-3} to 3×10^{-3} pore/ μm^2 as the weight percentage of PEG in the polymer increased from 10 to 40 wt %. From the cloud point temperature–polymer concentration curves illustrated in Figure 8, the polymer concentration in the solution in which phase separation occurs at 30 °C was calculated, and it is illustrated in Figure 12. As the PEG fraction in the PS/PEG ratio was reduced from 60/40, 70/30, and 80/20 to 90/10, the polymer concentration at the onset of phase separation increased and the PS concentration in the solution increased from 11.4 (60/40), 15.23 (70/30), and 20.96 (80/20) to 30.78 wt % (90/10). This means that a reduction of PEG in the solution increases the miscibility of the polymer blend in toluene and that PEG phase separation was delayed until a state of higher polymer concentration was achieved. In

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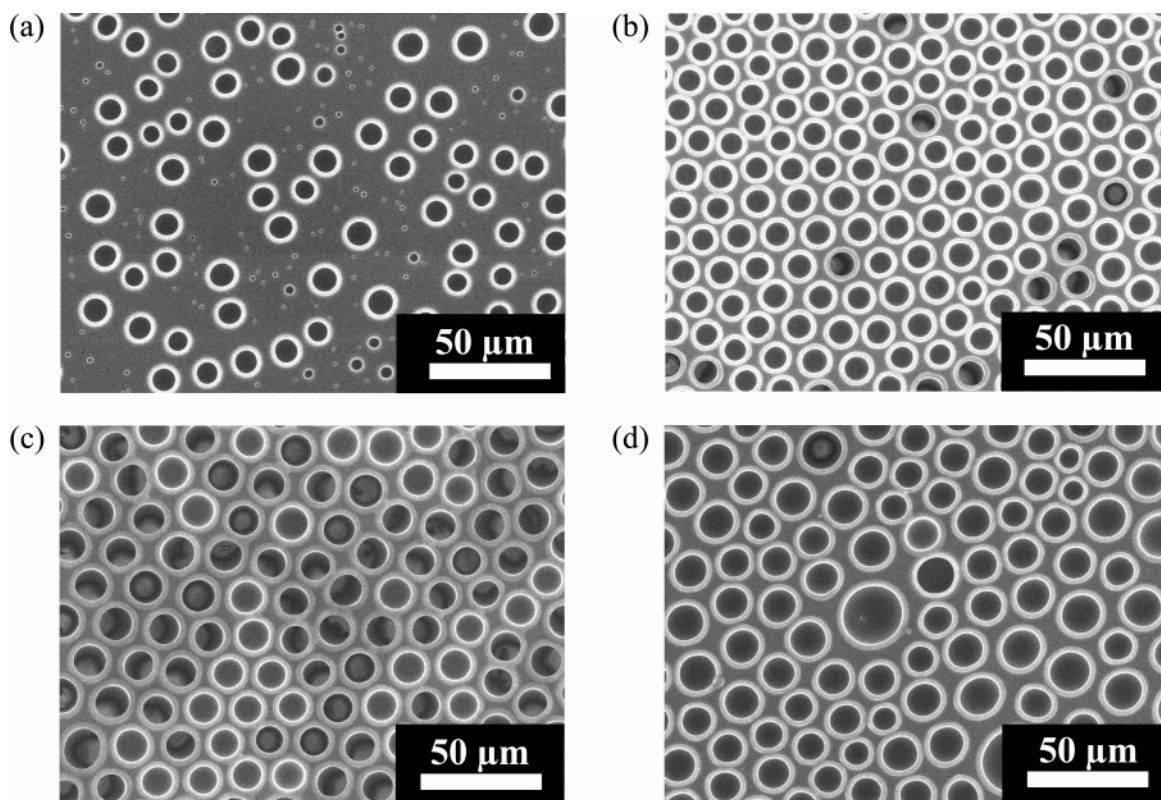


Figure 10. SEM micrographs of PS/PEG200 cast films obtained from toluene solution at 10 wt % polymer with different PS/PEG weight ratios of (a) 90/10; (b) 20/80; (c) 30/70; and (d) 60/40 wt %. The solution was dried under a 3 L/min N_2 flow rate.

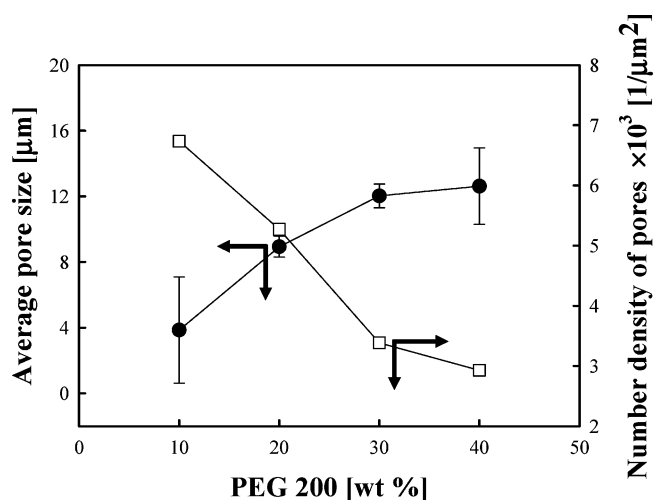


Figure 11. Average pore size and number density of pores plotted against the initial amount of PEG200 in the polymer component of the solution: (●) average pore size and (□) number density of pores.

other words, the concentration of PS in the solution increased while the PEG fraction in the polymer blend decreased at the onset of phase separation at 30 °C. Thus, the decrease in the PEG fraction in the polymer blend increases the polymer concentration; that is, the PS concentration in solution at the onset of PEG phase separation and the viscosity of the solutions at the onset of phase separation become higher as the PEG fraction in the polymer blend is lowered. The higher viscosity of the solution suppressed coalescence of the PEG-rich droplet shape domain after the phase separation because the droplets were floating in the solution. Therefore, the pore size decreased with the decrease in PEG wt % in the polymer blend. Due to the mass balance of

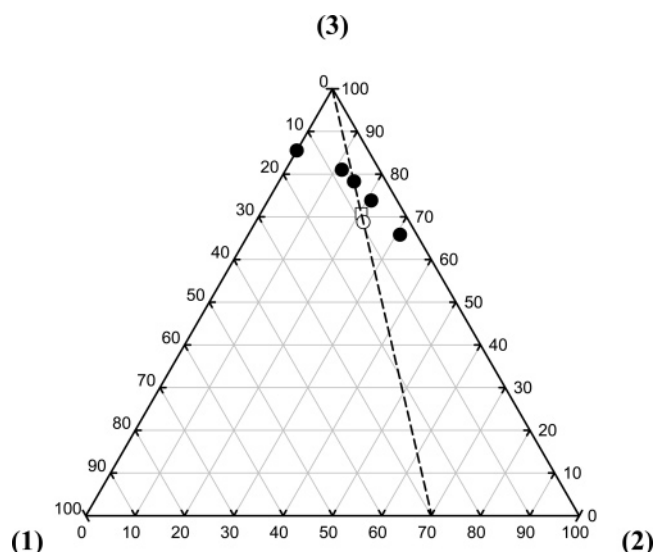


Figure 12. Phase diagram of PEG (1)/PS (2)/toluene (3) solutions at 30 °C: (—) PS/PEG polymer blend with 70/30 wt % PS/PEG weight ratio and cloud point concentration at 30 °C of (●) PEG200; (□) PEG400; and (○) PEG600.

PEG, the number density of pores became larger as the pore size became smaller. The variance of pore size, which is depicted in Figure 11 by error bars, became 3.23, 0.64, 0.72, and 2.33 μm for 10, 20, 30, and 40 wt % PEG in the polymer, respectively. The uniformity of the pore size should increase with the increase in the packing ratio of PEG droplets. However, since coalescence was enhanced as the PEG weight fraction in the polymer blend increased, the degree of variability in pore size became smaller as the PEG fraction in the polymer blend increased, but it became larger as the PEG fraction increased further.

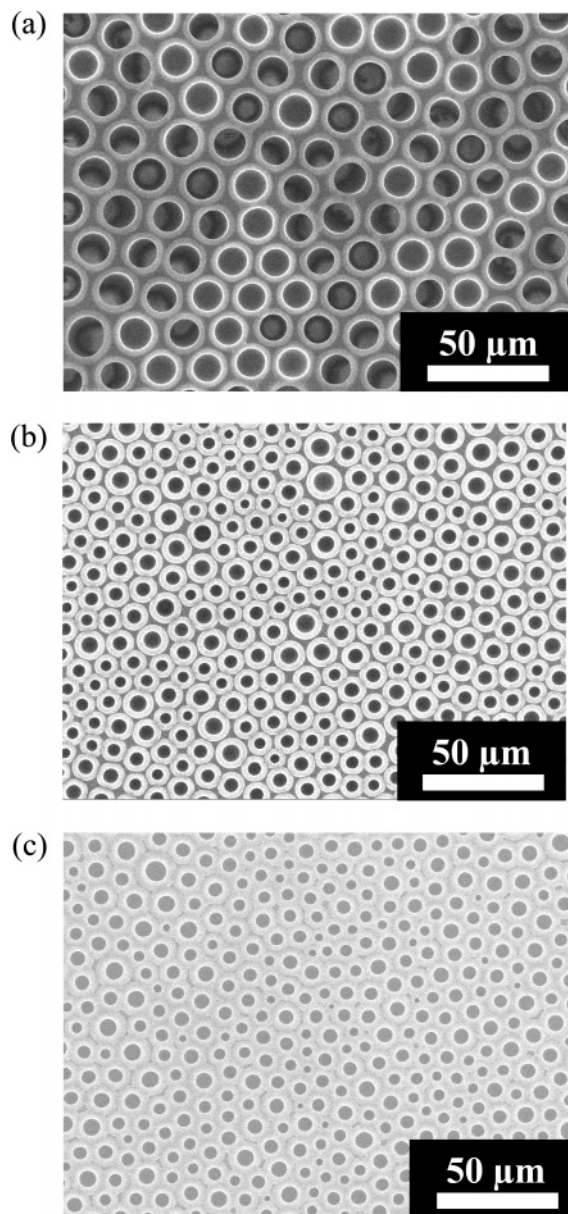


Figure 13. SEM micrographs of PS/PEG cast films obtained by drying PS/PEG/toluene solution under a 3 L/min N₂ flow rate. The initial polymer concentration was 10 wt % with different molecular weights of (a) PEG200; (b) PEG400; and (c) PEG600.

Effect of the Molecular Weight of PEG on the Formation of Pore Structure. The effects of the molecular weight of PEG on the uniformity of pore size and the number density of pores were investigated. As listed in Table 1, four different molecular weights of PEG were blended with PS at a weight ratio of 70/30 in the polymer blend and dissolved into toluene by 90 wt % of the solvent concentration. The PS/PEG/toluene solutions were cast and dried in the incubator. Figure 13 shows SEM micrographs of the film surface made using four different molecular weights of PEG. As shown in Figure 13, the pore size and the number density of pores on the film surface changed with the increase in PEG molecular weight. The average pore size, the number density of pores, and the variability of pore size were calculated from the SEM micrographs. The results are illustrated in Figure 14. The average pore size decreased and the number density of pores increased with the increase of PEG

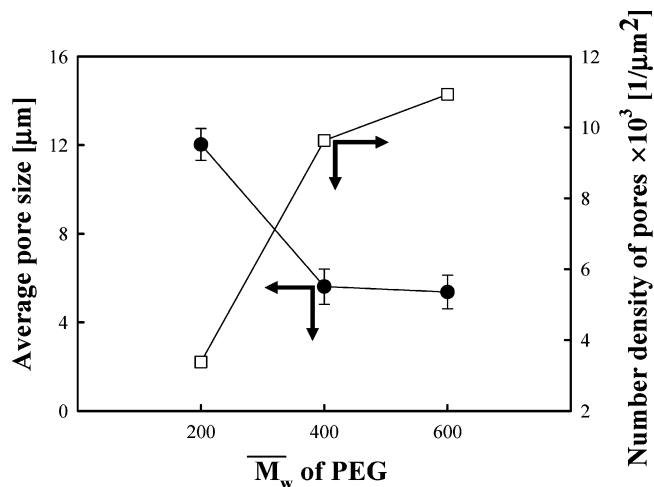


Figure 14. Average pore size and number density of pores versus molecular weight of PEG: (●) average pore size and (□) number density of pores.

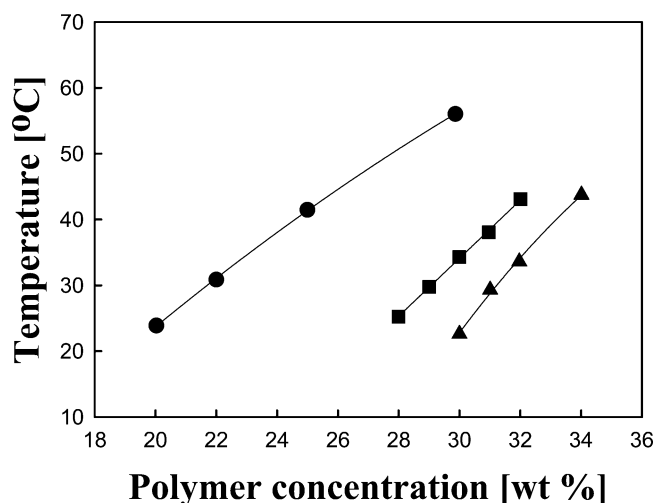


Figure 15. Cloud point temperature of PS/PEG/toluene solutions versus polymer concentration in solutions with a weight ratio of PS/PEG at 70/30 wt %: (●) PEG200; (■) PEG400; and (▲) PEG600.

molecular weight. The variability of pore size was not changed by the molecular weight of PEG; it was about 0.7 μm for all solutions.

To explain the effect of the molecular weight of PEG, the miscibility of PEG200, PEG400, and PEG600 to toluene was investigated. The miscibility of polymer to solvent is often evaluated by the Flory–Huggins interaction parameter (χ), which is given by

$$\chi = \frac{V_i}{RT}(\delta_i - \delta_j)^2 + \beta$$

where V is the molar volume of the solvent, δ is the Hildebrand solubility parameter for the solvent (i) and polymer (j), R is the gas constant, and T is the absolute temperature.²⁸ The term β corresponds to the entropic component, and a value of 0.34 is generally used for nonpolar systems.

Table 1 shows the Flory–Huggins interaction parameters (χ) for toluene and PEG200, PEG400, and PEG600. These parameters were calculated without an entropic component ($\beta = 0$) because of the polarity of PEG that was used. Grulke stated that a polymer

(28) Mark, J. E. *Physical properties of polymers handbook*; Springer: New York, 1996.

was considered to be miscible to the solvent when χ became lower than 0.5. That is, the smaller the value of χ , the higher the miscibility of the polymer to solvent. The interaction parameters of each PEG and toluene pair were calculated to be $\chi_{\text{PEG200/toluene}} = 2.68$, $\chi_{\text{PEG400/toluene}} = 1.03$, and $\chi_{\text{PEG600/toluene}} = 0.79$. This indicates that, with the increase of PEG molecular weight, the miscibility of PEG to toluene increased. The cloud point temperatures of the PS/PEG200/toluene, PS/PEG400/toluene, and PS/PEG600/toluene solutions were measured experimentally by varying the initial polymer concentration in solution. The resulting cloud point temperatures were plotted in Figure 15. The concentrations of PEG/PS/toluene at the cloud point at 30 °C for the three solutions, whose PS/PEG weight ratios were 70/30, were plotted in Figure 12. As can be seen in Figure 12, the PEG concentrations at the onset of the PEG phase separation were 6.53 wt % for PEG200, 8.76 wt % for PEG400, and 9.38 wt % for the PEG600/PS/toluene solution, and the concentrations of PS at the onset were 15.23 wt % for PEG200, 20.44 wt % for PEG400, and 21.88 wt % for PEG600 due to the 70/30 weight fraction of PS/PEG in the polymer blend. That is, the higher molecular weight PEG delayed PEG phase separation such that there were higher concentrations of PEG and PS when the solution was dried. The viscosity of the solution at the onset of the phase separation increased as the molecular weight of PEG increased. The high viscosity of the PEG-poor phase (in other words, the PS-rich phase) suppressed the coalescence of the PEG-rich droplet shape domain after the phase separation. Therefore, the pore size decreased with the increase of PEG molecular weight.

Conclusions

Polymeric porous films, which have a uniform pore size on their surfaces, could be prepared by phase separation that is induced by solvent evaporation. A unique porous structure in which the rim of each pore is surrounded by a PEG ring was created. The porous structure was exclusively formed on the film surface and substrate side. The formation mechanism of the porous structure was considered to be two step phase separation. The phase separation into PEG-rich and PEG-poor (PS-rich) phases occurred first at the surface area of the ternary solutions, where polymers were condensed due to solvent evaporation. The PEG-rich domains were precipitated as droplets and were arranged in an ordered structure on the surface due to capillary interaction. The droplet coalescence was controlled by the viscosity of the matrix phase, that is, the PEG-poor (PS-rich) domain. Secondary phase separation then followed in the PEG droplet and formed into solvent-rich and PEG-rich domains. Further solvent evaporation created a cavity in each PEG droplet. The formation mechanism can be applied to any immiscible polymer blend and solvent system, where one of the polymers has a higher solubility in the solvent and the other has poor solubility and phase separation can be induced by drying. The obtained porous film will be applied to a template material for the fabrication of a microscale feature on optical devices and polymer products.

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