

Microporous Polystyrene Membranes Produced *via* Thermally Induced Phase Separation

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열적으로 유도된 상 분리에 의해 제조된
폴리스티렌 미세 다공성 막

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Abstract: The effects of coarsening on microstructure formation in polystyrene-cyclohexane solutions and membranes made from them were studied by scanning electron microscopy(SEM). Thermal analysis of the polymer solutions was carried out with a differential scanning calorimeter and the binodal curve was determined from the onset temperature of the heat of demixing peak. Using thermally induced phase separation(TIPS) and a freeze drying technique, it was demonstrated that polymer membrane microstructure can be changed significantly by controlling coarsening time and quench route. For systems undergoing phase separation by spinodal decomposition, resulting in a well interconnected, microporous structure with nearly uniform pore sizes, it was found that extending the phase separation time prior to freezing and solvent removal can result in a significant increase in pore or cell size which is highly dependent on both quench depth and coarsening time. Also this study has revealed the important role of polymer concentration in dictating the material continuity of the membranes.

요 약 : 폴리스티렌과 싸이클로헥산 용액으로부터 제조된 멤브레인의 미세구조 형성에 미치는 coarsening의 효과를 주사전자현미경(SEM)을 이용하여 연구하였다. 고분자 용액의 열 분석은 DSC를 이용하여 행하여졌으며 demixing peak의 개시 온도로부터 binodal 곡선이 결정되었다. 열적으로 유도된 상 분리(TIPS) 공정과 freeze drying 기법을 이용하여 제조된 고분자 막의 미세 구조는 coarsening 시간과 quench 경로에 의해 큰 영향을 받음이 확인되었다. Spinodal decomposition이 상 분리 기구인 경우에는 멤브레인의 미세 구조가 서로 잘 연결되고 거의 일정한 cell 크기를 갖게 되며, 용매를 제거하기 이전에 상 분리 시간을 증가시킴으로써 멤브레인의 pore 크기를 증가시킬 수 있음이 판명되었다. 또한 멤브레인의 cell 또는 pore 크기 증가는 coarsening time과 quench depth에 크게 의존함이 확인되었다. 본 연구에서는 특히 고분자 용액의 농도가 이로부터 제조되는 고분자 막의 구조에 미치는 역할을 규명하였다.

1. Introduction

Membranes can be prepared from a variety of materials in various ways. Thermally induced phase separation (TIPS) is distinguished from the more common nonsolvent induced phase inversion (NIP1) method of membrane preparation in at least one important way: a homogeneous solution from which the membrane is formed is converted to a two-phase mixture *via* the removal of thermal energy rather than by the slower exchange of nonsolvent for solvent. The microstructure of polymer membranes produced *via* TIPS of polymer solutions is a strong function of both the early-stage (by spinodal decomposition or nucleation and growth) and the late-stage phase separation (referred to in general as coarsening) [1-2]. Since membrane transport properties correlate directly with their morphology and the microstructure is strongly influenced by the different preparation variables, the ability to analyze quantitatively the conditions controlling the structure formation is of great practical importance.

The microstructure of the two-phase system will continue to evolve even after the early stage development of structure, in response to its tendency to reduce the surface energy associated with interfacial area. This process, called coarsening, often results in a reduction in the number of droplets and an increase in their size [3-4] which is manifested in polymeric membranes as an increase in pore or cell size [6-8]. The coarsening process is of both fundamental and practical interest in materials science and has been the subject of significant theoretical and experimental studies.

2. Experimental

2.1. Materials

Atactic, monodisperse polystyrene (PS) standards (Pressure Chemical, USA) were used. PS was chosen because of the extensive characterization data available. PS is available commercially in a wide

Table 1. Molecular Weight of Polystyrene*

Polystyrene	M_w	M_n	M_w/M_n
PS (1.9×10^5)	1,921,000	1,524,000	≤ 1.3
PS (2.9×10^4)	288,800	274,600	≤ 1.06

* M_w : Weight-average molecular weight

M_n : Number-average molecular weight

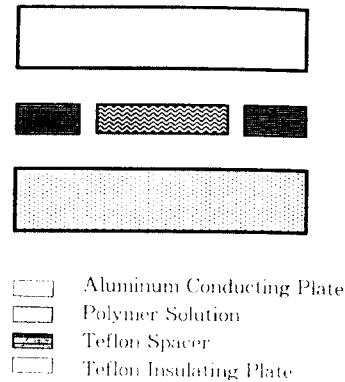


Fig. 1. Schematic diagram of the membrane casting cell for the thermally induced phase separation (TIPS) process.

range of molecular weights, and even high molecular weight PS can be obtained with a narrow molecular weight distribution. The molecular weight characteristics of the PS samples under study are given in Table 1. Cyclohexane and methyl cyclohexane were obtained in reagent grade from Aldrich and used without further purification.

2.2. Preparation of Membranes

The casting cell for the TIPS membrane is shown in Fig. 1. PS was dissolved in a solvent, and the homogeneous solution was transferred into the casting cell which has a diameter of 80mm. The casting cell is composed of a thin aluminum sheet (0.4mm thick), Teflon block (1/4inch thick), and Teflon spacer (400 μ m). The surface of the aluminum sheet is highly polished. Teflon block is used because it is a good thermal insulator. The casting cell was sealed by nuts and bolts. The homogeneous polymer solution is confined within a casting cell and placed into the water bath held at constant temperature

below the binodal point.

After the coarsening process, the solution is fast-frozen by pouring liquid nitrogen on the casting cell (top surface of thermal conducting plate). After the membrane is frozen, the cell is opened, and the solvent is removed by freeze drying. In the case of freeze drying, a VirTis bench top freeze-dryer was used. A Hitachi S-570 scanning electron microscope was used for the characterization of membranes. Cross-sections of the resulting membranes were prepared by freeze-fracturing method under liquid N_2 , and membrane samples were gold sputtered before analysis by scanning electron microscopy.

2.3. Construction of Phase Diagrams

Thermal analysis of the polymer solutions was carried out with a differential scanning calorimeter

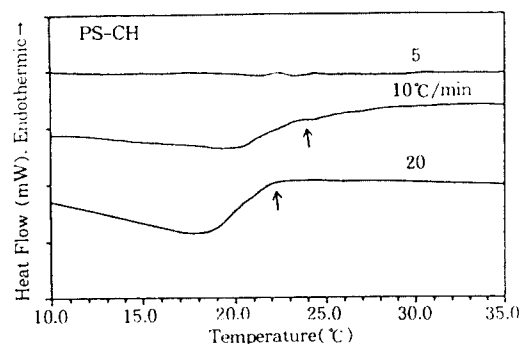


Fig. 2. Differential scanning calorimetry of a 15 wt% PS-cyclohexane solution ($M_w = 2.9 \times 10^5$) at different cooling rates.

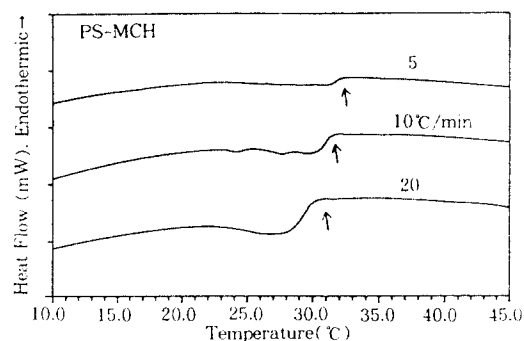


Fig. 3. Differential scanning calorimetry of a 13 wt% PS-methyl cyclohexane solution ($M_w = 3.1 \times 10^5$) at different cooling rates.

(Perkin-Elmer DSC-7). The binodal curve was determined from the onset temperature of the heat of demixing peak. Approximately 10 mg of polymer solution was placed into an aluminum pan and hermetically sealed. The sample was then scanned at cooling rates ranging from 1 to 40 °C/min. A dry-ice/methanol mixture was used as the cooling medium. The initial temperature of polymer solution for the thermal analysis was well above the expected cloud point, and the solution was allowed to remain at that temperature for 5 min to ensure that it was homogeneous.

3. Results and Discussions

Figs. 2 and 3 show typical thermograms for PS-

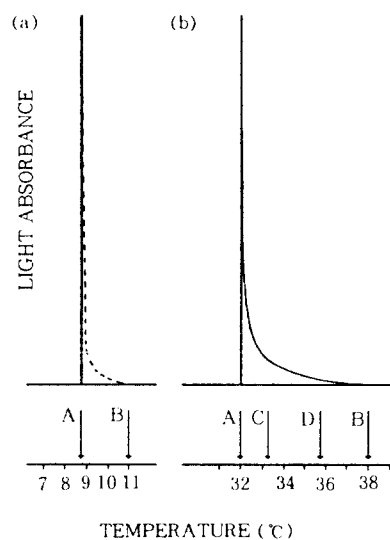


Fig. 4. Determination of cloud points in polymer solutions by various measurements. Solid curve (a) denotes the light-absorbance of a PS-methyl cyclohexane solution, and dotted curve (b) denotes a light-absorbance of a PS-cyclohexane solution: (A) peak temperatures of light-absorbance; (B) onset temperatures of light-absorbance peak; (C) cloud point determined by thermal analysis; (D) cloud point determined by a refractive index measurement [13].

cyclohexane and PS-methyl cyclohexane solutions. The onset temperature obtained from the extrapolation of the cooling rate to 0°C/min was taken as the binodal point for the polymer solution. For a monodisperse polymer sample dissolved in a single solvent (hence a binary system), the cloud point curve coincides with the binodal. The threshold cloud point (the maximum of the cloud point curve) is the critical point. These features do not hold for solutions of polydispersed polymers [9].

Turbidimetry measurements were also employed to determine the binodal points [10-12]. An IBM 9410 UV-visible spectrophotometer was used as a turbidimeter in this study. Initially homogeneous solution is cooled at a sufficiently low rate (such as 0.3°C/min) until a sharp increase in optical density is observed. A transmission wavelength of 800nm, not absorbed by the polymer solution, is used to follow turbidity.

Fig. 4 shows the cloud points of PS-solvent systems determined by various measurements. A refractive index measurement was done by Dobashi et

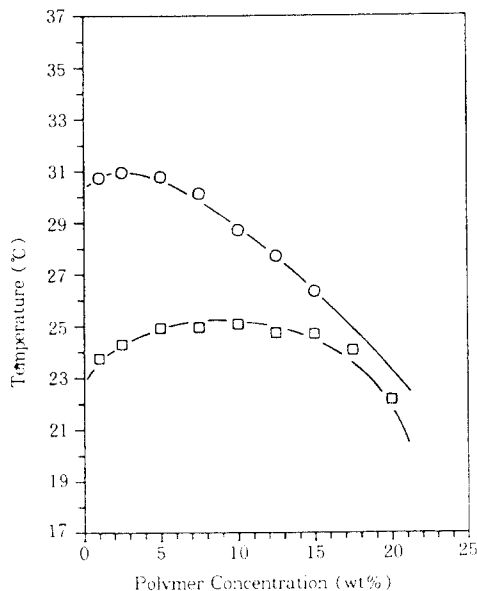


Fig. 5. Cloud point curves for PS-cyclohexane system prepared from differential scanning calorimetry : (○) $M_w = 1.9 \times 10^4$; (□) $M_w = 2.9 \times 10^4$.

al. [13] employing a 13wt% of PS-methyl cyclohexane solution. Even though the M_w of PS ($M_w = 3.5 \times 10^4$) used in the refractive index measurement is slightly different from the M_w of PS ($M_w = 3.1 \times 10^4$) used in differential scanning calorimetry/turbidimetry measurements, the cloud points determined by these three measurements are comparable. From Fig. 4, it should be noted that a thermal analysis employing differential scanning calorimetry provides more clear information about the cloud point temperature than turbidimetry. A relatively wide range between onset and peak temperatures in light-absorbance curves often makes it difficult to determine an exact cloud point, even though the cloud

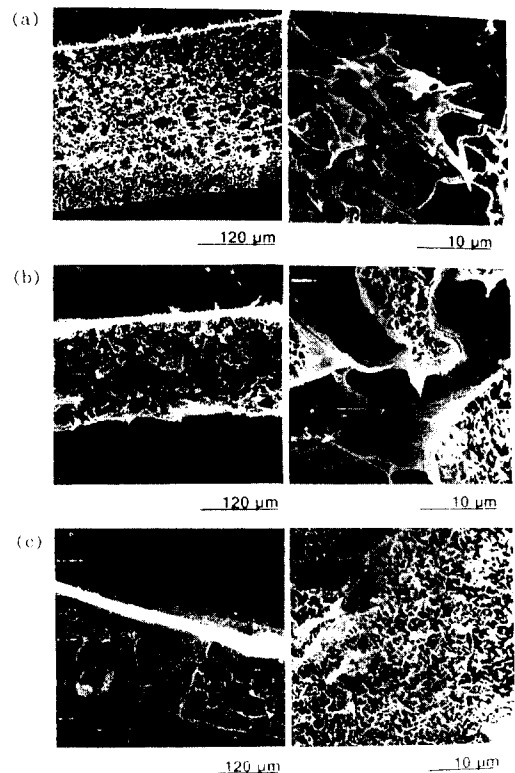


Fig. 6. Scanning electron micrographs of the cross-section of PS membranes as a function of coarsening time : (a) 2 min; (b) 20 min; (c) 60 min. Membranes were prepared by quenching a 5wt% PS-cyclohexane ($M_w = 1.9 \times 10^4$) solution to 24°C prior to freeze-drying.

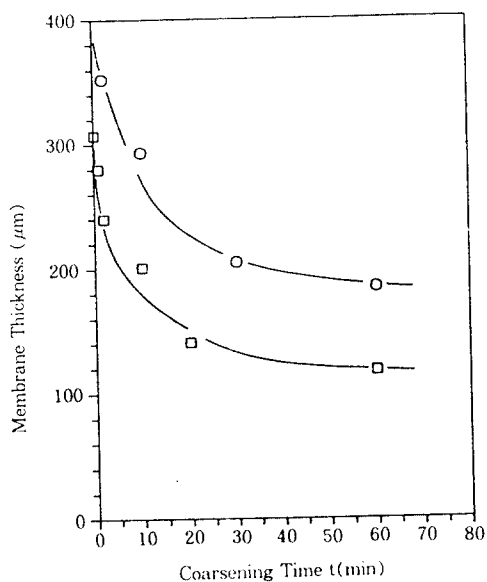


Fig. 7. Change of the thickness of PS membranes due to gravitational sedimentation: (○) 10 wt% PS-cyclohexane ($M_w = 2.9 \times 10^5$) at 20°C; (□) 5 wt% PS-cyclohexane ($M_w = 1.9 \times 10^5$) at 24°C.

point temperature is usually defined as the cross point of extrapolated base line and extrapolated peak line. The range between onset and peak temperature is strongly dependent on the molecular weight distribution of polymer and the characteristics of solvent.

The cloud point curves for the PS-cyclohexane systems used in this study are given in Fig. 5 and are consistent with others reported in the research literature [14]. Fig. 6 shows scanning electron micrographs of the cross-section of the membranes during the coarsening process. Homogeneous polymer solutions (5wt% PS-cyclohexane, $M_w = 1.9 \times 10^5$) were prepared at 35°C and quenched to a temperature in the two-phase region of the phase diagram.

In Fig. 6, a big shrinkage in thickness mainly due to the sedimentation effect has been observed. The large density differences in the polymer-rich and polymer-lean phases in cyclohexane solutions lead to gravity-induced sedimentation (the densities of PS and cyclohexane are 1.047g/cm³ and 0.779g/cm³,

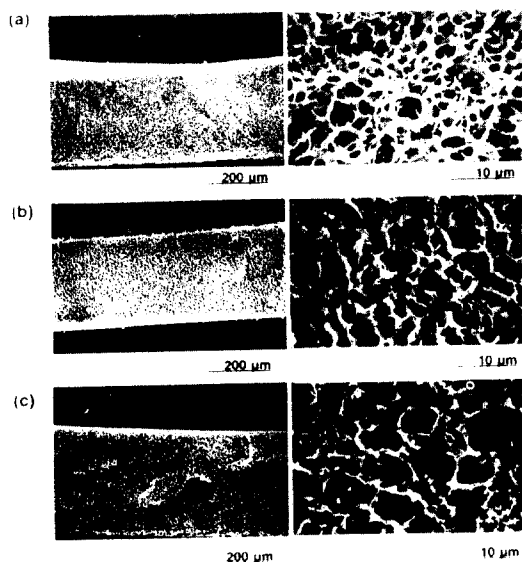


Fig. 8. Scanning electron micrographs of the cross-section of PS membranes as a function of coarsening time: (a) 1 min; (b) 2 min; (c) 60 min. Membranes were prepared by quenching a 7.5 wt% PS-cyclohexane ($M_w = 1.9 \times 10^5$) solution to 29°C prior to freeze-drying.

respectively). The microstructure changed significantly with increasing phase separation time, but the sedimentation seemed to overshadow the coarsening effects. The extreme effects of gravity on the PS-cyclohexane system are evident in selected cases from the inability to make 400μm-thick membranes even at short coarsening times (the solvent-rich phase layers on top of the polymer-rich phase due to buoyancy). Fig. 7 shows the change in thickness during the coarsening process. The sedimentation effects are dominant in low-viscosity systems even at very short times after initiation of phase separation. Thus, long-time coarsening is not observable. It must be noted that attempts to prepare membranes useful for characterization of coarsening phenomena over a reasonable range of time scales (10min or longer) was not possible using the $2.9 \times 10^5 M_w$ PS system.

By using a much higher molecular weight PS sample, $1.9 \times 10^6 M_w$, at a concentration of 7.5wt%,

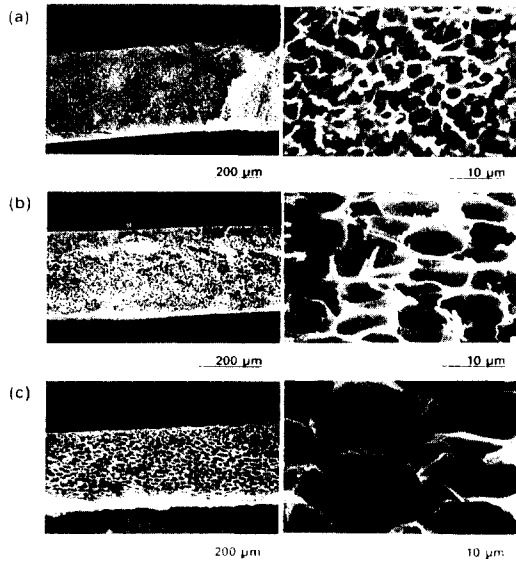


Fig. 9. Scanning electron micrographs of the cross-section of PS membranes as a function of coarsening time : (a) 2min; (b) 10min; (c) 60min. Membranes were prepared by quenching a 7.5wt% PS-cyclohexane ($M_w = 1.9 \times 10^6$) solution to 27°C prior to freeze-drying.

it was possible to avoid these significant layering effects on relatively short time scales and to investigate how coarsening time and quench depth affect membrane microstructure. (The high viscosity of this PS solution significantly retards the sedimentation effects.) Figs. 8 and 9 show the effects of coarsening time on the microstructure developed over a period of 1 hr at phase separation temperatures of 29°C and 27°C. In Fig. 8, for membranes produced by phase separation at 29°C, which is very close to the cloud point temperature, there is at most a modest increase in cell or pore size over the first hour. In contrast, with a slightly deeper quench to 27°C (Fig. 9), a much more substantial growth in cell size with coarsening time is observed.

Fig. 10 shows the quench temperature dependence of the cell size growth rate for a 7.5wt% solution of 1.9×10^6 M_w PS in cyclohexane as determined from scanning electron microscopy. For the highest quench temperature examined, the growth

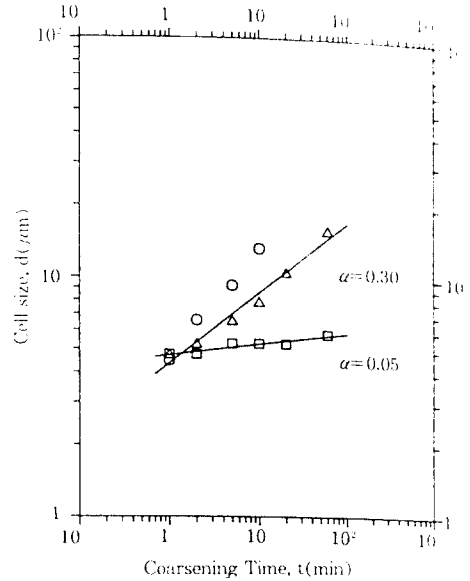


Fig. 10. Coarsening time dependence of cell size for a 7.5wt% PS-cyclohexane ($M_w = 1.9 \times 10^6$) system obtained at various quench temperatures (α denotes the slope of the line) : (○) 20°C; (△) 27°C; (□) 29°C. Cloud point determined by differential scanning calorimetry was 30.1°C.

rate exponent is 0.05. As the quench temperature is decreased to 27°C, the growth rate exponent at short time increases to 0.30. Noteworthy in Fig. 10 is that at 20°C the growth rate exponent at "short" coarsening time (≤ 10 min) apparently exceeds the value of 1/3, considered by some [15] to be a limiting exponent at short coarsening times. The apparently high value of the short time growth rate exponent may be due to a fact that on time scales exceeding 10min gravitational effects dominate at 20°C and characterization of cell size is not meaningful, leaving conclusions to be drawn from few data points.

Finally, the study of membrane microstructures in systems prepared from PS-cyclohexane have revealed the important role of polymer concentration in dictating the material continuity of the membranes, consistent with conclusions from previous

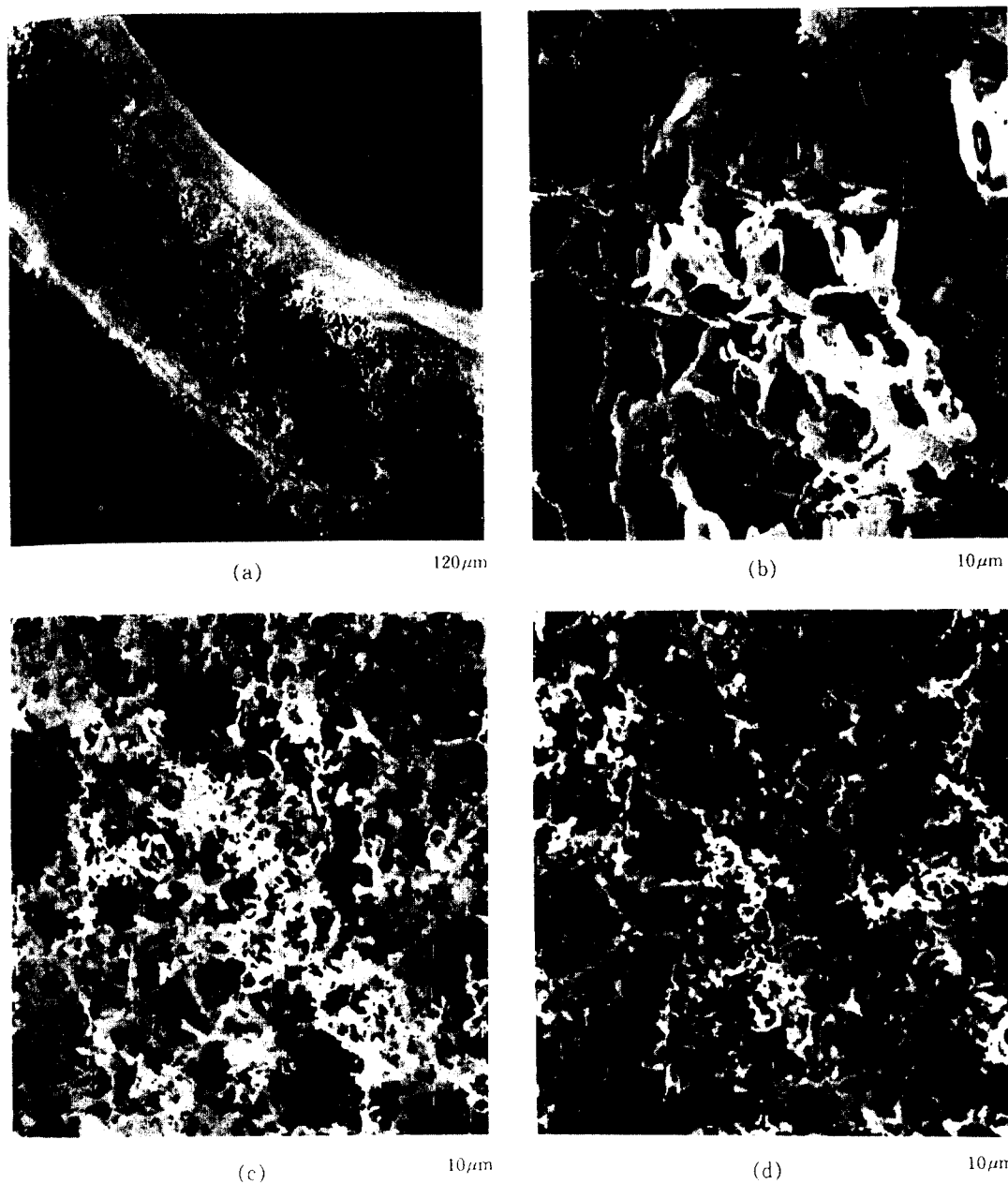


Fig. 11. Scanning electron micrographs of PS membranes : (a) cross-section (low magnification) ; (b) cross-section (high magnification); (c) top surface ; (d) bottom surface. Membranes were prepared by quenching a 1wt% PS-cyclohexane solution ($M_w = 1.9 \times 10^6$) directly with liquid N_2 prior to freeze-drying.

investigation [16]. Figs. 11~13 show the microstructure of membranes prepared from three different concentrations of PS-cyclohexane solution.

Each figure shows the cross-section and two surfaces (top and bottom) of the PS membrane. The top surfaces were directly contacted with an aluminum

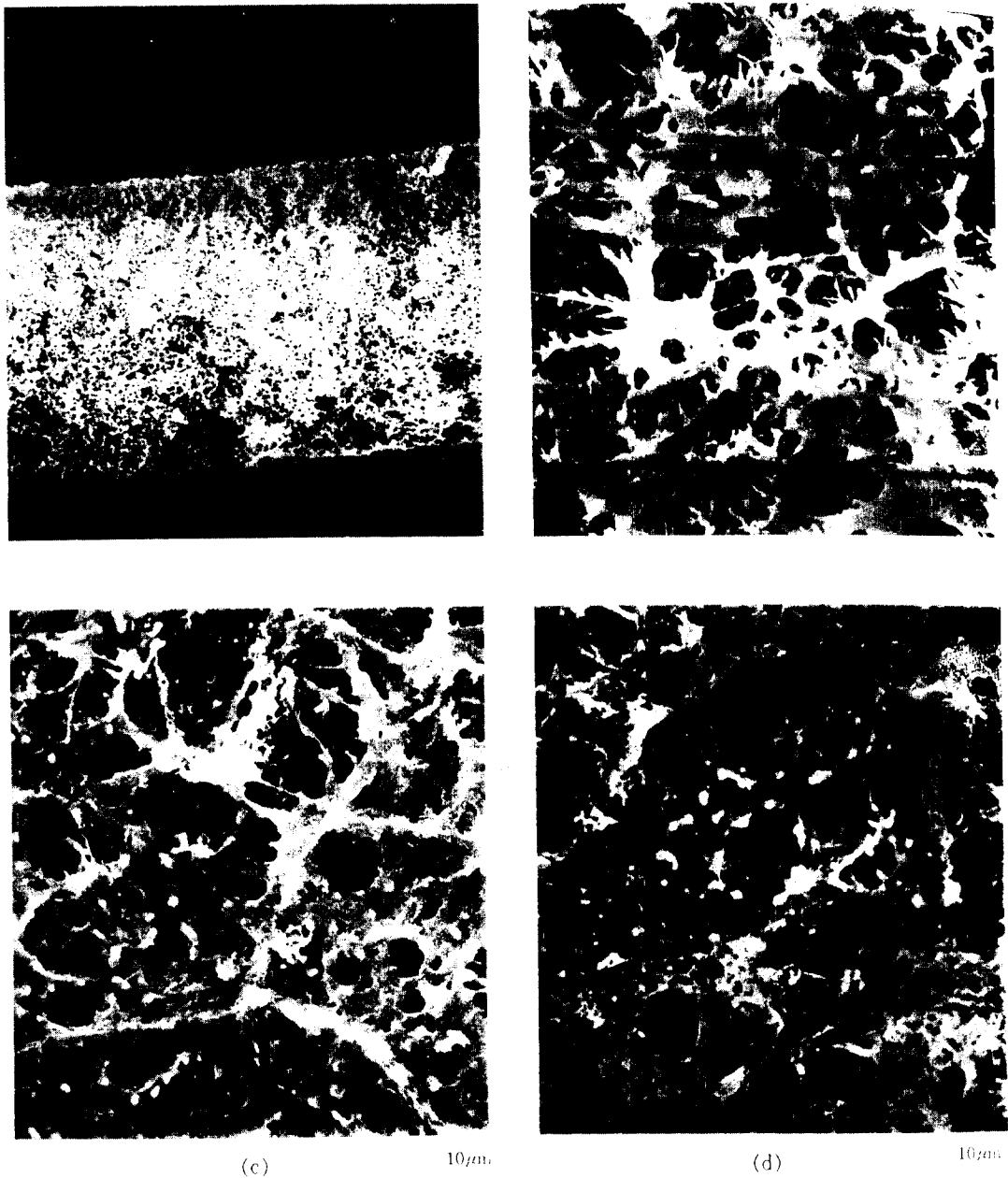


Fig. 12. Scanning electron micrographs of PS membranes : (a) cross-section (low magnification) ; (b) cross section (high magnification); (c) top surface ; (d) bottom surface. Membranes were prepared by quenching a 2.5wt% PS-cyclohexane solution ($M_w = 1.9 \times 10^5$) directly with liquid N₂ prior to freeze-drying.

conducting plate in the casting cell, while the bottom surfaces were contacted with the Teflon[®] insulating plate. Membranes were prepared by quenching a PS

-cyclohexane solution directly with liquid N₂ followed by solvent extraction *via* freeze-drying. Even from a 1wt% polymer solution, interconnected

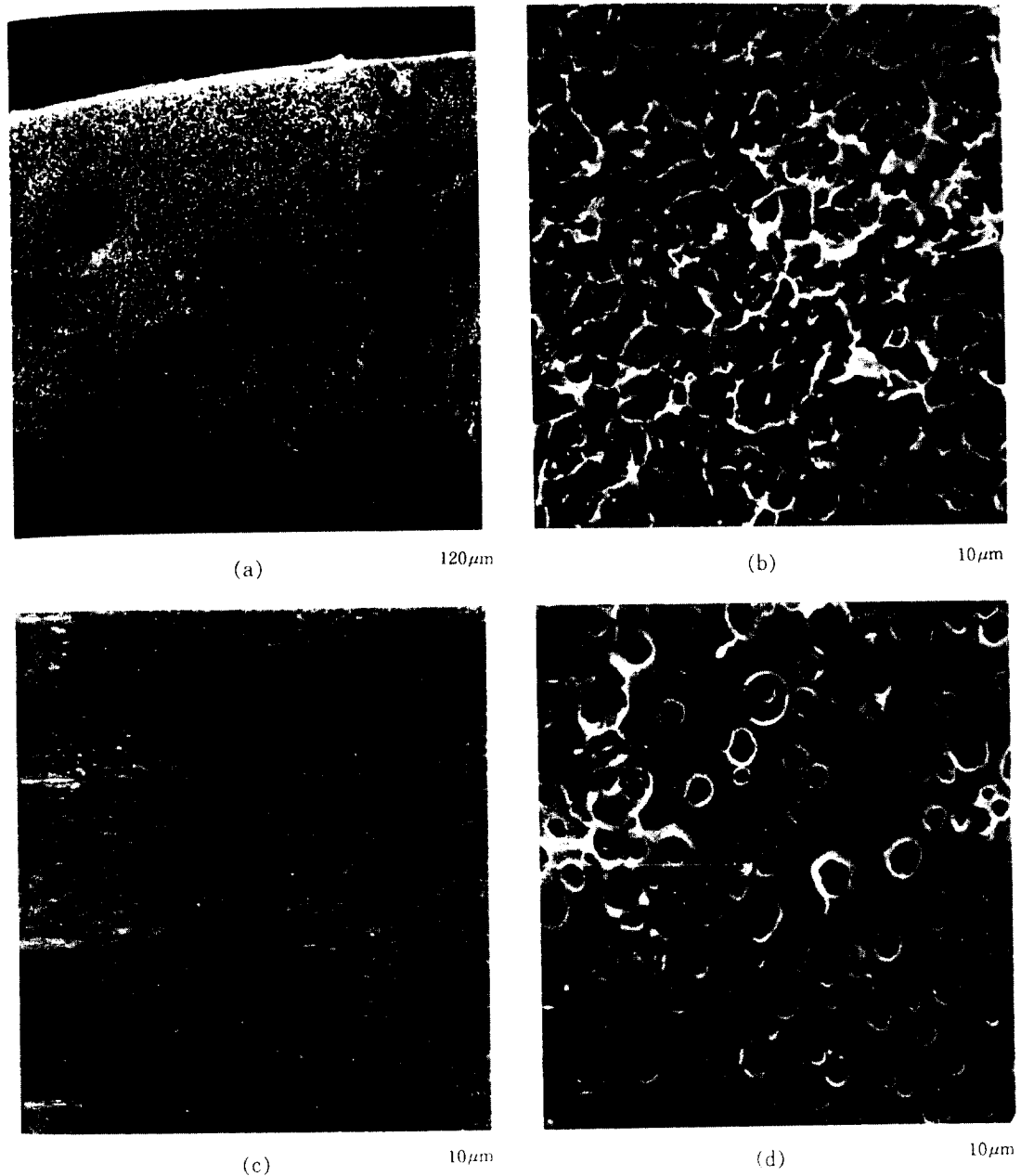


Fig. 13. Scanning electron micrographs of PS membranes : (a) cross-section (low magnification) ; (b) cross-section (high magnification); (c) top surface ; (d) bottom surface. Membranes were prepared by quenching a 15wt% PS-cyclohexane solution ($M_w = 1.9 \times 10^6$) directly with liquid N₂ prior to freeze-drying.

morphologies can be obtained (Fig. 11). However, membranes made from such a low concentration are very fragile. By increasing the polymer concen-

tration up to 2.5wt%, substantially stronger membranes can be prepared (Fig. 12), and from a 15wt% polymer solution (Fig. 13), very strong and even

flexible membranes can be obtained; the membranes can be bent over 90° without breaking them. It is also obvious that the membrane surface evolves toward a smaller pore-size structure as the polymer concentration is increased, and the top surfaces show a much more dense skin than the bottom surfaces. For all polymer concentrations investigated in this study, the top surfaces have smaller pores as compared with the bottom surfaces. Fig. 13 shows the asymmetric characteristics of the membrane surfaces which have quite different pore sizes; the top surface has very dense skin in which pores can not be observed at high magnification ($\times 3000$) while the bottom surface has porous structure in which large pores (about $3\mu\text{m}$) are formed.

4. Conclusions

The effects of coarsening on microstructure formation in polystyrene membranes were studied by scanning electron microscopy (SEM). Thermal analysis of the polymer solutions was carried out with a differential scanning calorimeter and the phase diagram was determined from the onset temperature of the heat of demixing peak. The onset temperature obtained from the extrapolation of the cooling rate to 0°C/min was taken as the binodal point for the polymer solution. By using a high molecular weight PS sample, $1.9 \times 10^6 M_w$, at a concentration of 7.5wt%, it was possible to avoid significant layering effects on relatively short time scales and to investigate how coarsening time and quench depth affect membrane microstructure. Using thermally induced phase separation (TIPS) and a freeze-drying technique, it was demonstrated that polymer membrane microstructure can be changed significantly by controlling coarsening time and quench route. For systems undergoing phase separation by spinodal decomposition, resulting in a well interconnected, microporous structure with nearly uniform

pore sizes, it was found that extending the phase separation time prior to freezing and solvent removal can result in a significant increase in pore or cell size which is highly dependent on both quench depth and coarsening time. Also this study has revealed the important role of polymer concentration in dictating the material continuity of the membranes.

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