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The presence of nanopores in mesophase of syndiotactic polystyrene estimated from gas sorption behaviour

Kimiaki Tsutsui, Yoshiharu Tsujita*, Hiroaki Yoshimizu and Takatoshi Kinoshita
Department of Materials Science and Engineering, Polymeric Materials Course, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466-8555, Japan
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Thermal and spectroscopic properties of the annealed cast syndiotactic polystyrene (SPS) films were investigated and it was shown that the sample annealed at lower temperature than 170°C exhibited the presence of a conformational order but lack of crystalline regularity. This result indicated the formation of mesophase by annealing cast SPS films. CO_2 sorption properties of such a film were also examined and dual-mode sorption model was applied to clarify the SPS structure. The hole saturation constant for the Langmuir sorption (C_H') evaluated from the dual-mode sorption model reflected the fine structure of the annealed SPS (mesophase) and depended on the annealing time when annealed at a certain temperature. From these results we supposed that the samples annealed at lower temperature contained many nanopores between SPS chains of mesophase, i.e. desorption sites of solvent. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: syndiotactic polystyrene; mesophase; nanopore)

INTRODUCTION

Recently, highly syndiotactic polystyrene (abbreviated as SPS) was synthesized using a homogeneous catalytic system using a titanium compound and a methylaluminoxane[1]. This polymer has attractive characteristics such as high melting temperature (270°C) and fast crystallization rate[2–5] in addition to the properties of commercial atactic polystyrene and will be widely used in a variety of fields in the future. SPS exhibits a very complex polymorphic behaviour and crystallizes in two different conformations depending on crystallization conditions[6–14]. One is the TT conformation, obtained when SPS is melt-quenched. It is well-known that the TT conformation constructs the α form[15–19]. The other is the TTGG helix conformation, formed by the solution-cast method and vapour sorption to amorphous SPS. There are two crystalline forms exhibited by the TTGG conformation[6,10]. The δ form is always prepared in the presence of a solvent and includes a certain amount of solvent molecule[20–29]. Its crystalline structure depends on the nature of the solvent used. By thermal treatment, the δ form is first transformed into the γ form and finally into the α form. This transition from δ to γ form has been investigated by various methods[30–33]. At present, there are unresolved problems on fine structure during the transition which one cannot clarify by various methods. The study of the transport properties of gases and organic vapours is a very useful method for examining the fine structure of the polymer films[34–36]. This is because sorption and diffusion of a penetrant molecule occurs in an amorphous part of the membranes and is reflected by the fine structure in addition to the physical properties such as the degree of crystallinity, fractional free volume (FFV), i.e. microvoid, and chain mobility. In particular, the information on microvoid which can be obtained from a glassy polymer–gas system cannot be obtained by thermal and spectroscopic studies. For example, Vittoria *et al.* investigated the structural organization on the transition from δ to γ form by studying dichloromethane transport properties of the SPS samples[37–42]. They concluded that the transition from δ to γ form occurred through the mesophase[43–46]. The mesophase is defined as the phase which has not crystalline regularity but conformational order.

In general, organic vapours are able to plasticize to some extent an amorphous part of the polymer and make it crystallizable due to much more mobility if it is a crystalline polymer. Accordingly, organic vapours are possible to change the structural organization of the permeation phase and make it complex to investigate the initial morphology of the membrane. On the other hand, CO_2 is less effective to plasticization than organic vapour. The extent of plasticization can be altered by changing CO_2 pressure[47–51]. In addition, the transport properties of the CO_2–polymer system have been widely studied and can be interpreted in terms of transport models[52–55]. In this article, the CO_2 sorption properties of SPS, which was prepared by the solution-cast method and annealing at different temperatures were investigated. Moreover, we obtained the information on mesophase, in other words, the structural organization that occurs on the transition from δ to γ form.

EXPERIMENTAL

Syndiotactic polystyrene (SPS) was kindly supplied by Idemitsu Petrochemical Co. Ltd and was used without further purification. The weight-averaged molecular weight is $M_w = 211\,000$ ($M_w/M_n = 3.45$). The film samples cast

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* To whom correspondence should be addressed

from a toluene solution were annealed at 100, 120, 140 and 170°C for various annealing times. The annealed SPS films have been abbreviated according to the following scheme: *XAY* where *X* is the annealing time (hour) and *Y* is the annealing temperature (°C).

Differential scanning calorimetry (d.s.c.) thermograms in the range 25–300°C were performed using Perkin Elmer DSC 7 at the heating rate of 20°C/min under a nitrogen gas purge. Thermogravimetric analysis (t.g.a.) data in the range 25–450°C were obtained using Seiko TG/DTA220 at the heating rate of 20°C/min under a nitrogen gas purge. Wide-angle X-ray diffraction patterns in the range 5–25° of 2Θ were recorded with nickel-filtered Cu K α radiation by Rigaku RAD-RC-type at the scan rate of 1°/min and the collection number was 5. Infrared spectra were obtained using a Jasco IR-700-type i.r. spectrometer with the 1 cm^{-1} resolution in the range 4000–400 cm^{-1} and the number of accumulation cycles was 1.

CO_2 sorption isotherms at 25°C were obtained by the Quartz Crystal Microbalance (QCM) method. QCM has become a popular method for the detection of a very small amount of weight because its resonance frequency can sensitively decrease upon the increase of mass on the QCM in the nanogram level. The advantages of the QCM method for CO_2 sorption measurement are (1) no buoyancy correction which should be considered for sorption measurement using electro micro balance such as Cahn model, (2) fast sorption equilibrium time (only a very small amount of material is needed for measurement) and (3) possible high pressure sorption measurement. The thin films were coated on the electrode on QCM by spin-casting and annealed under the appropriate conditions.

The CO_2 used in this sorption study was at least 99.9% purity and was used without further purification.

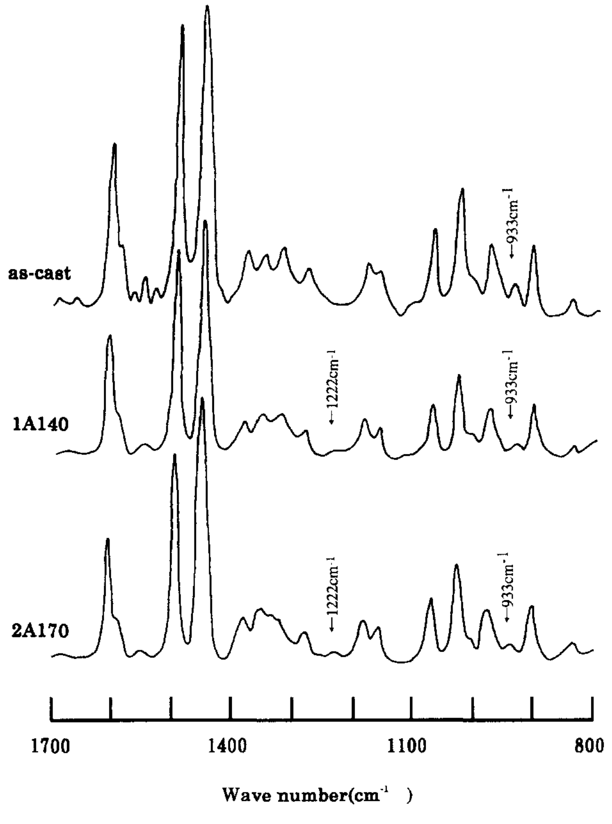

Figure 1 Infrared spectra of as-cast, 1A140 and 2A170

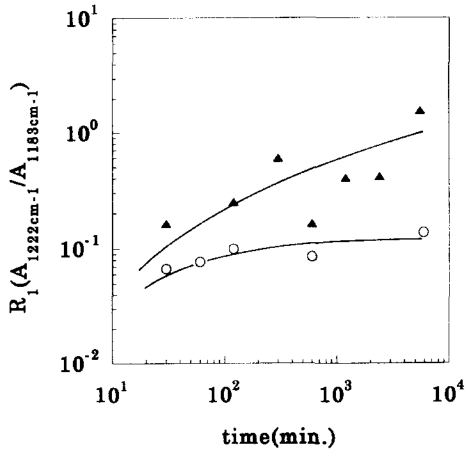

Figure 2 Relative absorbance of the 1222 cm^{-1} band (R_1) against annealing time; annealing temperature: 140°C (○) and 170°C (▲)

RESULTS AND DISCUSSION

Characterization of the annealed cast SPS

The films prepared by the solution cast method consist of δ form as mentioned above. When they are annealed below 190°C, they are first reorganized into γ form and subsequently from γ to α form at 190–200°C. This transition from γ to α form of SPS morphology is accompanied by the conformational change from TTGG to TT. We examined i.r. spectra to detect the conformational transition as well as the transition from γ to α form. I.r. spectra at 933 and 1222 cm^{-1} are assigned to the TTGG and TT conformations, respectively. Typical i.r. spectra of three samples are shown in *Figure 1*. The as-cast film has a band at 933 cm^{-1} and both 1A140 and 2A170 have two bands at 933 and 1222 cm^{-1}. From this result, it is found that TTGG conformation exists in as-cast film, 1A140 and 2A170, and TT conformation exists only in the 1A140 and 2A170. The transition from γ to α form occurs at 190°C, but the change of conformation from TTGG to TT seems to occur below 190°C. *Figures 2 and 3* show the annealing time-dependence of the relative absorbance of TT and TTGG conformations of the cast SPS annealed at 120, 140 and 170°C, respectively. The band absorbance (R_1 and R_2) at 1222 and 933 cm^{-1} are normalized by the band absorbance at 1183 cm^{-1} as an internal standard to correct for the film thickness. In the case of annealing at 120°C, R_1 remains zero even if the cast films of the δ form were annealed for more than 100 h. Annealing of the cast film at 140 or 170°C

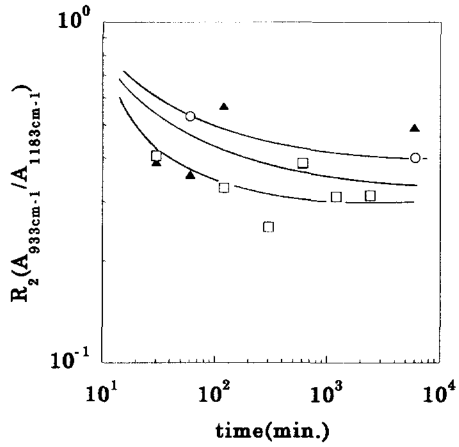

Figure 3 Relative absorbance of the 933 cm^{-1} band (R_2) against annealing time; annealing temperature: 120°C (○), 140°C(▲) and 170(□)

makes R_1 increase with the annealing time. It can be seen from *Figure 2* that the higher the annealing temperature is, the more R_1 changes. The value of R_2 of the cast film is 1.24 and when annealed at 120, 140 and 170°C, the values decrease rapidly and become gradually constant with the annealing time as shown in *Figure 3*. The results obtained may indicate that the transition from TTGG to TT conformation occurs below the transition temperature (*Tc* = 190°C) which corresponds to the maximum transition temperature of the conformation for a large crystallite. In other words, it is possible that the conformational transition from TTGG to TT conformation for a small crystallite occurs at lower temperature than *Tc*. In the case of the annealing in the vicinity of *Tc*, both conformations exist but when annealed below 120°C, at much lower temperatures than *Tc*, the TTGG conformation decreases slightly and the conformational transition to TT conformation never occurs by annealing.

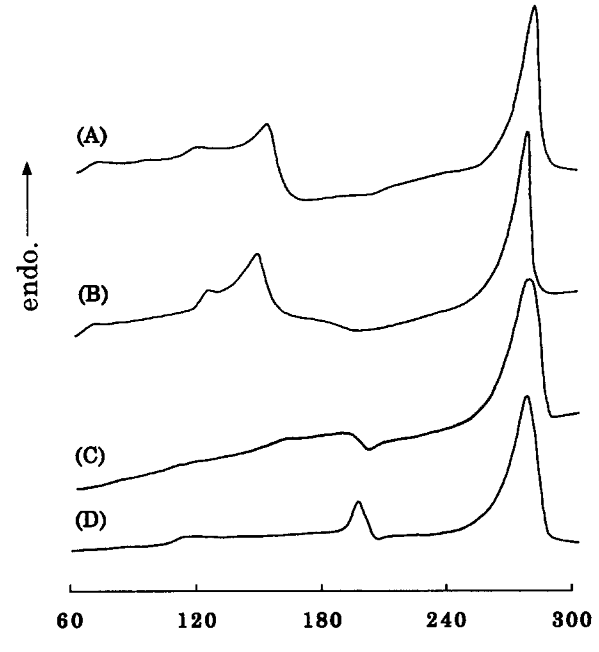

Figure 4 D.s.c thermograms of (A) as-cast, (B) 1A120, (C) 1A140 and (D) 1A170

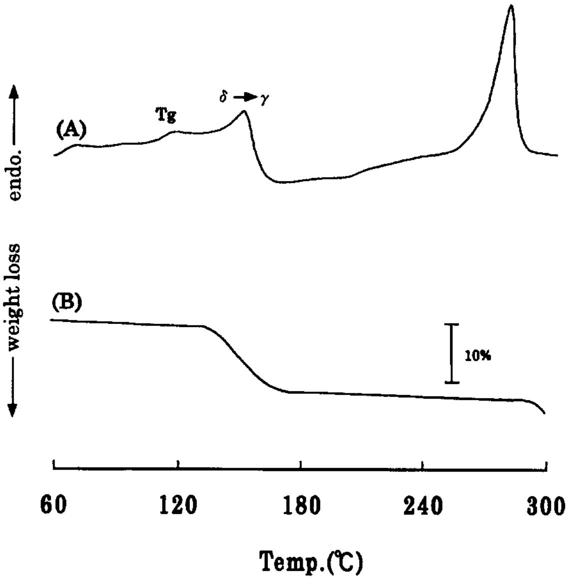

Figure 5 Thermal analysis of as-cast SPS; (A) d.s.c. thermogram and (B) t.g. curve

The thermal properties of SPS have been widely investigated[4,32,33]. In particular, the cast SPS samples exhibit very complex behaviour. It is reported that the solvents that form complex structures (δ form) with SPS desorb from its crystal lattice of the δ form at 150°C (transition from δ to γ form). *Figure 4* shows the d.s.c. thermograms of the cast films, 1A120, 1A140 and 1A170. The endothermic peaks at 270°C observed in all samples correspond to the melting of the α form and Tgs are 105~110°C, which are higher than Tg of amorphous SPS (100°C). This results from the restriction of SPS amorphous chain mobility by the presence of the crystal regions. A large endothermic peak of the cast film and 1A120 appears at 150°C, which is due to the desorption of the solvent complexed as demonstrated from thermogravimetric analysis (t.g.a.) (*Figure 5*). It is probable to induce the reorganization of the SPS amorphous chain judging from the observation of the broad exothermic peak appearing at 150~200°C. On the other hand, the thermograms of the annealed samples near *Tc* indicated that there is no endothermic peak at 150°C and the other endothermic peaks, which are sharper as the annealing temperature approaches to *Tc*, involved the transition from γ to α form. It is probable that the crystalline size of the γ form might be small and there might be many crystal defects in the γ form transformed from the δ form by annealing at low temperature. Therefore, such a γ form may transform into the α form in the d.s.c. scan below *Tc*. In the case of annealing near *Tc*, the transition from δ to γ form is likely to occur and the transformed γ form may be large in the crystalline size with small crystal defects. An endothermic peak resulting from the transition from δ to γ form is observed at 190°C because there exists a stable γ form by annealing near *Tc*. The d.s.c. thermograms of the annealed samples for 100 h at 100, 120, 140 and 170°C are shown in *Figure 6*. The solvents still exist in 100A100 but no solvent exists in 100A120 and 100A140. The absence of endothermic peaks around *Tc* indicates the presence of small and imperfect γ form for 100A100. The important feature of these results exhibits TTGG conformation according to the i.r. spectra but small and imperfect γ form crystals

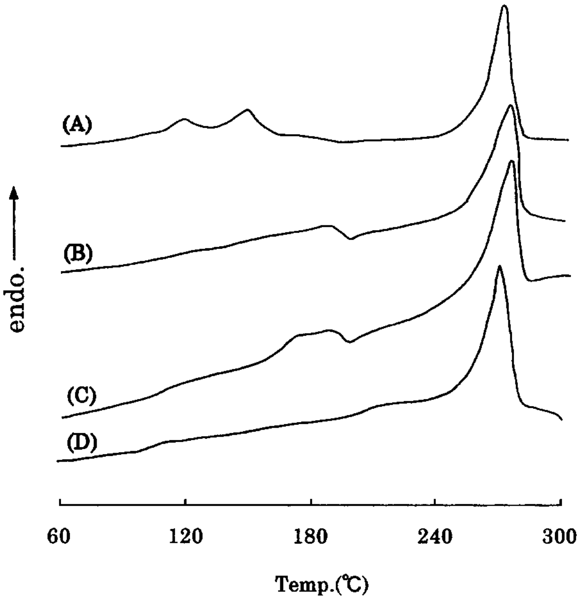

Figure 6 D.s.c. thermograms of (A) 100A100, (B) 100A120, (C) 100A140 and (D) 100A170

Table 1 Dual-mode sorption parameters of various annealed samples

Sample	C_H'	$k_D \times 10^2$	$b \times 10^3$
1A120 (APS)	5.86	1.29	3.10
1A120	7.19	1.10	2.97
100A120	13.27	0.58	1.53
1A170	13.55	0.57	1.71
1A170 (slowly cooled)	10.40	0.53	1.74
5A170	8.53	0.68	2.54

C_H': Langmuir sorption capacity; cm^3 STP/cm^3 polymer.
k_D: Henry's law solubility coefficient; cm^3 STP/cm^3 polymer.cm Hg.
b: affinity constant of Langmuir site; cm Hg^{-1}.

according to d.s.c. study. That is, the mesophase, which has an ordered TTGG conformation but lacks crystalline regularity, exists in 100A120. This is also confirmed by X-ray profiles shown in *Figure 7*. The X-ray profiles of (A), (B), (C) and (D) are typical of the samples consisting of δ form, mesophase, γ form and α form, respectively[46]. These results suggest the existence of a relatively regular nanopore in mesophase different from a microvoid in a glassy polymer. Hereafter we propose it to be a nanopore.

CO_2 sorption properties of the annealed SPS samples

The study of transport properties of gases and organic vapours is a very available method for examining the fine local structure of the membranes as well as spectroscopic and thermal studies. It is well-known that gas sorption behaviours of glassy polymeric membrane are explained by a dual-mode model and the dual-mode sorption parameter C_H' (hole saturation constant of Langmuir sorption) represents a microvoid content between polymer segments. We have tried to obtain informations on the fine structure of annealed cast SPS by understanding CO_2 sorption properties. The sorption isotherms of the SPS samples annealed at 120 and 170°C are shown in *Figures 8 and 9*, respectively. No correction of the degree of crystallinity was made for sorption amount. Atactic polystyrene (APS), which is annealed at 120°C for 1 h (1A120 (APS)), is also shown in the figures. The sorption isotherms of all the samples are typical of glassy polymers. The CO_2 sorption amount of the annealed SPS is smaller than that of 1A120 (APS) because of the presence of the crystallinity of the annealed SPS. It is suggested that the CO_2 sorption amount of the annealed SPS may be larger than that of 1A120 (APS) when the correction of the degree of crystallinity was made for sorption amount because of lack of crystalline regularity, i.e. the sorption into the nanopores between the polymer chains of the mesophase occurs. One can assume that the sorption into the nanopores is regarded as Langmuir-type sorption. The plasticization by CO_2 can be ignored until 25 atm as both sorption and desorption isotherms are almost identical. To evaluate the CO_2 sorption behaviour more fully, the dual-mode sorption model represented by equation (1) has been applied to the obtained sorption isotherms. This can explain the gas sorption properties of glassy polymers and dual-sorption parameters are calculated by the non-linear least square method.

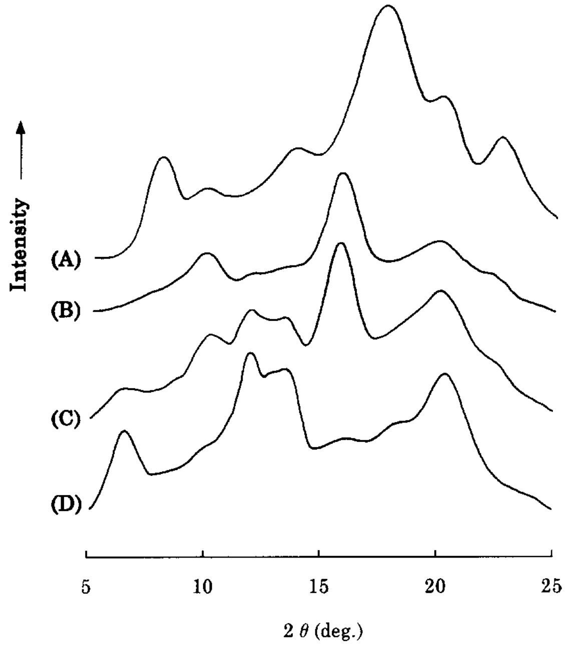

Figure 7 X-ray diffraction profiles of (A) as-cast, (B) 100A120, (C) 5A170 and (D) 100A170

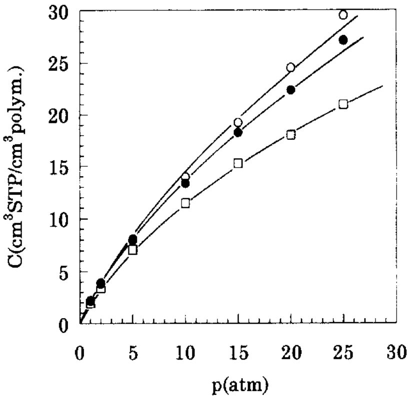

Figure 8 CO_2 sorption isotherms at 25°C of 1A120 (APS) (○), 1A120 (●) and 100A120 (□)

$$C = k_d p + \frac{C_H' b p}{1 + bp} \tag{1}$$

where k_d is the Henry's law parameter (cm^3 STP/cm^3 polymer.cm Hg), C_H' is the hole saturation constant for the Langmuir sorption (cm^3 STP/cm^3 polymer), b is the affinity constant for the Langmuir sorption (cm Hg^{-1}), p is the pressure (cm Hg), and C is the concentration (cm^3 STP/cm^3 polymer). The dual-mode sorption parameters obtained are shown in *Table 1*. The parameters k_d and b of the SPS samples annealed at 120°C decrease as annealing time increases. On the other hand, C_H' increases with annealing

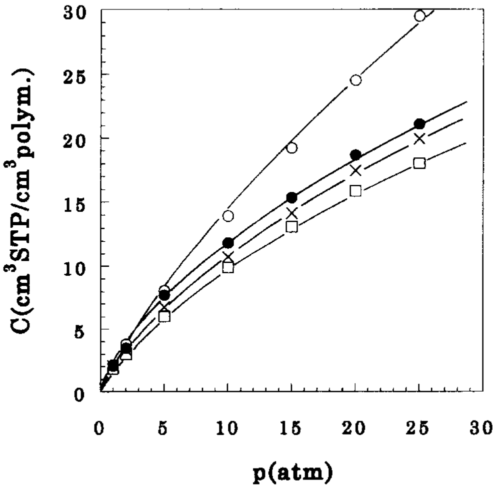

Figure 9 CO_2 sorption isotherms at 25°C of 1A120 (APS) (○), 1A170 (●), 1A170 (slowly cooled) (□) and 5A170 (×)

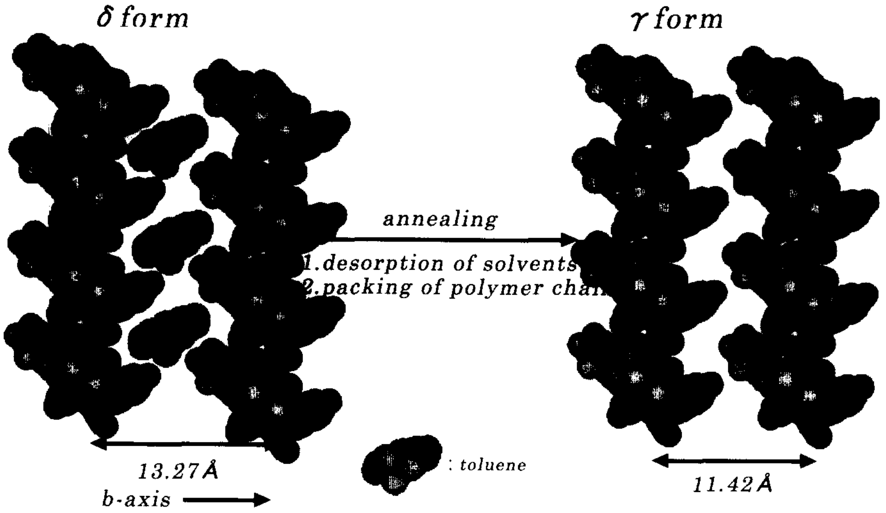

Figure 10 Schematic representation of reorganization from δ form to γ form in the case of SPS–toluene system

time. C_H' reflects the amount of microvoid in unit polymer volume and it is interesting that C_H' of the annealed SPS is larger than that of the amorphous APS, irrespective of the presence of crystalline phase. In the case of annealing at 170°C, k_d does not change markedly with annealing time increases but C_H' decreases remarkably. The difference of the annealing time-dependence of C_H' between 120 and 170°C is very important for understanding the reorganization from δ to γ form. Chatani *et al.* investigated X-ray analysis of the SPS samples complexed with the solvents and reported that they exhibited a monoclinic system (P_21/a) of the crystal lattice of $a = 17.48$ Å, $b = 13.27$ Å, $c = 7.71$ Å, $\gamma = 122°$ containing eight monomers $(TTGG)_2$, the two chains of TTGG conformation, and the two solvent molecules which are sandwiched between the two chains in the unit lattice[20]. From these results, we propose that the solvent first desorb from the unit lattice by annealing and subsequently the two chains pack in the direction of b axis depending on annealing temperature (*Figure 10*). D.s.c. and i.r. measurements mentioned above showed that annealing at 120°C induced full desorption of the solvent but resulted in an imperfect γ form. This may result in the increase of C_H' as the desorption site of the solvent still remains, that is, there are many nanopores between the polymer chains of mesophase. On the other hand, the reorganization from δ to γ form may occur perfectly by annealing at 170°C, indicative of the decrease in the number of micropores. This may cause the decrease of C_H' with annealing time.

From CO_2 sorption measurements it was found that annealing at low temperature induces the formation of the mesophase including many nanopores. Finally, the reorganization of a crystalline form and mesophase is represented schematically in *Figure 11*. One can see much more nanopores for an SPS sample annealed at low temperature and for a long time.

CONCLUSION

Thermal and spectroscopic analyses of the annealed cast SPS samples were performed and it was suggested that the sample annealed at lower temperature exhibited

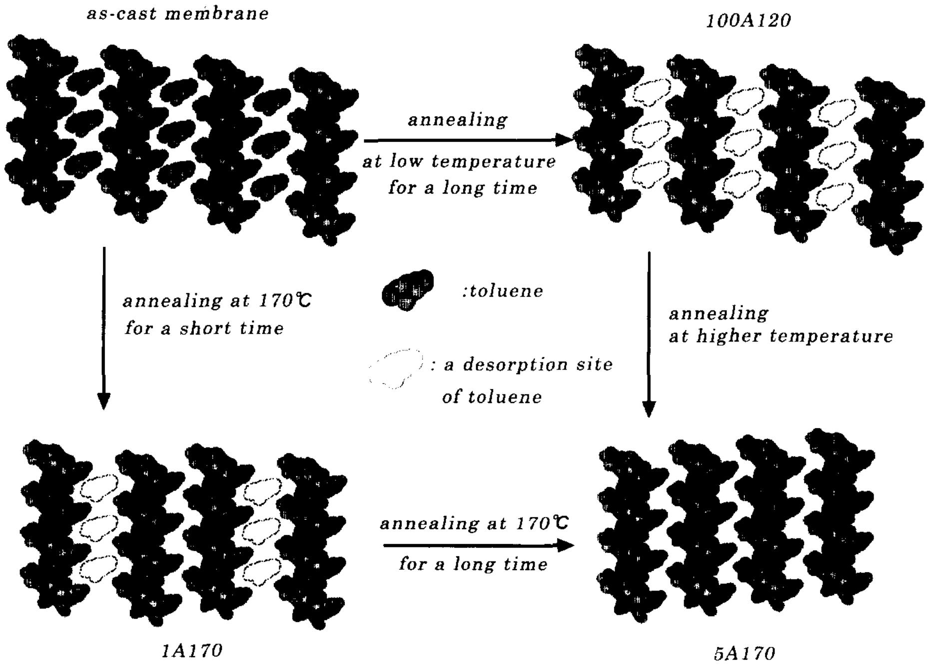

Figure 11 Schematic representation of reorganization of the annealed as-cast SPS membrane

conformational order but lack of crystalline regularity. From CO_2 sorption measurement it is apparent that the samples annealed at lower temperature contain many desorption sites of solvent as nanopores. Taking the formation mechanism of the desorption sites of solvent into consideration, it is possible that the site memorizes solvent structure and properties. So we will investigate the selective sorption into such a site in a following article.

REFERENCES

1. Ishihara, N., Kuramoto, M. and Uoi, M., *Macromolecules*, 1988, **21**, 3356.
2. Gvozdic, N. V. and Meier, D. J., *Polym. Commun.*, 1991, **32**, 183.
3. Gvozdic, N. V. and Meier, D. J., *Polym. Commun.*, 1991, **32**, 493.
4. Arnauts, J. and Berghmans, H., *Polym. Commun.*, 1990, **31**, 343.
5. Cimmino, S., Di Pace, E. , Martuscelli, E. and Silvestre, C. , *Polymer*, 1991, **32**, 1080.
6. Kobayashi, M., Nakaoki, T. and Ishihara, N., *Macromolecules*, 1989, **22**, 4377.
7. Doherty, D. C. and Hopfinger, A. J., *Macromolecules*, 1989, **22**, 2472.
8. Greis, O., Xu, Y., Asano, T. and Peremann, J., *Polymer*, 1989, **30**, 590.
9. Zimba, C. G., Rabolt, J. F. and English, A. D., *Macromolecules*, 1989, **22**, 2867.
10. Gomez, M. A. and Tonelli, A. E., *Macromolecules*, 1991, **24**, 3533.
11. Grassi, A., Longo, P. and Guerra, G., *Macromol.Chem., Rapid Commun.*, 1989, **10**, 687.
12. Gomez, M. A. and Tonelli, A. E., *Macromolecules*, 1990, **23**, 3385.
13. Capitani, D., De Rosa, C., Ferrando, A., Grassi, A. and Segre, A. L., *Macromolecules*, 1992, **25**, 3874.
14. Capitani, D., Segre, A. L., Grassi, A. and Ferrando, A., *Macromolecules*, 1991, **24**, 623.
15. Guerra, G., Vitagliano, V. M., De Rosa, C., Petraccone, V. and Corradini, P., *Macromolecules*, 1990, **23**, 1539.
16. De Rosa, C., Guerra, G., Petraccone, V. and Corradini, P., *Polym. J.*, 1991, **23**, 1435.
17. Sun, Z. and Miller, R. L., *Polymer*, 1993, **34**, 1963.
18. Napolitano, R. and Pirozzi, B., *Macromolecules*, 1993, **26**, 7225.
19. Auriemma, F., Petraccone, V., Poggetto, F. D., Rosa, C. D., Guerra, G., Manfredi, C. and Corradini, P., *Macromolecules*, 1993, **26**, 3772.
20. Chatani, Y., Shimane, Y., Inagaki, T., Ijitsu, T., Yukinari, T. and Shikuma, H., *Polymer*, 1993, **34**, 1620.
21. Roels, T., Deberdt, F. and Berghmans, H., *Macromolecules*, 1994, **27**, 6216.
22. Deberdt, F. and Berghmans, H., *Polymer*, 1994, **35**, 1694.
23. Deberdt, F. and Berghmans, H., *Polymer*, 1993, **34**, 2192.
24. Daniel, C., Deluca, M. D., Guenet, J.-M., Brulet, A. and Menelle, A., *Polymer*, 1996, **37**, 1273.
25. Daniel, C., Dammer, C. and Guenet, J.-M., *Polymer*, 1994, **35**, 4243.
26. Roels, T., Deberdt, F. and Berghmans, H., *Progr. Colloid Polym. Sci.*, 1996, **102**, 82.
27. Prasad, A. and Mandelkern, L., *Macromolecules*, 1990, **23**, 5041.
28. Kobayashi, M., Yoshioka, T., Kozaka, T., Tashiro, K., Suzuki, J., Funahashi, S. and Izumi, Y., *Macromolecules*, 1994, **27**, 1349.
29. Kobayashi, M., Yoshioka, T., Imai, M. and Itoh, Y., *Macromolecules*, 1995, **28**, 7376.
30. Chatani, Y., Shimane, Y., Inoue, Y., Inagaki, T. and Ishioka, T., *Polymer*, 1992, **33**, 488.
31. Chatani, Y., Shimane, Y., Inagaki, T., Ijitsu, T. and Yukinari, T., *Polymer*, 1993, **34**, 1625.
32. Reynolds, N. M., Stidham, H. D. and Hsu, S. L., *Macromolecules*, 1991, **24**, 3662.
33. Wang, Y. K., Savage, J. D., Yang, D. and Hsu, S. L., *Macromolecules*, 1992, **25**, 3659.
34. Crank, J. and Park, G. S., *Diffusion in Polymers*. Academic Press, London, 1968.
35. Rogers, C. E., *Physics and Chemistry of the Organic Solid State*. Interscience, New York, 1965.
36. Peterlin, A., *J. Macromol. Sci. Phys.*, 1975, **B11**, 57.
37. Vittoria, V., *Macromol. Chem., Rapid Commun.*, 1988, **9**, 765.
38. Vittoria, V., Russo, R. and Candia, F. D., *J. Macromol. Sci.-Phys.*, 1989, **B28**, 419.
39. Filho, A. R. and Vittoria, V., *Macromol. Chem., Rapid Commun.*, 1990, **11**, 199.
40. Vittoria, V., Filho, A. R. and Candia, F. D., *J. Macromol. Sci.-Phys.*, 1991, **B30**, 155.
41. Vittoria, V., Filho, A. R. and Candia, F. D., *Polym. Bull.*, 1991, **28**, 445.
42. Vittoria, V. and Filho, A. R., *J. Appl. Polym. Sci.*, 1993, **49**, 247.
43. Vittoria, V., Filho, A. R. and Candia, F. D., *J. Macromol. Sci.-Phys.*, 1990, **B29**, 411.
44. Vittoria, V., Filho, A. R. and Candia, F. D., *J. Macromol. Sci.-Phys.*, 1992, **B31**, 133.
45. Petraccone, V., Auriemma, F., Poggetto, F. D., Rosa, C. D., Guerra, G. and Corradini, P., *Makromol. Chem.*, 1993, **194**, 1335.
46. Candia, F. D., Guadagno, L. and Vittoria, V., *J. Macromol. Sci.-Phys.*, 1994, **B33**, 347.
47. Wang, W.-C. V. and Kramer, E. J., *J. Polym. Sci.: Polym. Phys. Ed.*, 1982, **20**, 1371.
48. Chiou, J. S., Barlow, J. W. and Paul, D. R., *J. Appl. Polym. Sci.*, 1985, **30**, 2633.
49. Sanders, E. S., *J. Membrane Sci.*, 1988, **37**, 63.
50. Mizoguchi, K., Hirose, T., Naito, Y. and Kamiya, Y., *Polymer*, 1987, **28**, 1298.
51. Kamiya, Y., Mizoguchi, K., Hirose, T. and Naito, Y., *J. Polym. Sci: Part B: Polym. Phys.*, 1989, **27**, 879.
52. Bourbon, D., Kamiya, Y. and Mizoguchi, K., *J. Polym. Sci: Part B: Polym. Phys.*, 1990, **28**, 2057.
53. Naito, Y., Bourbon, D., Terada, K. and Kamiya, Y., *J. Polym. Sci.: Part B: Polym. Phys.*, 1993, **31**, 693.
54. Kumazawa, H., Wang, J.-S., Naito, K., Messaoudi, B. and Sada, E., *J. Appl. Polym. Sci.*, 1994, **51**, 1015.
55. Bandis, A., Wen, W.-Y., Jones, E. B., Kaskan, P., Zhu, Y., Jones, A. A., Inglefield, P. T. and Bendler, J. T., *J. Polym. Sci: Part B: Polym. Phys.*, 1994, **32**, 1707.