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Polymerization of Monomers Containing Functional Silyl Groups. 7. Porous Membranes with Controlled Microstructures

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ABSTRACT: Porous membranes have been prepared from the films of the block copolymers that were synthesized through the anionic living polymerization of (4-vinylphenyl)dimethyl-2-propoxysilane (1) and isoprene, by cross-linking the segregated poly(1) domain and by decomposing the polyisoprene block with ozone. The characterizations of the porous membranes produced were carried out by IR measurement, elemental and gravimetric analyses, scanning electron micrographic (SEM) observation, and BET measurement. The pore widths of the membranes produced from the five block copolymers are estimated to be 28, 27, 17, and 7 nm by SEM observation, corresponding to the widths of polyisoprene domain, and 30, 31, 21, and 11 nm for the respective block copolymers. Thus, the microstructure of the porous membrane could be controlled by block lengths of the original copolymer. Large surface area and nitrogen permeability of the membranes indicate that the hollow domain is continuous through the membrane.

Introduction

Porous membranes were produced by various methods using spinodal decomposition, annealing under tension, and sintering processes.[1] Control of pore size and the size distribution have been emphasized in each case to obtain selective permeable membranes. However, precise regulation of pore size of the membrane is not easy because even slight fluctuation of the processing conditions might cause a broad size distribution. In our previous studies,[2] a new attempt was presented to make a microporous membrane from the film of the block copolymer, which was synthesized through the anionic living polymerization of (4-vinylphenyl)dimethyl-2-propoxysilane (1) and isoprene, by cross-linking the poly(1) domain and by ozonolysis of polyisoprene block. The TEM and SEM observations of the block copolymer and the resulting porous membrane revealed that the lamellar structure of the original block copolymer film directly reflected in the shape and size of the micropores. Accordingly, it is thought that the microstructure of the porous membrane can be controlled chiefly by the morphology of the segregated microphase depending on architecture of block copolymer and casting conditions of the film. Narrow molecular weight distributions of the block lengths of the copolymer cause uniform micropores. Furthermore, the SEM of the cross section of the membrane shows the continuous structure of micropores through the membrane. A large surface area estimated by BET measurement also substantiates the penetrating structure. On the surface of the micropore, formyl and acetyl groups attached to the polymer chain are formed by the oxidative cleavage of the carbon–carbon double bond of polyisoprene.

In this paper, the elaboration is fully described on the control of microstructure of porous membrane prepared from the block copolymers of 1 and isoprene with different block lengths.

Experimental Section

(4-Vinylphenyl)dimethyl-2-propoxysilane, 1. According to our prevous method, 1 was prepared.[3] A solution of (4-vinylphenyl)magnesium chloride was prepared from 4-vinylphenyl chloride (12.4 g, 89 mmol) and magnesium (4.4 g, 180 mmol) in dry tetrahydrofuran (THF, 120 mL). The resulting Grignard reagent was added dropwise over 1-h period to a solution of (2-propoxy)dimethylchlorosilane (13.7 g, 89 mmol) in dry THF (80 mL). The temperature was maintained at 10 °C during the addition. The reaction mixture was stirred at room temperature overnight under a nitrogen atmosphere. After removal of the THF, the crude product obtained by direct distillation was purified by fractional distillation at 75–78 °C (1 mmHg) (11.1 g, 56.4%). The resulting monomer, 1, was again distilled from a mixture of 1 and phenylmagnesium bromide in THF through a vacuum line into a glass tube equipped with a breakseal for use in the anionic living polymerization.

Block Copolymerization. The anionic living polymer of isoprene (28.0 mmol) was prepared with oligo(α-methylstyryl)dipotassium (0.045 mmol) in dry THF (28 mL) at −78 °C for 3 h in a sealed glass tube equipped with breakable seals. For the characterization of the central segment, an aliquot of the reaction mixture (10 mL) was withdrawn. To the residual THF solution (18 mL) of the anionic living polyisoprene was added a second monomer, 1 (6.94 mmol) in THF (6.8 mL) at −78 °C and it was kept for 5 min at the same temperature to complete the polymerization. The living polyisoprene and the block copolymer (II) were quenched with methanol. The polymers were precipitated by pouring them into a large excess of methanol. The polymers collected were purified by reprecipitation and freeze-drying.

Preparation of Film. The resulting block copolymer dissolved in methyl isobutyl ketone (MIBK) was poured onto an Afron film, and the solvent was allowed to evaporate gradually at 25 °C for 12 h. The as-cast films were about 15–25 μm thick and somewhat brittle to tender corresponding to the content of polyisoprene block.

Cross-Linking. To immobilize the microdomain of poly(1) block, an as-cast film (140 mg, 8.0 cm × 8.0 cm × 20 μm) of the block copolymer from MIBK was immersed in a 2 N HCl aqueous solution (100 mL) at room temperature for 2 days, rinsed with water repeatedly, and dried in vacuo. Progress of the cross-linking reaction was traced by IR measurement.

Ozonolysis. A dichloromethane solution of ozone (5.0 mmol/L) was prepared by passing a stream of oxygen containing about 1.5 mol % of ozone generated by a discharge apparatus. The concentration of ozone was determined by iodometric titration with a neutral 2% solution of potassium iodide and 0.1 N sodium

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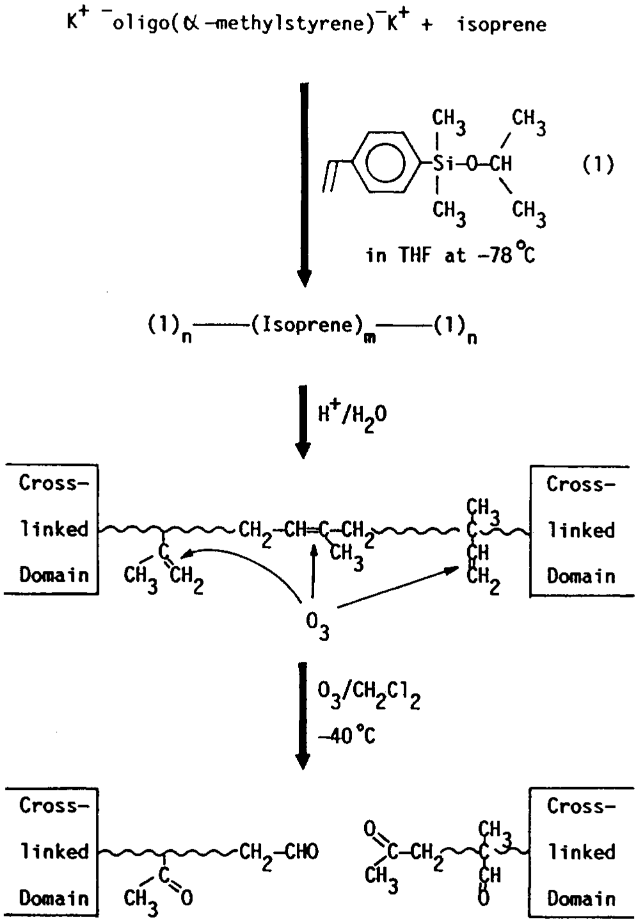
Scheme I



thiosulfate solution with soluble starch as an indicator.[4] Cleavage of the carbon–carbon double bond of the polyisoprene chain was performed by soaking the film (16 mg, 2 cm × 4 cm × 20 μm) in a dichloromethane solution of ozone (100 mL, 5.0 mM) at -40 °C for 2–8 h (Scheme I). The ozonide produced was decomposed with trimethyl phosphite in methanol at -30 °C for 2 h followed by elevation of the reaction temperature to 20 °C.[5]

Leaching. The film was soaked in methanol at room temperature for 24 h and at 50 °C for 3 h to leach out the decomposed polyisoprene chains. The degree of leaching was checked by weight loss and IR measurement at 1500–1900 cm^{-1}. Any change was not observed in the IR spectrum after further soaking at 50 °C for 20 h.

Permeability Measurement. The volume of permeated nitrogen gas through the membrane (15 μm × 0.8 cm) with 18 mmHg of pressure difference was measured at 20 °C for the membranes I, II, IV. The value of dp/dt was measured in the low-pressure side (Δp = 1520 mmHg) at 20 °C for the membrane V.

Instruments for Measurements. Gel permeation chromatograms (GPC) were obtained at 40 °C by using a Toyosoda HLC-802 instrument with RI detector, THF being the elution solvent, at a rate of 1.4 mL/min. The $\bar{M}_w/\bar{M}_n$ values were calculated by the method described by Tung with some modification.[6] ^{1}H NMR spectra were run with a JEOL FX 90Q instrument. Vapor-pressure osmometric (VPO) measurements for the number-average molecular weight determinations were made with a Corona 117 instrument in benzene. IR spectra were run with a JIR-AQS20M, JEOL. The glass transition temperature (T_g) of the polymer was evaluated from differential scanning calorimetric (DSC) diagrams recorded on a Perkin-Elmer DSC-2 instrument at a 10 °C/min heating rate. The very thin films of block copolymers cast from MIBK was stained with OsO_4 and observed by transmission electron microscope, JEM-100CX, JEOL. The scanning electron micrographs of surface and cross section of the ozone-treated and rinsed membrane were obtained with slightly gold-coated samples prepared by using S-800, Hitachi. The surface area of the porous membrane was measured by the nitrogen-adsorption technique using a BET apparatus, SA-1000, Shibata Science Technology Ltd.

Table I
Anionic Block Copolymerization of Isoprene and 1[a]

polymer	$10^{-4}\bar{M}_n$ calcd	$10^{-4}\bar{M}_n$ obsd	$\bar{M}_w/\bar{M}_n$
block copolymer I	6.5	5.8	1.18
polyisoprene block	4.4	3.8	1.12
block copolymer II	9.7	8.0	1.24
polyisoprene block	4.3	3.6	1.10
block copolymer III	8.5	7.3	1.24
polyisoprene block	4.1	3.6	1.11
block copolymer IV	7.2	6.8	1.20
polyisoprene block	2.8	2.4	1.09
block copolymer V	6.2	6.5	1.16
polyisoprene block	1.4	1.5	1.09

[a] $\bar{M}_n$ of block copolymer was estimated from $\bar{M}_n$ of polyisoprene and the composition of block copolymer measured by VPO and ^{1}H NMR, respectively.

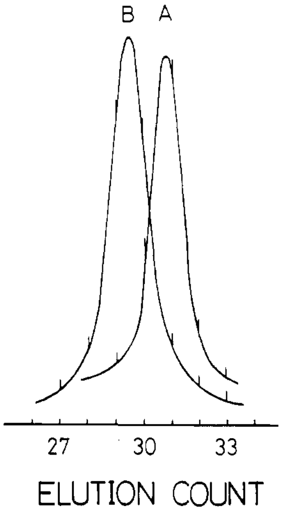


Figure 1. GPC curves for isoprene homopolymer (A) and block copolymer, IV (B).

Results and Discussion

Block Copolymerization. The triblock copolymers of isoprene and 1 were obtained in quantitative yield by using the anionic living polymerization technique investigated in our previous work.[2] As shown in Table I, the molecular weights of the isoprene homopolymers for central blocks and the block copolymers observed by VPO and ^{1}H NMR measurement fairly agree with the calculated ones. The polydispersity indexes, $\bar{M}_w/\bar{M}_n$, of the polyisoprene and the copolymers are estimated to be 1.09–1.24 from the GPCs by using a calibration curve based on standard polystyrene, indicating that the block lengths of the copolymers are nearly monodispersed. Figure 1 shows that a representative GPC curve of polyisoprene corresponding to the central block clearly shifts to a unimodal one of the block copolymer without shoulder in higher molecular weight region. The anionic living nature of isoprene and poly(1) enable the design the block copolymers of $(1)_n$–$(\text{isoprene})_m$–$(1)_n$ with different block lengths, n and m, and with narrow molecular weight distributions. The degrees of polymerization ($\overline{\mathrm{DP}}$) of central polyisoprene blocks are controlled 600, 600, 400, and 200, while those of the terminal poly(1) blocks are almost constant (n = 100) for block copolymers II, III, IV, and V, respectively, assuming that equivalent propagation occurs at the both ends of living polyisoprene. The block copolymer, I, with a short poly(1) block (n = 50) and long polyisoprene block (m =

Table II
Swelling Test of Block Copolymer at 20 °C

solvent	$(L/L_0)^3$
THF	2.40
benzene	2.68
hexane	2.11

600) was also prepared. Thus, five block copolymers with well-defined chain structures are obtained. Various morphology of segregated microdomains are formed depending on the relative block lengths of polyisoprene and poly(1). The transmission electron micrographs of the very thin films of the copolymers cast from MIBK are shown in Figure 3 (Ia, IIa, IVa, Va), where the lamellar, cylindrical, and sphere microdomains of polyisoprene are observed.

From the ^{1}H NMR spectroscopic measurement, the microstructure of the polyisoprene segments in the block copolymers are found to contain 8.0 ± 2.7% 1,4, 33.3 ± 6.1% 1,2, and 58.7 ± 8.3% 3,4 linkage.

Formation of Porous Membrane. The block copolymer dissolved in MIBK was cast as a 20-μm-thick thin film, which was soaked in dilute aqueous hydrochloric acid solution to fix the microphase separated structure by cross-linking. The hydrolysis of the isopropoxysilyl group in the poly(1) domain affords the silanol followed by condensation of the silanols to form siloxane linkage. The progress of the reaction was followed by IR spectroscopic measurement. The strong absorption of the original film at 1170 cm^{-1} due to the Si–O–C stretching completely disappeared, and alternatively a new broad band appeared at 1050 cm^{-1}, which was ascribed to the stretching of Si–O–Si bond cross-linking the poly(1) chains after acid treatment. As shown in Table III, the results of elemental analysis of the cross-linked polymer film agree with the calculated values, assuming that isopropoxysilyl groups are quantitatively converted into siloxane linkages.

The resulting cross-linked film is insoluble in organic solvents and swells with THF, benzene, and hexane as shown in Table II. Since the cross-linked homopoly(1) does not absorb organic solvents, the swelling seems to occur in the polyisoprene domain. The dry film is a rubberlike elastic material, although the poly(1) domain is highly cross-linked. Pairs of T_g's of the film (II) before and after acid treatment were evaluated as 284, 461 K and 321, 465 K, respectively, by DSC measurement. Lower T_g's can be attributed to polyisoprene block. Elevation of the T_g after hydrolysis suggests partial restriction of the segment motion of polyisoprene by cross-linking, whereas higher T_g's due to poly(1) block are almost unchanged. The clearly separated two T_g's suggest that the structure of microseparated domains is retained even after hydrolysis.

The cross-linked film was immersed in dichloromethane solution of ozone at −40 °C and then treated with triethyl phosphite in methanol to cleave the carbon–carbon double bond of polyisoprene block, affording a somewhat brittle and opaque film. The main chain of the polyisoprene block is cleaved at the carbon–carbon double bond of the 1,4 linkage, while vinyl and isopropenyl groups of 1,2 and 3,4 linkages are oxidized to give formyl and acetyl groups attached on the main chain. A huge IR absorption of the film around 1740 cm^{-1} observed just after ozonolysis (Figure 2a) indicates that the oxidized fragments bearing carbonyl groups remained in the film. When the film was washed in methanol, the strong absorption band of carbonyl groups around 1740 cm^{-1} decreased the intensity as shown in Figure 2a–c, indicating that the degraded compounds were leached out. After thorough rinse in hot methanol, the weak bands were still observed at 1770 and 1735 cm^{-1} assigned to formyl and acetyl groups on the short polymer chain which was covalently bonded to terminal of cross-linked poly(1). The methanol solution containing decomposed polyisoprene fragments was collected and condensed for GPC measurement. From the GPC curve, $\overline{DP}$ of the fragment was estimated to be 23–26.[7] Assuming that all of the 1,4 linkage, the content of which is 8% in the polyisoprene chain, is cleaved, the $\overline{DP}$ of the fragment is calculated to be 12. Reaction time with ozone affects degree of C=C bond scission as shown in Figure 2, where rather strong absorption at 1640 cm^{-1} of unreacted carbon–carbon double bond was observed for 2 h of oxidation. The IR bands of C=C stretching (1640 cm^{-1}) and of olefinic C–H deformation (910 and 870 cm^{-1}) almost diminished after soaking the film in the dichloromethane solution of ozone for 6 h. The results of elemental analysis of the film obtained agree with the calculated ones[8] as shown in Table III. The polyisoprene domain becomes a hollow by leaching out the cleaved fragments that have been packed therein, and the wall of the micropores produced would be covered with formyl and acetyl groups attached to the cross-linked polymer chain.

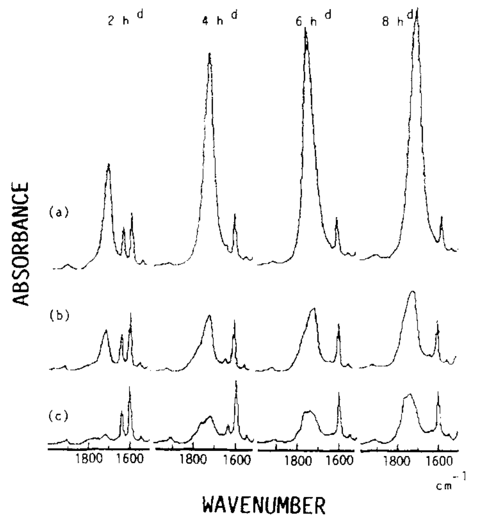


Figure 2. Change of IR absorbance with repeating a soak of the oxidized film (II) in methanol for 0 h (a), 24 h at 20 °C (b), 24 h at 20 °C, and 3 h at 50 °C (c). (d) Reaction time for ozonolysis.

Table III
Elemental Analysis of Polymer Film IV

treatment	calcd, % C	calcd, % H	measd, % C	measd, % H
as cast film	76.88	10.01	77.84	10.15
hydrolysis	78.00	9.35	77.92	9.59
ozonolysis	70.59	7.84	70.31	7.82

Gravimetric Analysis. The weights of the films obtained in each step reduced by condensation of silanols and thereby leaching out the decomposed polyisoprene fragments. Table IV summarizes the weight percent of the cross-linked and the ozonized films based on the corresponding original films (I, III, IV, and V) in comparison with their calculated values. From the contents of the poly(1) block, the weight losses by condensation reaction are calculated to be 6–15%, which fairly agree with the calculated values. After leaching out the decomposed fragmental polymer chains, the weight loss approximately equivalent to the weight of polyisoprene block was observed. The small differences between the measured and calculated values might correspond to the oxidized short polyisoprene chain attached to the micropore by the co-

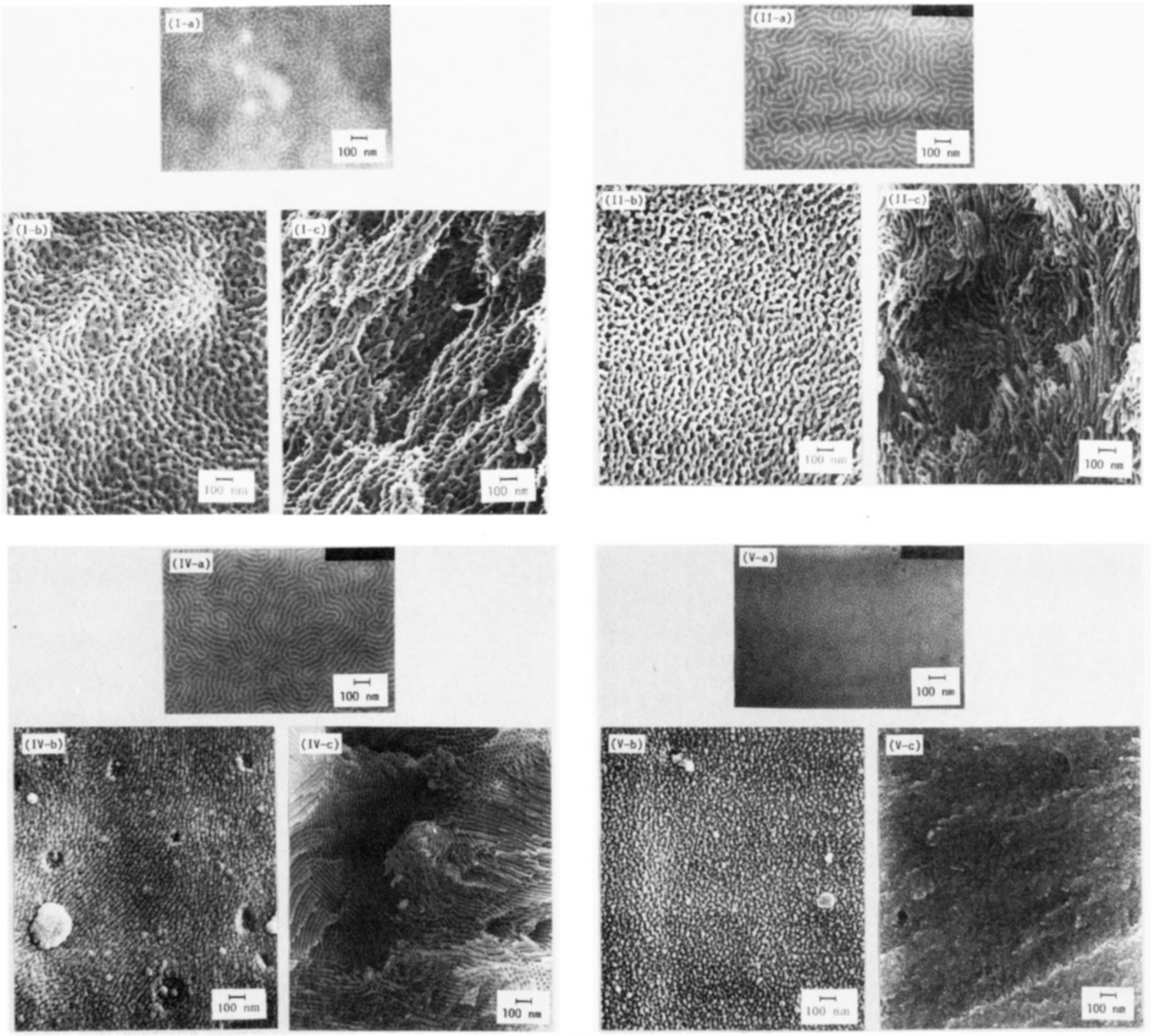


Figure 3. TEM of the thin films of block copolymers I, II, IV, and V cast from MIBK (Ia, IIa, IVa, and Va) and SEM of the surface (Ib, IIb, IVb, and Vb) and the cross section (Ic, IIc, IVc, Vc) of the corresponding microporous membranes.

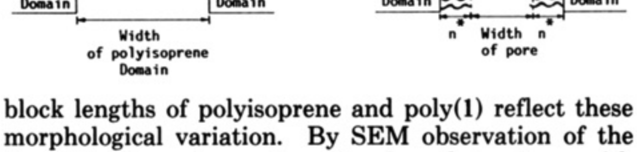
valent bond, provided the cleaved fragments are completely removed from the membrane. Hence, on the basis of the calculated and observed weight percent, the $\overline{\mathrm{DP}}$ of the residual polyisoprene chain, n^*, can be estimated to be 26–46 as shown in Table IV. These values are close to that observed by GPC rather larger than that calculated ($\overline{\mathrm{DP}} = 12$) from the content of 1,4 linkage in the polyisoprene chain as mentioned above. This is presumably due to the remaining 1,4 linkage, which is still observed in the IR spectrum at 1640 cm^{-1} (Figure 2). A typical result of elemental analysis of the porous membrane (IV) shown in Table III agrees well with the calculated one by assuming that all isopropoxysilyl groups are converted into siloxane linkages and that the polyisoprene chain ($\overline{\mathrm{DP}} = 46$) remains with formyl and acetyl groups.

Electron Micrographic Observation. Microstructures of the original films of the block copolymer and the porous membrane obtained by ozonolysis were investigated by transmission and scanning electron microscopies, respectively. The lamellar structures of segregated microdomains were observed on the surfaces of the films of block copolymer I, II, and IV, as shown in Figure 3. In the case of block copolymer V, the polyisoprene domain stained with osmium tetroxide becomes discontinuous, suggesting sphere and/or cylinder type microphase separation. The block lengths of polyisoprene and poly(1) reflect these morphological variation. By SEM observation of the O_3-oxidized membrane, lamellar-shaped structures with the same sizes as original films were emerged on the surfaces of the membrane (I and II). On the surface of the

Table IV
Gravimetric Analysis after Cross-Linking and Ozonolysis

block copolymer	block length[a] n–m–n	after cross-linking, % calcd[b]	obsd	after ozonolysis, % calcd[c]	obsd[d]	n^*
I	44–565–44	92.2	93.6	25.7	32.1	26
III	85–530–85	88.2	90.3	41.8	49.1	38
IV	100–340–100	84.8	88.5	50.4	60.0	46
V	115–210–115	81.9	85.4	59.9	69.2	43

[a] $(1)_n$–(isoprene)$_m$–$(1)_n$. [b] $[2\cdot100n(220-51)+68m]/(2\cdot220n+68m)$. [c] $2\cdot100n(220-51)/(2\cdot220n+68m)$. $n^* = (\text{wt }\%^d - \text{wt }\%^c)(2\cdot220n+68m)/2\cdot70\cdot100$, $\overline{\mathrm{DP}}$ of remaining polyisoprene after ozonolysis:



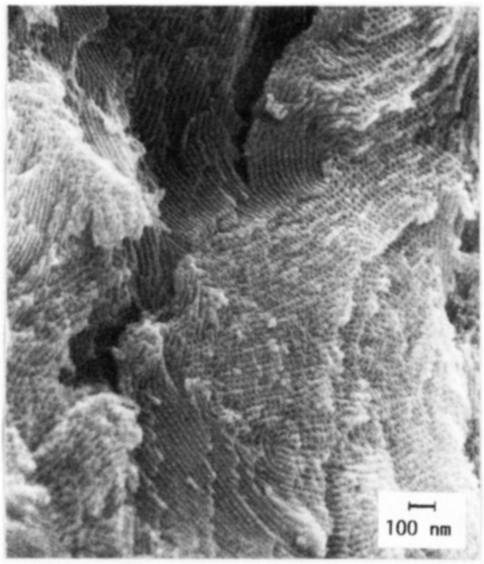


Figure 4. SEM of the cross section at the middle of the membrane (IV). SEM of the cross section beneath the surface is shown in Figure 3 (IVc).

porous membrane made from block copolymer (IV), the hollow lamellae were very narrow and a rugged pattern of microphase separation was observed corresponding to narrower polyisoprene domain due to shorter block length compared with that of I and II. Cylindrical hollows were partly observed in the cross section of the membrane (IV). A more finely divided spherelike structure was observed on the surface and cross section of the membrane derived from V. The surface and cross-section structures of the porous membranes observed by SEM reflect the microphase separated structures of the original films. The SEMs of the cross section observed beneath the surface and at the middle of the membrane (IV) show almost the same lamellar structure, suggesting the formation of continuous channels through the membrane (Figure 4). On the other hand, the hollow domain in the cross section of the membrane (V) seems closed corresponding to the discontinuous sphere like microphase separation of the original film. The periodicities of the lamellar structures of the original films and the microporous membranes measured by TEM and SEM, respectively, are listed in Table V. The widths of polyisoprene domains in as-cast films unequivocally correspond to the size of hollow domain in the porous membrane. The pore sizes are somewhat smaller than the polyisoprene domain sizes. Such shrinkage of pores might be caused by the partly remaining polyisoprene chains onto the cross-linked domain as shown in the scheme in the Table IV, by mechanical deformation of the porous membrane and thereby gold coating on the sample for SEM measurement.

Table V
Characterization of the Porous Membranes

block copolymer	width: polyisoprene domain, nm	width: pore, nm	surface area, m^2/g	N_2 permeability[a] $\times 10^6$
I	30 ± 5	28 ± 5	50	4.0–12
II	31 ± 4	27 ± 3	91	1.5–5.6
IV	21 ± 1.5	17 ± 2	74	0.22–0.43
V	11 ± 1.5	7 ± 2	*b*	0.0028

[a] $cm^3(STP)cm/cm^2{\cdot}s{\cdot}cmHg$. [b] Adsorption of nitrogen was not detected.

Surface Area and Permeability. The surface area of the porous membranes were measured by BET method. The results are listed in Table V. The large specific surface areas of the membranes I, II, and IV indicate that the hollow domain is not a closed and/or shallow groove but a continuous channel through the membrane. The BET curves leveled off at around 1.7, 2.0, and 4.6 h for the membrane, I, II, and IV, respectively, suggesting a width of the channel narrows in this order. Adsorption of nitrogen into the membrane V was not observed, which means that the hollow domain are almost closed, as suggested by electron micrographic observation.

The N_2 permeabilities of porous membranes shown in Table V are correspond to the pore sizes of the membranes. The high permeability of I, II, and IV indicates that the hollow channels are opened through the membranes, while the closed hollow domain of V causes low N_2 permeability.

In conclusion, the structure of the microporous membrane, which was prepared from the block copolymer of isoprene and 1, was characterized by IR and BET measurements, elemental and gravimetric analyses, and electron micrography. The microstructure of the porous membrane was found to be precisely controlled by block lengths of the original block copolymer.

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(7) Ozonolysis of isoprene homopolymer, which was prepared in the same condition as that of block copolymerization, was also performed. The $\overline{DP}$ of the scission products was evaluated to be 23 from the GPC curve.

(8) The elemental composition is calculated on the following assumptions: All isopropoxysilyl groups are converted to siloxane linkages, 70 wt % of polyisoprene chain is decomposed and removed, and the all C═C bonds of residual polyisoprene chains are oxidized.