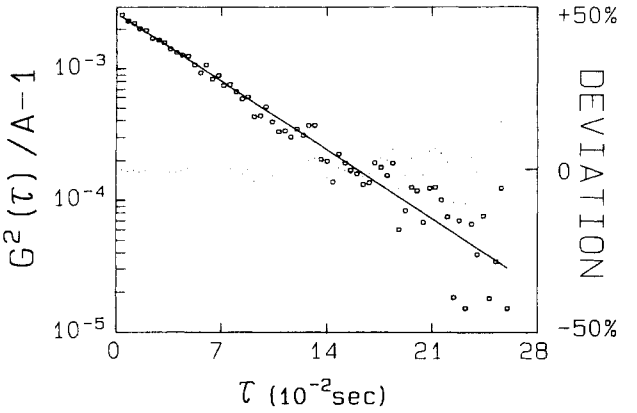

Figure 1. Plot of $G^{(2)}(K,\tau)/A - 1$ and percent deviation versus τ. Hollow circles denote measured data at 35 °C; solid line denotes $G^{(2)}(K,\tau)/A - 1 = 0.0028 \exp(-17.4\tau)$ with τ expressed in seconds. $\theta = 6.9°$; $C \approx 3 \times 10^{-8}$ g/mL for PS polymer with $M_w = 4.83 \times 10^7$ g/mol. DEVIATION = 1 - log $(G^{(2)}_{calcd}(K,\tau)/A - 1)$/log $(G^{(2)}_{measd}(K,\tau)/A - 1)$.

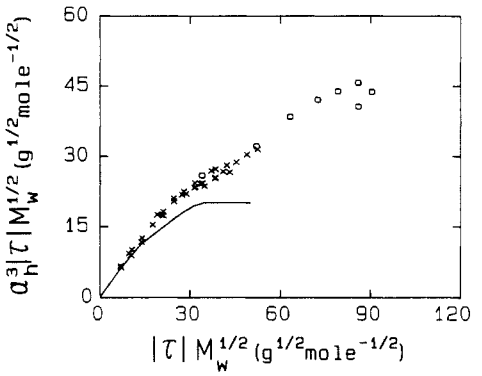

Figure 2. Plot of $\alpha_h^3|\tau|M_w^{1/2}$ versus $|\tau|M_w^{1/2}$. Solid line denotes $\alpha_s^3|\tau|M_w^{1/2}$. Crosses denote earlier results[2] using lower molecular weight PS polymers at higher concentrations; hollow circles denote this work using a PS sample with $M_w = 4.83 \times 10^7$ g/mol, $M_w/M_n \leq 1.03$, $C \approx 3 \times 10^{-8}$ g/mL, and measured at small scattering angles ($KR_g \leq 1$).

solvent due to polymer solute scattering represent, to our knowledge, light-scattering experiments in the most dilute solution and small-angle scattering limits ever performed. (3) The agreement between the measured and computed base line is typically $A_{meas} = 8.656\,33 \times 10^6$, $A_{compt} = 8.656\,10 \times 10^6$, i.e., one part in 3.8×10^4. This means that our system including polymer solution clarification has achieved an extremely high operating efficiency.

Figure 2 shows a plot of scaled expansion factor of hydrodynamic size $\alpha_h^3|\tau|M_w^{1/2}$ ($g^{1/2}$ $mol^{-1/2}$) versus scaled reduced temperature $|\tau|M_w^{1/2}$ ($g^{1/2}$ $mol^{-1/2}$) where $\alpha_h = R_h(T)/R_h(\Theta)$ with R_h and Θ being the hydrodynamic radius and the Θ temperature, respectively. By using a $M_w = 4.83 \times 10^7$ g/mol, PS polymer of extremely narrow MWD ($M_w/M_n \leq 1.03$), and a concentration of 3×10^{-8} g/mL, we have reached the collapsed state for polystyrene in cyclohexane based on the hydrodynamic size. The crosses represent our earlier results[2] and circles denote the present work. The solid line denotes a plot of $\alpha_s^3|\tau|M_w^{1/2}$ versus $|\tau|M_w^{1/2}$ with $\alpha_s = R_g(T)/R_g(\Theta)$, R_g being the root-mean-square z-average radius of gyration. The ratio of the plateau values for $\alpha_h^3/\alpha_s^3 = (43.2 \pm 2.0)/(20.2 \pm 0.8) = 2.14 \pm 0.19$, in reasonable agreement with a value of 2.08, based on the blob theory.[9] A more detailed analysis and further measurements are under way.

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Registry No. PS, 9003-53-6; cyclohexane, 110-82-7.

References and Notes

(1) Chu, B. *J. Polym. Sci., Polym. Symp. Ed.* **1985**, *73*, 137; *Polym. J., Jpn.* **1985**, *17*, 225.
(2) Park, I. H.; Wang, Q.-W.; Chu, B. *Macromolecules* **1987**, *20*, 1965.
(3) Chu, B.; Park, I. H.; Wang, Q.-W.; Wu, C. *Macromolecules*, in press.
(4) Park, I. H.; Fetters, L.; Chu, B. *Macromolecules*, in press.
(5) Chu, B. *Proceedings of International Symposium on Dynamics of Ordering Processes in Condensed Matter*, Kyoto, Japan, August 1987, to be published.
(6) Chu, B.; Xu, R.-L.; Maeda, T.; Dhadwal, H. S. *Rev. Sci. Instrum.*, submitted for publication.
(7) Chu, B.; Park, I. H.; Ford, J. R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1983**, *24*, 237.
(8) Chu, B. U.S. Patent 456 544.
(9) Akcasu, A. Z.; Han, C. C. *Macromolecules* **1979**, *12*, 276.

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Polymerization of Monomers Containing Functional Silyl Groups. 5. Synthesis of New Porous Membranes with Functional Groups

Microporous membranes are commercially produced from polymers by using phase-separation process.[1] In this paper, a new attempt is described to make microporous membranes from the film of a block copolymer with well-defined chain structure which is prepared by anionic living polymerization. This method involves casting a block copolymer film with a microphase-separated lamellar structure, fixation of one microdomain by cross-linking between the polymer chains, oxidative decomposition of the other microdomain, and leaching out the degraded low molecular weight compounds from the inside of micropores formed by oxidation. The lamellar structure of the original block copolymer film was found to be directly reflected in the shape and size of the micropores produced by these steps. Thus, the microstructure of the porous membrane can be controlled through these procedures chiefly by the morphology of the segregated microphase depending on architecture of block copolymer and casting conditions of the film. Regulated pore size of the membrane may control the permeability of a fluid. Furthermore, it is observed that the resulting membrane contains carbonyl groups by oxidative cleavage of the polymer chain, which will enable some functions such as enzymes and metal complexes to be linked in the micropores.

Experimental Section. Block Copolymerization. The anionic living polymer of isoprene (20.4 mmol) was prepared with oligo(α-methylstyryl)dipotassium (0.05 mmol) in dry THF (26 mL) at -78 °C for 3 h in a sealed glass tube equipped with breakable seals. For the characterization of homopolyisoprene, an aliquot of the reaction mixture (12 mL) was withdrawn. (4-Vinylphenyl)dimethyl-2-propoxysilane (1) (5.63 mmol) in 5.5 mL of THF was added to the residual THF solution (15 mL) of anionic living polyisoprene at -78 °C and was kept at the same temperature for 5 min to give a triblock copolymer, 2, as shown in Scheme I. The living polyisoprene and block copolymer were quenched with methanol. The polymers

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Scheme I
Anionic Block Copolymerization

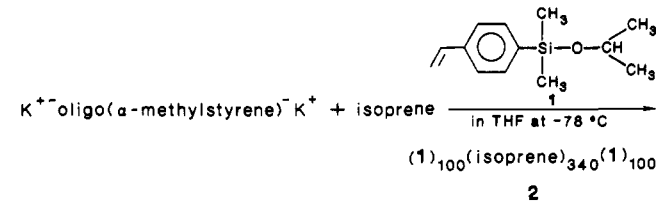

Table I
Anionic Block Copolymerization of Isoprene and 1

polymer	$\bar{M}_n \times 10^{-4}$ calcd	obsd
polyisoprene (central block)	2.8	2.4[a]
block copolymer (2)	7.2	6.8[b]

[a] Measured by vapor-pressure osmometry, $\bar{M}_w/\bar{M}_n$ = 1.10. [b] Estimated from $\bar{M}_n$ of polyisoprene and the composition of 2 measured by ^{1}H NMR, $\bar{M}_w/\bar{M}_n$ = 1.20.

obtained were purified by reprecipitation and freeze-drying.

Cross-Linking. In order to immobilize a microdomain of the poly(1) block, a film (200 mg; 8 cm × 8 cm × 20 μm) of **2** cast from methyl isobutyl ketone (MIBK) was immersed in a 2 N HCl aqueous solution (50 mL) at room temperature for 2 days, rinsed with water repeatedly, and dried in vacuo.

Ozonolysis. Cleavage of the carbon–carbon double bond of the polyisoprene chain was performed by soaking the film (30 mg; 2 cm × 4 cm × 20 μm) in 50 mL of dichloromethane containing 0.25 mmol of ozone at −40 °C for 6 h.[2]

Leaching. To leach out the cleaved compounds from the micropore, the film was soaked repeatedly in methanol (50 mL) at 20 and 50 °C for several hours.

Measurements. IR spectra were run with a IR-810, JASCO. The film of **2** cast from MIBK was stained with OsO_4 and observed by transmission electron microscope, JEM-100CX, JEOL. Surface and cross section of the ozone-treated and rinsed membrane were slightly coated with gold and observed by using scanning electron microscope, 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.

Results and Discussion. Block Copolymerization. The block copolymer was obtained in quantitative yield. From the ^{1}H NMR spectroscopic measurement, the microstructure of polyisoprene block was found to contain 8% 1,4-, 38% 1,2-, and 54% 3,4-linkage. The parameters of molecular weight distribution, $\bar{M}_w/\bar{M}_n$, of the polyisoprene and **2** were estimated to be 1.1–1.2 from GPC by using a calibration curve based on standard polystyrene. The calculated molecular weights of the polymers based on the molar ratios of monomer to initiator agree with those measured by vapor-pressure osmometry (VPO) and ^{1}H NMR spectroscopy as shown in Table I. These results arise from the living nature of the propagating end of **1** which was already substantiated by our previous study.[3]

Cross-Linking. The electron micrograph of the film in Figure 2A shows the lamellar morphology of the segregated phase which will be discussed later compared with the microstructure of the porous membrane. Soaking the film in dilute aqueous hydrochloric acid solution readily caused cross-linking via hydrolysis of the isopropoxysilyl group and subsequent condensation of the resulting silanols in the poly(1) block domain. The insoluble cross-linked film was elastic and swelled in THF, benzene, hexane, and dichloromethane. The IR spectra shown in Figure 1A,B unequivocally followed the progress of the reaction. The strong absorption of the film of **2** at 1170 cm^{-1} due to the Si–O–C stretching completely disappeared and a new broad band appeared at 1050 cm^{-1}, corresponding to the Si–O–Si cross-linking between the poly(1) chains after acid treatment. The results of elemental analysis of the cross-linked polymer film agree with the calculated values, assuming that all isopropoxysilyl groups are converted into siloxane linkages: Anal. Obsd: C, 77.92; H, 9.59. Calcd: C, 78.00; H, 9.35%.

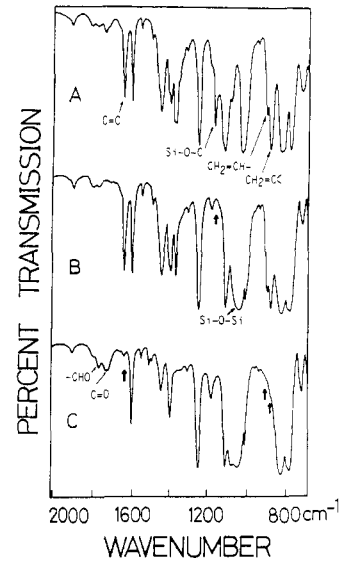

Figure 1. IR spectra for the as-cast film of **2** (A), the acid-treated film (B), and the ozone-treated and rinsed film (C).

Ozonolysis. Ozonolysis of the film was performed in dichloromethane to give a somewhat brittle and opaque membrane. The reaction predominantly results in the cleavage of the carbon–carbon double bond of polyisoprene block to form carbonyl functions. This was proved by IR spectra of the film as shown in Figure 1C. Before ozonolysis, the characteristic strong absorptions due to the isoprene unit were observed at 1640 ($\nu_{C=C}$), 910 ($\delta_{CH_2=CH-}$), and 870 cm^{-1} ($\delta_{CH_2=C<}$). They diminished after the film was immersed in the dichloromethane solution of ozone.

Leaching. Through ozonolysis, the main chain of the polyisoprene block was cleaved at the 1,4-linkage to form low molecular weight compounds, which packed together in the interior of the pores which previously contained the polyisoprene block domain. The strong absorption band of the carbonyl group at around 1740 cm^{-1} due to degraded molecules decreased in intensity when the film was repeatedly soaked in methanol. When all cleaved compounds were leached out, weak bands were observed at 1770 and 1728 cm^{-1}, attributable to aldehyde and ketone groups, respectively, which were presumably attached to the chain end and pendant groups of the short polymer chain which was still linked to the terminal of poly(1) block. A small peak assigned to the C=C bond still remained at 1640 cm^{-1}. The weight of the resulting membrane was reduced to 60% of the original value, indicating that about 70% of polyisoprene chain was cleaved and leached out.[4] The results of elemental analysis of the porous film obtained here agree fairly well with the calculated composition based on the loss of degraded polymer chains:[5] Anal. Obsd: C, 70.31; H, 7.82. Calcd: C, 70.59; H, 7.84%.

Electron Micrographic Observation and Measurement of Surface Area. Microstructures of the original

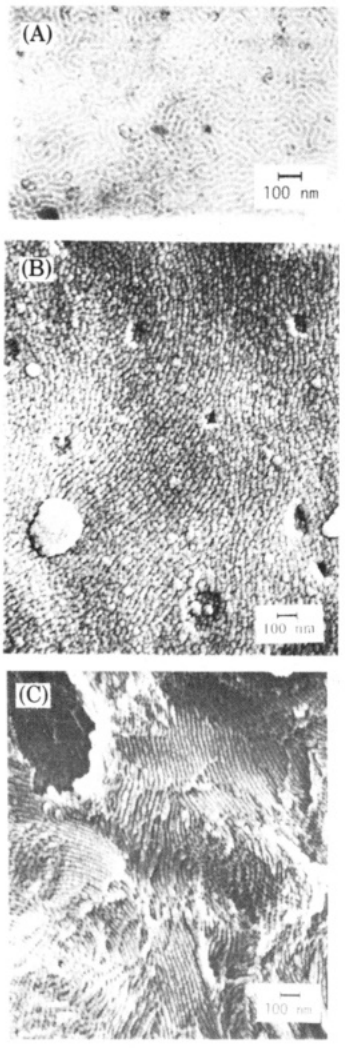

Figure 2. Electron micrographs of the thin film of block copolymer **2** cast from MIBK observed by TEM (A) and the surface (B) and the cross section (C) of the ozone-treated and rinsed film observed by SEM, the scale mark indicates 100 nm.

film, **2**, and the porous membrane were investigated by means of transmission and scanning electron microscopies, respectively. The lamellar structure of the segregated microphase was observed on the surface of the original film as shown in Figure 2A. After the film was rinsed and treated with ozone and methanol, a rugged surface of a similar lamellar pattern emerged (Figure 2B). The shadowed and ridged lines may correspond to the etched polyisoprene and remaining poly(**1**) domains, respectively. The scanning electron micrograph of a cross section of the treated film also exhibited lamellar morphology (Figure 2C), suggesting that the hollow domain continued through the film. The pore width seems to be 10 nm although the periodicity distance of the polyisoprene domain of the original film is about 20 nm, which is also reasonable value based on the polyisoprene block length. Such shrinkage of pores might be caused by leaching out the cleaved products and gold coating on the sample would also affect the electron microscopic observation.

The surface area of the porous membrane was measured by BET method to be 74 m^2/g. This large value indicates that the hollow domain is not a closed and/or shallow groove but rather is a continuous channel.

The results of IR and BET measurement, elemental and gravimetric analyses, and electron micrographic observation substantiated the formation of the microporous membrane, whose structure was similar to that of segregated microphase of the original block copolymer. A further work on the synthesis and detailed characterization of the membranes with different controlled pore sizes is now in progress.

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Registry No. (Isoprene)((4-vinylphenyl)dimethyl-2-propoxysilane) (block copolymer), 102394-54-7.

References and Notes

(1) Strathmann, A.; Kock, K. *Desalination* **1977**, *21*, 241.
(2) Ho, K. W. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 2467.
(3) Hirao, A.; Nagawa, T.; Hatayama, T.; Yamaguchi, K.; Nakahama, S. *Macromolecules* **1985**, *18*, 2101.
(4) Assuming that isopropoxysilyl group was almost converted into siloxane linkage and that polyisoprene chains were completely cleaved and leached out, the weight of original film (**2**, 250 mg) should reduce to 120 mg, but the weight of produced porous film was actually 150 mg. The difference (30 mg), corresponding to about 30 wt % of polyisoprene block (88 mg) of the original film, may be attributable to residual polymer chain attached to the micropore by a covalent bond.
(5) The elemental composition is calculated on the following assumptions: all isopropoxysilyl groups are converted into siloxane linkages, 70 wt % of polyisoprene chain is decomposed, and the all C=C bonds of residual polyisoprene chains are oxidized.

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Ferrocenyl Containing Polysilanes[1]

Organopolysilanes, high molecular weight polymers containing only Si atoms in the backbone, $(R''R'Si)_n$, have attracted considerable recent interest due to their use as photoresists,[2-4] perceramic and ceramic doping materials,[5,6] dopable semiconductors,[6] and photoconducting[7] and nonlinear optical materials.[8] To date, the substituent groups R″ and R′ have been limited to organic radicals such as phenyl, alkyl, and trimethylsilyl groups.

We have been interested for a long time in the chemical and physical properties of transition-metal-substituted silanes, including oligosilane, and have found that the location of a transition-metal center in an oligosilane dramatically alters these properties. For example, oligosilanes are significantly more susceptible to photochemical deoligomerization when directly bonded to the iron atom in $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]$ systems, while migration from the iron atom to the cyclopentadienyl ligand removes this activation.[9,10]

Such dramatic changes in photochemical properties suggested to us that preparation of transition-metal-substituted high molecular weight polysilanes would produce a new class of these interesting polymers with many unique properties. In this initial report on our studies we present the first example of such compounds in which copolymerization of ferrocenylmethyldichlorosilane, $FcMeSiCl_2$, Fc = $(\eta^5\text{-}C_5H_4)Fe(\eta^5\text{-}C_5H_5)$, and phenylmethyldichlorosilane, $PhMeSiCl_2$, has been successfully accomplished.

Copolymerization was effected by the procedure of Wurtz-type coupling as outlined in reaction 1.[11]

$$FcMeSiCl_2 + n\,PhMeSiCl_2 \xrightarrow{Na/solvent} [(FcMeSi)(PhMeSi)_n]_m \quad (1)$$