

Syntheses and Gas-Transport Properties of Alkylsilane-Modified SBS Membranes

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ABSTRACT: Alkylsilane-modified styrene-butadiene-styrene (SBS) polymers were prepared via two steps. In the first step, dimethylchlorosilane $\text{HSi}(\text{CH}_3)_2\text{Cl}$ and SBS (Korea Kumho Petrochem. Co.; 35% vinyl content; $M_w = 48,000$, $M_w/M_n = 1.05$) were reacted in toluene using H_2PtCl_6 catalyst to produce a hydrosilylated polymer. In the second step, chloride in the silyl group was replaced with alkyl by reaction with RLi ($\text{R} = \text{Me}, n\text{-Bu}$). Under severe conditions, silylation occurs on all the double bonds of the polymer so that their elastomeric nature disappears. However, under mild conditions, selective hydrosilylation of the pendant vinyl groups of SBS could be accomplished so that the polymer retained its elastomeric properties with two low T_g values. These modified SBS polymers were easily dissolved in THF, and thus could be formed into film-type membranes by solvent casting on teflon plates. From the measurements of their gas permeability for O_2 and N_2 , they showed higher selectivity for O_2 compared with the unmodified SBS. The permeability for oxygen was dependent on the size of the alkylsilyl group. Methylsilane and butylsilane-modified SBS membranes showed the higher permeability values of 31.2 and 37.5 barrer ($1 \text{ barrer} = 1 \times 10^{-10} \text{ cm}^3 (\text{STP}) \text{ cm cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$) at 30°C , respectively, compared with 2.39 barrer of the unmodified SBS. Furthermore, their selectivities for O_2 over N_2 were increased to 3.0 and 3.2, respectively, from 2.5 of the unmodified SBS case. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1117-1122, 1997

Key words: gas permeability; elastomeric membrane; SBS polymer; hydrosilylation; O_2/N_2

INTRODUCTION

Organosilicon polymers have been widely studied as one of the most attractive membrane materials for gas transport because of their superior gas permeabilities.¹⁻³ Some of these polymers such as polydimethylsiloxane, polytrimethylsilylpropyne, etc., show very high permeabilities because of the large void volume among polymer segments generated by the disruption of the polymer packing in the presence of the bulky silicon moiety and flexible Si—C bonds. In general, however, the ho-

mopolymers having silyl groups show low selectivities in gas separation. Several studies have shown that introduction of silane moiety by copolymerization, blending, and chemical modification could improve the above properties.⁴⁻⁶ We have recently been developing elastomeric membranes containing silyl groups for gas separation. The segments of elastomer can rotate freely along the main chain bonds, providing a high degree of chain mobility. Therefore, elastomers generally exhibit high permeabilities compared to glassy polymers. Styrene-butadiene-styrene (SBS) block copolymer, one of the most popularly used thermoplastic elastomers, has properties of resin and rubber ($T > T_g$), which makes possible preparation into elastomeric membranes and fibers sim-

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ply from solutions of the material. Furthermore, the microstructures 1,2- or 1,4-addition of polybutadiene blocks in SBS can be controlled by changing polymerization conditions⁷ such as temperature, time, and polar additives. Because the pendant vinyl groups generated by 1,2-addition of butadiene have higher reactivity compared with the double bonds in the polymer backbone, formed by 1,4-addition, the polymer could be easily modified by hydrosilylation using Pt catalyst without the loss of elastomeric properties. In this article, we report the syntheses and gas transport properties of the hydrosilylated SBS as gas transport elastomeric membranes.

EXPERIMENTAL

Materials

The host polymer, SBS (Korea Kumho Petrochem. Co.; 35% vinyl content; $M_w = 48,000$, $M_w/M_n = 1.05$), was used after 1 day of drying in a vacuum oven. Hydrogen hexachloro platinate hydrate ($H_2PtCl_6 \cdot xH_2O$), as a catalyst purchased from Aldrich Chemical Co., was handled and stored under N_2 atmosphere. Toluene, as reaction solvent, was distilled in the presence of P_2O_5 before use. Methyl lithium (1.5M in ether, Aldrich Co.), *n*-butyl lithium (2.5M in ether, Aldrich Co.), and other solvents were used without further purification. O_2 and N_2 gases used were of ultrapure grade (99.9999%).

Syntheses of Alkylsilane-Modified SBS Polymers

$H_2PtCl_6 \cdot xH_2O$ (0.016 mmol) and $HSi(CH_3)_2Cl$ (6.8 g, 70 mmol) were added to a solution of SBS (10 g, 45 mmol of pendant double bonds) in dry toluene (100 mL). The solution was allowed to stir at 30–60°C for 2–6 h under argon atmosphere. After cooling the reaction mixture to 5°C, methyl or *n*-butyl lithium (80 mmol in ether) was added dropwise and subsequently the reaction was allowed to proceed for 1 h at 5°C. The resulting pale yellow solution was poured into methanol (2 L) to produce the white precipitate of polymer. The precipitate was rinsed three times in methanol and dried under vacuum at room temperature to give 5.3 g of white elastomeric solid. The microstructures of the alkylsilane-modified polymers were analysed by 1H -NMR ($CDCl_3$) and IR spectroscopy (see Figs. 1 and 2).

Measurements of Properties

1H -NMR and IR spectroscopic measurements of the modified SBS polymers were carried out using a Varian (200 MHz) NMR spectrometer using $CDCl_3$ as solvent and an IR spectrometer (BIORAD Co., FTS-60A), respectively. The glass transition temperature of the polymers were determined by using a differential scanning calorimeter (DSC: Netzsch Co., DSC 200) from –100 to 120°C at a heating rate of 10°C/min under N_2 atmosphere. The mechanical properties, such as tensile strength, elongation, and Young's modulus, were determined from the strain–stress curve measured by UTM (Instron Co.).

Membrane Preparation and Gas Permeation Measurements

A solution of toluene or THF containing 15 wt % of the SBS polymers was cast on a teflon plate and covered. The solvent was slowly evaporated overnight. The thickness of the membranes ranged between 100–300 μm . To measure the gas permeabilities, polymer membranes were further dried in vacuum for 1 day. Gas permeabilities of membranes were measured by using the gas permeability analyzer (K-315N-02, Rikaseiki Co.). Before measuring gas transport properties, the system was kept under a constant vacuum to remove residual air to obtain accurate measurements. The sample film, totally devoid of adsorbed gases, comes in contact with test gas at the top side surface. A few minutes are required for the gas to generate a steady flow, depending on the state of the membranes. The gas permeation coefficients and permeabilities were determined from the slope of the curve of the pressure on the permeation side vs. time (dP/dt) at this steady state, whereas time lag (θ), period of time for reaching the steady state, is taken for measurement of diffusion coefficient using the following equations:

$$Q = \frac{V \times 273}{A \times (273 + T) \times P \times dt}$$

$$p = \frac{L}{P \times A \times t} \times Q$$

$$D = L^2/6\theta; \quad p = D \cdot S; \quad S = p/D$$

where Q is the permeation coefficient [$cm^3(STP) m^{-2} h^{-1} atm^{-1}$]; V , the volume of low-pressure side of the cell (cm^3); A , the effective membrane area (m^2); p , permeability (barrer); T , the tem-

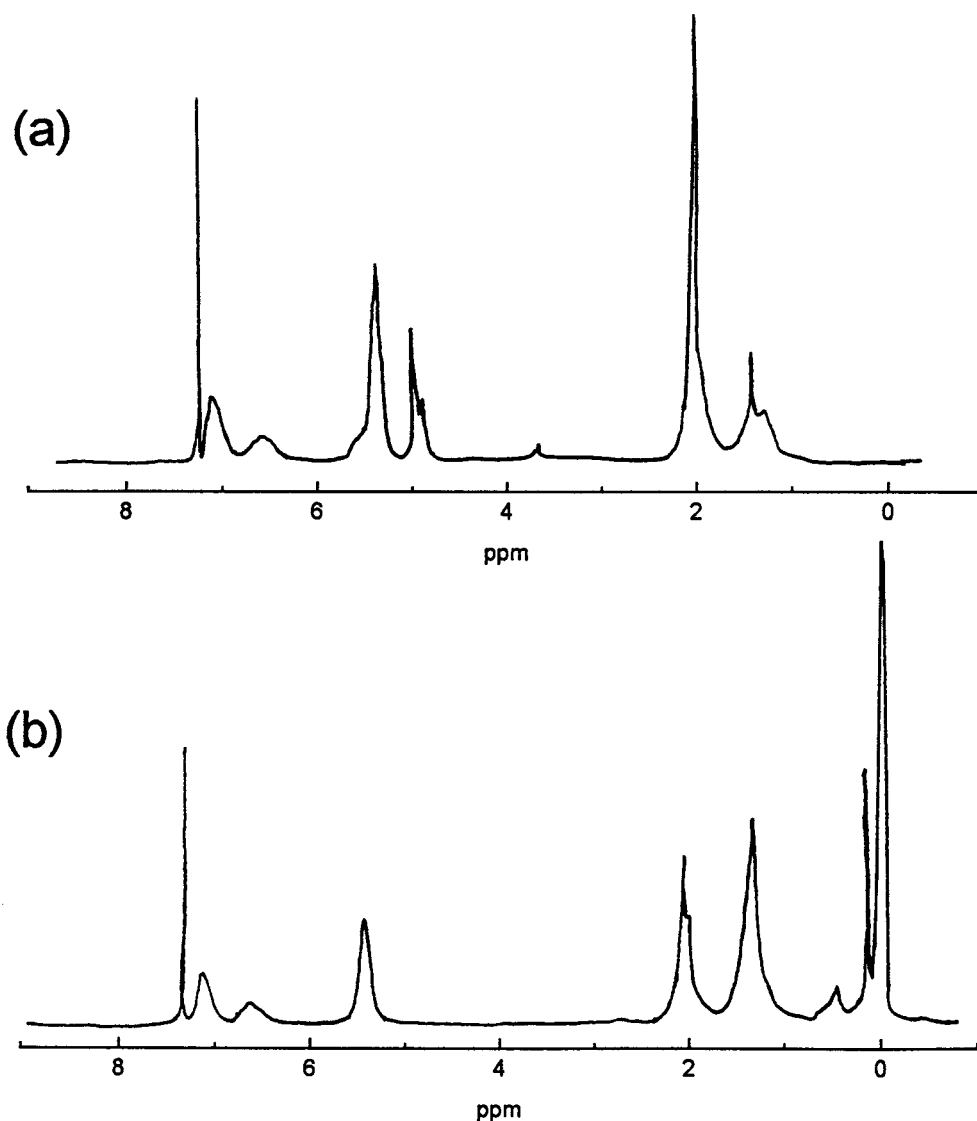


Figure 1 (a) $^1\text{H-NMR}$ (CDCl_3) spectrum for SBS. (b) $^1\text{H-NMR}$ (CDCl_3) spectrum for methylsilane-modified SBS (**2a**).

perature of low-pressure side of the cell; P , the pressure difference on both sides of the membrane (mmHg); dt , the required time to increase 1 mmHg pressure in the low-pressure side of the cell (h); L , the membrane thickness (cm); D , diffusion coefficient (cm^2/s); θ , time (s); and S , solubility coefficient [cm^2 (STP) cm^{-1} cmHg^{-1}].

RESULTS AND DISCUSSION

Alkylsilane-Modified SBS

Alkylsilane-modified SBS polymers were prepared by two-step reactions as shown in Scheme

1. The first step is the hydrosilylation reaction on pendant vinyl groups of the SBS (35% vinyl content) with dimethylchlorosilane (DMCS) using H_2PtCl_6 as a catalyst in toluene to prepare compound **1**. The second step is the alkylation step reacting chlorosilane-modified SBS with alkyl lithium to prepare alkylsilane-modified compound **2**. The SBS with high vinyl content that was produced under the conditions favorable for 1,2-addition of butadiene, has better hydrosilylation reactivity than the one with low vinyl content. But the former case is more vulnerable to gelation during the reaction with DMCS because of its high sensitivity to the reaction conditions such as moisture, air, temperature, and so forth.⁸

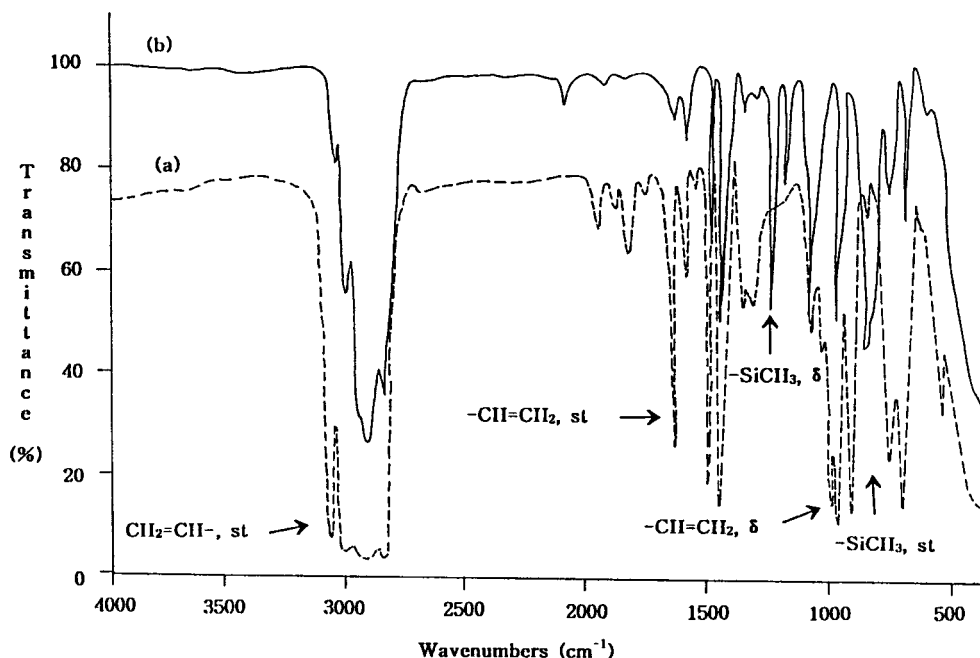
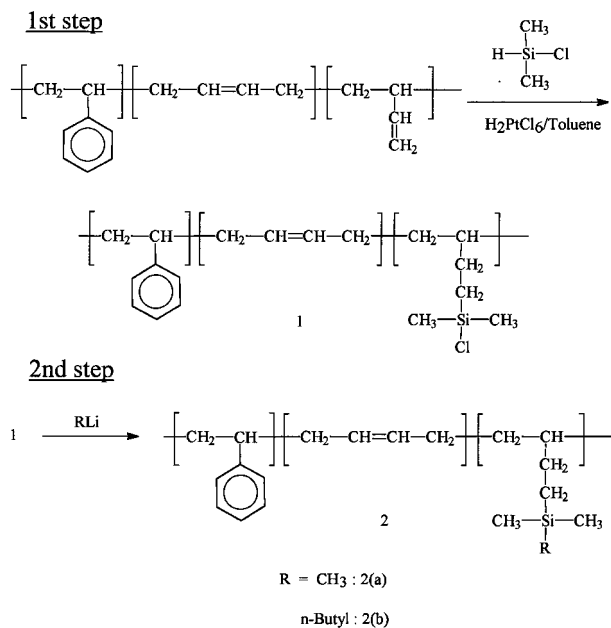


Figure 2 (a) IR spectrum for SBS. (b) IR spectrum for methylsilane-modified SBS (2a).

On the other hand, the latter has lower reactivity that necessitates severe reaction conditions.^{9,10} (The SBS with vinyl content lower than 10% especially required reaction temperature higher than 80 and a time longer than 1 day to achieve complete hydrosilylation on the pendant vinyl groups. In this case, hydrosilylation also occurred on dou-

ble bonds in the polymer main chain.) When the silylation occurs on all double bonds of the polymer, their elastomeric nature is almost totally lost. However, the selective hydrosilylation of the double bonds in the side chains of SBS was accomplished without gelation under mild conditions (30–60°C, 2–6 h) and under dry argon atmosphere. Figure 1 shows the ¹H-NMR data. The peaks, at 4.95 and 5.5–5.6 ppm corresponding to the pendant vinyl group (—CH=CH₂) of SBS, disappeared completely and two new peaks appeared due to silylation at around 0 ppm. From the calculation, based on integration, hydrosilylation occurred in all pendant vinyl groups. The IR spectra (Fig. 2) also showed a complete disappearance of the absorbances due to the terminal C=C bonds (3100 and 910 cm⁻¹) and new absorbances at 1235 cm⁻¹ due to CH₂ wagging, and at 1410 cm⁻¹ due to CH₂ scissoring, from the —SiCH₂— in the hydrosilylated SBS. These synthetic methods gave only the anti-Markownikoff addition products, which showed hydrosilylation on the terminal carbon of pendant vinyl group as Guo et al.¹¹ reported.



Scheme 1

Properties of SBS Membranes

These modified SBS polymers were easily dissolved in THF and were formed into dense films by casting THF solution on teflon plates. Table I

Table I The Physical Properties of SBS Polymers

Sample	T_g (°C) ^a	Tensile Strength (kgf/mm ²)	Elongation (%)	Young's Modulus (kgf/mm ²)
SBS	-70	0.93	800	1.55
SBS (2a)	-49/16	0.90	830	0.27
SBS (2b)	-60/14	0.69	950	0.15

^a The T_g values of butadiene block in SBS polymers.

shows values for T_g and mechanical properties of SBS polymers that were obtained from DSC and strain–stress curves, respectively. DSC measurements showed only broad endothermic peaks that necessitated differentiation to clearly locate T_g values. Table I shows only the T_g values for the butadiene blocks in the polymers that are involved in chemical modification. Butadiene blocks, in unmodified SBS membrane, showed an endothermic peak at -70°C , while the hydrosilylated SBS membranes showed two broad peaks each at -49 and 16°C in the methyl case (**2a**), and -60 and 14°C in the butyl case (**2b**), respectively. These observations indicate that two domains were formed in the modified butadiene block by silylation. All these T_g values are lower than room temperature, even though these values were increased by silylation. In comparison with physical properties, tensile strength and Young's modulus are decreased while elongation is increased after modification. The noticeable decrease in Young's modulus, which is the ratio of stress/strain, can be interpreted as a considerable increase in flexibility of polymer chains after silylation. Nevertheless, little change was observed for tensile strength and elongation. These results, the low T_g values together with the retention of major mechanical properties, imply that alkylsilylated SBS

membranes still maintain elastomeric properties after silylation.

Gas Transport Properties of SBS Polymer Membranes

The elastomeric membranes for O_2 , N_2 gas transport properties, permeabilities, diffusion and solubility coefficients, and selectivities, are shown in Table II. When the alkylsilylated SBS membranes were used as gas transport membranes, better oxygen transport behaviors (methylsilyl case (**2a**): 31.2 barrer in permeability and $\alpha = 3.0$ in selectivity; butylsilyl case (**2b**): 37.5 barrer in permeability and $\alpha = 3.2$ in selectivity at 30°C) were shown, compared with the unmodified SBS (23.9 barrer in permeability and $\alpha = 2.5$ in selectivity at 30°C). Between the alkylsilane-modified SBS membranes, *n*-butylsilane–modified SBS, which has more flexibility as shown in Young's modulus data, showed better oxygen transport behaviors than the methylsilane-modified one. From these results, it is interpreted that the presence of alkylsilyl groups in place of vinyl groups in the polymer backbone not only provides higher flexibility of the polymer segments to increase the void volume for better permeability, but also enhances the oxygen solubility for improved selectivity.

Table II Oxygen and Nitrogen Transport Properties of SBS Polymer Membranes

Sample	Diffusion Coefficient (10 ⁶ cm ² /s)		Solubility Coefficient [10 ⁴ cm ³ (STP) cm ⁻³ cmHg ⁻¹]		Permeability (barrer) ^a		Selectivity (PO ₂ /PN ₂)
	O ₂	N ₂	O ₂	N ₂	O ₂	N ₂	
SBS	2.4	1.4	9.8	6.9	23.9	9.7	2.5
SBS (2a)	2.8	1.6	11.1	6.6	31.2	10.4	3.0
SBS (2b)	2.4	1.9	15.5	6.3	37.5	11.7	3.2

^a 1 barrer = 1×10^{-10} cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹.

CONCLUSION

The selective alkylsilylation of pendant vinyl groups of SBS could be performed under mild conditions (30–60°, 2–6 h) with H₂PtCl₆ as a catalyst. The SBS polymers retain not only the elastomeric nature such as low T_g , low Young's modulus, and high elongation values, but also the solubility in THF, which facilitate the fabrication of their membranes. The silylated SBS membranes, which have more flexibility in polymer segments, show higher selectivities and higher permeabilities for O₂/N₂ than those made with unmodified SBS membrane.

REFERENCES

1. M. Masuda, Y. Iguchi, B. Tang, and T. Higashimura, *Polymer*, **29**, 2041 (1988).
2. K. Takada, H. Matsuya, T. Masuda, and T. Higashimura, *J. Appl. Polym. Sci.*, **30**, 1605 (1985).
3. R. Srinivasan, S. R. Auvil, and P. M. Burban, *J. Membr. Sci.*, **86**, 67 (1994).
4. T. Kendo, *New Developments in Gas Separation Technology*, Toray Research Center Inc., Japan, 1992, p. 137.
5. D. R. Paul and Yu. P. Yampol'skii, *Polymeric Gas Separation Membranes*, CRC Press, Inc., Boca Raton, FL, 1994.
6. Y. Nakassaki, Y. Hashimoto, and M. Kato, *Macromol. Rapid Commun.*, **15**, 619 (1994).
7. J. L. Speier, J. A. Webster, and H. Barnes, *J. Am. Chem. Soc.*, **79**, 974 (1957).
8. A. Iraqi and S. Seth, C. A. Vincent, D. J. Cole-Hamilton, M. D. Watkinson, I. M. Graham, and D. Jeffrey, *J. Mater. Chem.*, **2**, 1057 (1992).
9. X. Guo and G. L. Rempel, *Macromolecules*, **25**, 883 (1992).
10. Y. Nagasaki, K. Kurosawa, M. Suda, T. Tsuruta, K. Ishihara, and Y. Nagase, *Makromol. Chem.*, **191**, 2103 (1990).
11. X. Guo, R. Farwaha, and G. L. Rempel, *Macromolecules*, **26**, 5047 (1990).