Synthesis and Gas Permeation Behavior of Organosilicon-Containing Poly(*p*-allylstyrene)s

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(Received December 22, 1993)

ABSTRACT: New synthetic routes for silicon-containing styrene derivatives were investigated using *p*-allylstyrene (AST) as starting material. Lithium diisopropylamide induced a lithiation reaction of AST to form *p*-(1-lithioallyl)styrene (LiAST) without any side reaction such as polymerization under appropriate reaction conditions. Utilizing this carbanion as intermediate, synthesis of organosilicon-containing AST monomers was carried out. By adding trimethylsilyl chloride to the reaction system, mono-trimethylsilylated AST, [*p*-(3-trimethylsilyl-1-propenyl)-styrene; SAS] and bis(trimethylsilylated) AST, [*p*-[1,3-bis(trimethylsilyl)-2-propenyl]styrene; BSAS] were obtained by one pot. The yields of SAS and BSAS attained up to 91.7% and 88.5%, respectively under the appropriate reaction conditions. Radical polymerization of these monomers proceeded smoothly to form high molecular weight polymers without any gel formation even in bulk polymerization. The resulting polymers showed good membrane formabilities. Permeabilities of oxygen were in the range of 17–26 Barrers, keeping their selectivities against nitrogen through these membranes to be 3.3–3.5.

KEY WORDS Silicon-containing Polymers / *p*-Allylstyrene / Lithium Diisopropylamide / *p*-(3-Trimethylsilyl-1-propenyl)styrene [SAS] / *p*-[1,3-Bis(trimethylsilyl)-2-propenyl]styrene [BSAS] / Oxygen Permselective Membrane /

Gas separations through membrane are one of the most attractive fields for industries because of low and clean energy processes, easy to handle, etc.¹ Polydimethylsiloxane (silicone) is known to have one of the highest permeation coefficients for several gases. However, there are several problems for the oxygen permselective membrane such as low mechanical strength and low permselectivity in terms of oxygen against nitrogen, etc. There are several approaches to create new gas separation membranes with high performances such as high permeability coefficients, high permselectivities, and high mechanical strength. Silicon-

containing polymers such as poly(1-trimethylsilylpropyne)², polyfumarates³ and poly(trimethylvinylsilane),⁴ etc. are one of the promising materials.

Our strategies for creation of functional materials are to create new polymers through novel reaction routes, because of such polymers with new structure to have infinite opportunities as materials.

We have been studying on reactivity of lithium dialkylamide with different substituent(s) toward olefinic compounds. In the course of the studies, we found that lithium diisopropylamide (LDA) induced a metalation

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reaction of *p*-methylstyrene to form a *p*-benzylolithium (VBL) without any side reaction (eq 1).⁵ VBL can be regarded as a unique carbanion having reactive vinyl group and can be utilized as an intermediate to synthesize new functional monomers. When organosilyl chloride compound was dropped into the equilibrium system containing VBL, several kinds of silicon-containing styrene derivatives were synthesized.⁶

We investigated further on gas permeation properties of these silicon-containing poly(methylstyrene)s and found that the poly(*p*-methylstyrene)s with trimethylsilyl group(s) showed fairly high oxygen permselectivity against nitrogen ($P_{\text{O}_2}/P_{\text{N}_2}=3.8$) among common vinyl polymers, keeping high permeation coefficients of oxygen ($P_{\text{O}_2}=45$ Barrers; Barrer denotes $10^{-10} \cdot \text{cm}^3$ (STP) $\cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$).⁷ In addition, it was also found that the solubility of oxygen (S_{O_2}) into the membranes tends to increase with increasing the Si-content in the polymer.⁸

If another function can be introduced into such the polymers having high gas permselective properties, an opportunity as materials will be expanded. For this purpose, we chose *p*-allylstyrene (AST) as a starting material for the metalation and the silylation reactions, because the resulting polymer after polymerization should have reactive double bond in each monomeric unit and can be utilized for certain derivatizations or crosslinking reactions. This paper deals with the synthesis of new silicon-containing monomers starting from *p*-allylstyrene (AST) in the same manner as *p*-methylstyrene. The structure-gas permeation relations are also discussed.

EXPERIMENTAL

All procedures in terms of monomer synthesis were carried out under argon atmosphere to eliminate oxygen and moisture.

Materials

Commercial tetrahydrofuran (THF), diisopropylamine (DPA), trimethylsilyl chloride (TMSCl) were purified using conventional methods.⁹ Butyllithium (BuLi) was used as hexane (Hx) solution, the concentration of which was determined by double titration method.¹⁰ *p*-Allylstyrene was synthesized according to the previous paper¹¹ using allyl chloride and *p*-vinylphenylmagnesium chloride.

Synthesis of 4-[(3-Trimethylsilyl)-1-propenyl]-styrene (SAS)

To a stirred THF solution (21.4 ml) of DPA (10 mmol), a Hx solution (3.1 ml) of BuLi (5 mmol) was added to a 100 ml-round bottomed flask at room temperature. After stirring for a few minutes to complete the formation of LDA, the mixture was cooled to -48°C , then AST (5 mmol) was added by using a syringe. The color of the mixture was observed to turn red violet immediately, and then, TMSCl (5.5 mmol) was added into the mixture for silylation. After the reaction for 3 h, the products were analyzed directly by gas chromatography (GC). The low boiling materials were evaporated and then the product was distilled under reduced pressure (bp $78\text{--}80^\circ\text{C}/0.3$ mmHg).

Synthesis of 4-[1,3-Bis(trimethylsilyl)-2-propenyl]styrene (BSAS)

After the lithiated AST was prepared at -50°C in the same manner as stated above ($[\text{LDA}]_0/[\text{DPA}]_0/[\text{AST}]_0=15/5/5$ (mmol) in THF (22.8 ml)), TMSCl (5.5 mmol) was added into a 100 ml round bottomed flask. After the reaction for 2 h, temperature of the mixture was raised up to 0°C , then a THF solution

(6.2 ml) of TMSCl (11 mmol) was dropped slowly into the mixture for 1 h. The mixture was stirred for further 2 h, then, products were analyzed directly by gas chromatography (GC). The purification of the silylated monomer was carried out by fractional distillations after low the boiling materials were evaporated (bp 87–89 °C/0.18 mmHg).

Polymerization Procedure

One of the representative procedures of radical polymerizations of silylated-allylstyrene derivatives is described. 2,2'-Azobisisobutyronitrile (AIBN) (0.012 g, 0.069 mmol) and BSAS (2.0 g, 6.9 mmol) were filled in a glass tube. After sealing off the tube under high vacuum, the mixture was allowed to react at 60 °C for 22 h, then the tube was opened. The polymer obtained was dissolved in THF and then poured into methanol. The precipitates formed were purified by 2-fold successive reprecipitations from THF solution into methanol. The polymer sample collected was subjected to freeze drying with benzene to remove the solvent employed.

Membrane Preparation

A solution of an appropriate solvent such as toluene and benzene containing 5–20 wt% of the polymer was cast on a polytetrafluoroethylene sheet, and the solvent was evaporated for 2–3 days. To measure the gas permeabilities, the polymer membrane was further dried *in vacuo* for 1 day. The thickness of the membrane was in the range of 200–500 μm .

Gas Permeation Measurements

Gas permeation measurements were carried out by means of the apparatus reported in our previous paper⁸ using vacuum method. The permeability coefficients were determined from the slope of the time *vs.* pressure on the permeation side curve (dP/dt) at the steady state.

Measurement

Gas chromatograms were taken with a Shimadzu GC-14A gas chromatograph. For gel permeation chromatography (GPC) measurements, Shimadzu SCL-6A equipped with Shimadzu RID-6A RI detector was used. Number-average molecular weight (M_n) and weight-average molecular weight (M_w) were determined by GPC diagrams using a calibration curve obtained with polystyrene standard samples. GC/MS spectra were obtained using a HP5971A equipped with HEWLET PACKARD 5890 SERIES II gas chromatography. ¹H NMR spectra were observed on a JEOL EX-400 spectrometer at room temperature, using a 5 mm-glass tube containing a solution of the silylated AST sample in CDCl_3 (1.0 g dl^{-1}). Glass transition temperatures of the polymers were determined by using a differential scanning calorimeter (DSC) (Mettler DSC 30) at a heating rate of 10 °C min^{-1} from –100 °C to 200 °C.

RESULTS AND DISCUSSION

Synthesis of Trimethylsilylated *p*-Allylstyrene Derivatives

As stated above lithium diisopropylamide (LDA) induced a metalation reaction of *p*-methylstyrene (MST) at 20 °C to form *p*-vinylbenzyl lithium (VBL) without any side reactions such as an addition and a polymerization reaction (eq 1). It should be noted that toluene was not metalated by LDA under the same conditions, indicating that the para-standing vinyl group plays an important role for a stabilization of the carbanion owing to a 10π -conjugation. If this metalation reaction system can be applied to other styrenic compounds having active hydrogen(s), an opportunity for new synthetic route(s) will be expanded. As an allyl group is well known to carry active hydrogens, metalation of *p*-allylstyrene (AST) by LDA was examined.

When AST was added to the reaction mixture containing LDA at 20 °C, color of the

Figure 1. Gas chromatogram of the products resulting from the silylation reaction of *p*-allylstyrene under the same conditions as shown in Run 1 in Table I. (column: glass capillary DB-1; 30 m $\times$ 0.25 μ m; temp 100–250°C, 10°C min⁻¹; He 100 ml min⁻¹; split ratio 1/100) *: These signals were also identified to be 1- and 3-trimethylsilyl substituted *p*-allylstyrenes estimated by GC/MS spectroscopy.

mixture turned red violet immediately. After the reaction was stopped by adding a small amount of methanol, however, the polymerization product was obtained and almost no AST remained, indicating that AST was metalated by LDA, then the metalated AST attacked monomers to initiate an anionic polymerization of AST at 20°C. To prevent such the polymerization by lithiated AST, the reactions were carried out at low temperature. When the reaction was carried out at -48°C, no polymerization took place at least for a few minutes. When trimethylsilyl chloride (TMSCl) was added to the reaction mixture, a silylation reaction of LiAST proceeded. Figure 1 shows gas chromatogram of the products after the silylation reaction of AST with TMSCl. As can be seen in the figure, several new peaks appeared. From GC/MS analysis shown in Figure 2, the fragmentations can be explained reasonably, considering the products A and B (shown in Figure 1) to be mono- and bis-trimethylsilylated AST, respectively. ¹H NMR also supports the above consideration. Figure 3 shows ¹H NMR spectra of the products A and B after purifications by fractional distillations (bp A, 78–80°C/0.3 mmHg; B, 87–89°C/0.18 mmHg). According to our previous paper,^{6a} doublet signals appearing at 1.73 ppm in Figure

Figure 2. Mass spectra of (a) *p*-(3-trimethylsilyl-1-propenyl)styrene, SAS (the product assignable to peak A in Fig. 1) and (b) *p*-[1,3-bis(trimethylsilyl)-2-propenyl]styrene, BSAS (the product assignable to peak B in Figure 1).

3 (a) were assignable to silylmethylene protons adjacent to olefinic group. In addition, signals appearing at 6.2–6.4 ppm can be attributable to inner olefinic protons but not vinylic protons. From the two results, product A was assignable to *p*-(3-trimethylsilyl-1-propenyl)styrene (SAS). As can be seen in the Figure 3 (b), silylmethine protons between two unsaturated groups were appearing at 3.09 ppm as doublet. If the product B was *p*-[3,3-bis(trimethylsilyl)-1-propenyl]styrene, bis(trimethylsilyl)methine signals adjacent to olefinic protons must appear around 1.6 ppm,^{6a} indicating the product B to be assignable to *p*-[1,3-bis(trimethylsilyl)-2-propenyl]styrene (BSAS).¹² The coupling constants around double bonds in the substituents, $J_{5,6}$ in SAS and $J_{5,7}$ in BSAS, were determined to be 15.6 Hz and 18.5 Hz, respectively, which correspond to *trans*-configuration.¹⁴

On the basis of these results, it is found that AST was metalated by LDA below -40°C to

form *p*-(1-lithioallyl)styrene (LiAST) without polymerization, then LiAST reacted with TMSCl to form SAS. TMSCl was found to attack the γ -position of the allyl group selectively probably owing to the steric factor between trimethylsilyl and *p*-vinylphenyl groups. SAS was also metalated by LDA to

form a carbanion, LiSAS, then, it reacted with TMSCl again to form BSAS shown in eq 2–5. The second trimethylsilylation took place at the α -position of SAS. This way, trimethylsilylation in this reaction governed mainly by the steric factor.

At -48°C , the yields of the SAS and BSAS were 91.7 and 2.9%, respectively. Even when the initial concentration of LDA was increased up to twice as compared to AST, the yield of BSAS was only 9.9%, indicating the metalation reaction of SAS by LDA not to proceed easily below -40°C (Run 1 and 2 in Table I).

To increase the yield of the doubly-trimethylsilylated AST, a silylation of SAS as starting material was examined (Table I, Run 3–6). When the reaction was carried out at -45°C , the yield of BSAS was low as well as that from AST, supporting SAS to be hard to metalate below -40°C .

Since the metalation reaction of SAS at high temperature might not induce any side reactions such as polymerizations owing to low the metalation degree, we examined the metalation reaction by LDA at 0°C . As anticipated, no polymerization took place at 0°C at least for a few minutes. Then, the silylation reactions of LiSAS at 0°C were carried out. As TMSCl can react with LDA at 0°C , TMSCl was dropped slowly into the reaction system to avoid the possible coupling reaction. Our idea was to

Table I. Results on the silylation reaction of *p*-allyl-styrene (AST) derivatives by trimethylsilyl chloride (TMSCl) in the presence of lithium diisopropylamide (LDA) in THF^a

Run	[LDA] ₀ / [AST] ₀	Temp. °C	Silylation time min	Yield in %	
				SAS	BSAS
1	1	-48	180	91.7	2.9
2	2	-40	180	90.1	9.9
3 ^c	1	-45	1320	—	30.2
4 ^{c,d}	1	0	60 ^e	—	59.5
5 ^c	1	0	50 ^e	—	77.7
6 ^c	2	0	25 ^e	—	88.5
7 ^f	3	-50	120 ^g	—	83.6

^a Total amount of the reaction mixture: 25 ml; AST 5 mmol; [LDA]₀ = [DPA]₀; [TMSCl]₀/[DPA]₀ = 1.1.

^b Determined from GC results.

^c SAS was used as a starting material instead of AST.

^d Polymeric materials were obtained (29.3%).

^e TMSCl solution in THF (1.0 mol l^{-1}) was dropped slowly for indicated period.

^f After the first silylation at -50°C , temperature increased to 0°C then the second silylation by TMSCl was carried out. Detailed procedure was shown in the text.

^g The first silylation conditions were described.

Figure 3. 400 MHz ^1H NMR spectra of (a) *p*-(3-trimethylsilyl-1-propenyl)styrene, SAS and (b) *p*-[1,3-bis(trimethylsilyl)-2-propenyl]styrene, BSAS.

maintain the low concentration of TMSCl in the reaction system to proceed coupling between LiSAS and TMSCl predominantly. Note that the reaction between LDA and TMSCl was relatively slower in the reaction of TMSCl with VBL in the presence of LDA .⁶ When TMSCl was dropped for 60 min, the yield of BSAS increased to be 59.5%, though 29% of the polymer was formed owing to the long reaction period. When the dropping time of TMSCl was reduced to 25–50 min, BSAS was obtained in good yield (77–89%) without

any polymeric materials. This way, BSAS was obtained selectively under the appropriate reaction conditions.

Utilizing all knowledge mentioned above, BSAS was synthesized from AST as starting materials in good yield. Namely, in the initial stage of the metalation and the silylation, the reaction was carried out under lower temperature than -40°C to form SAS predominantly. After the formation of SAS , temperature of the mixture was raised up to 0°C , then, TMSCl was dropped into the system for a certain

period. According to the procedure, BSAS was obtained in the yield of 83.6% from AST by one-pot process (Run 7 in Table I).

Radical Polymerizations of Trimethylsilylated *p*-Allylstyrenes

To evaluate a polymerizability of the monomers thus obtained, radical polymerizations of SAS and BSAS were carried out, the results of which are listed in Table II. The bulk polymerizations of SAS and BSAS gave high polymers, which are soluble in several common solvents such as THF, benzene, toluene, etc. It

should be noted that a bulk polymerization of AST under the same conditions gave non-soluble gel owing to crosslinking reactions. The fact indicates that the pendent double bonds in poly(trimethylsilylated AST)s were less reactive against the growing radical attack due to the steric hindrance around the double bond. Actually, the molecular weight of poly(BSAS) thus obtained showed normal mono-modal distributions in GPC pattern shown in Figure 4, though small amount of the high molecular polymer eluted in void volume. On the basis of these results, it is concluded that the organosilicon-containing polystyrenes with the pendent double bonds can easily be obtained starting from *p*-allylstyrenes.

Table II. Radical polymerizations of the silylated *p*-allylstyrenes (AST)^a

Monomer	Time	Yield	$\bar{M}_n \times 10^{-3}$	T_g
	h	%		°C
AST	23	—	Gel formation	—
SAS	28	36 ^b	46	78
BSAS	22	74 ^c	>200	102

^a Bulk polymerization, $[\text{Monomer}]_0/[\text{AIBN}]_0 = 100$; temp = 60°C.

^b Methanol insoluble part.

^c Determined from GPC results.

Figure 4. Gel permeation chromatogram of poly(BSAS) (column: TSK-Gel G4000H8 + G3000H8 + G2500H8; Eluent: THF (98%) + *N,N'*-dimethylbenzylamine (2%), 1 ml min⁻¹).

Properties of Poly(trimethylsilylated AST)s

As membrane formabilities of poly(SAS) and poly(BSAS) were similar to that of polystyrene homologues, the membranes can be easily obtained by casting method from toluene solution. Before measuring the gas permeability of the polymer membrane, the glass transition temperatures (T_g) of the polymers were determined by DSC analysis, the results of which are listed in Table II. We reported previously that an introduction of trimethylsilyl group at para methyl position of poly(*p*-methylstyrene) decreased T_g (93→82°C), owing to a mobility of the trimethylsilylmethyl group.¹⁵ The introduction of the second trimethylsilyl group at the same position as that of the first one, however, increased T_g significantly (82→156°C). In this way, the branching structure at para position of polystyrene plays an important role for the mobility of the polymers. The results obtained in this study also showed the same tendency. Namely, the polymer with para-branching structure [poly(BSAS)] showed higher T_g than that of poly(SAS).

The gas permeation properties of the Si-containing poly(AST)s were examined, the results of which are summarized in Table III. The permeability of oxygen and its permselectivity were also measured.

Table III. Gas permeation coefficients through the silylated AST polymer membranes

Polymer	$P_{O_2}^a$	$P_{N_2}^a$	$\frac{P_{O_2}}{P_{N_2}}$	Si-content in wt %
Poly(SAS) ^b	17	5	3.5	13.0
Poly(BSAS) ^c	26	8	3.3	19.4
Poly(BSMS) ^d	45	12	3.8	21.4

^a Permeation coefficient in $10^{-10} \text{ cm}^3 (\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$.

^b The thickness of the membrane was in 478 μm .

^c The thickness of the membrane was in 217 μm .

^d Poly[4-[bis(trimethylsilyl)methyl]styrene]; ref 8.

tivity against nitrogen through the membrane thus obtained were in the range of 17–26 Barrer and 3.3–3.5, respectively. We reported previously that the solubility of oxygen in the membrane is in proportion to Si-content in the organosilicon-containing polystyrenes.⁸ The lower oxygen permeability of poly(BSAS) and poly(SAS) than that of poly[4-bis(trimethylsilyl)methyl]styrene [poly(BSMS)] may be due to the low Si-contents. Koros, *et al.*, reported that polymers with higher glass transition temperature showed the higher selectivity in diffusion of oxygen against nitrogen (D_{O_2}/D_{N_2}).¹⁶ The low permselectivities of poly(BSAS) and poly(SAS) may be explained by their lower T_g s than that of poly(BSMS).

In conclusion, the organosilicon-containing polymers with reactive double bonds as pendant were synthesized from *p*-allylstyrenes as starting materials. Their oxygen permselectivities against nitrogen were 3.3–3.5, keeping oxygen permeability in the range of 10^0 Barrer order.

Acknowledgments. One of the authors (Y. Nagasaki) would like to express his sincere appreciation to *Izumi Science Technology Foundation* for financial support of a part of this study. A part of this study was also supported financially by a Grant-in-Aid for Development Scientific Research from the Ministry of Education, Science, and Culture of

Japan. (No. 05555252)

REFERENCES AND NOTES

1. E. F. Vansant and R. Dewolfs, "Gas Separation Technology," Elsevier, Amsterdam, 1990.
2. T. Masuda, E. Isobe, T. Higashimura, and K. Takada, *J. Am. Chem. Soc.*, **105**, 7473 (1983).
3. S.-B. Choi, A. Takahara, N. Amaya, Y. Murata, and T. Kajiyama, *Polym. J.*, **21**, 433 (1989).
4. For reviews, see: Yu. P. Yampol'skii and V. V. Volkov, *J. Membrane Sci.*, **64**, 191 (1991).
5. Y. Nagasaki and T. Tsuruta, *Makromol. Chem.*, **187**, 1583 (1986).
6. (a) Y. Nagasaki and T. Tsuruta, *Makromol. Chem., Rapid Commun.*, **7**, 437 (1986); (b) Y. Nagasaki, K. Kurosawa, and T. Tsuruta, *Bull. Chem. Soc., Jpn.*, **63**, 3036 (1990).
7. Y. Nagasaki, M. Suda, T. Tsuruta, K. Ishihara, and Y. Nagase, *Makromol. Chem., Rapid Commun.*, **10**, 255 (1989).
8. Y. Nagasaki, K. Kurosawa, M. Suda, S. Takahashi, T. Tsuruta, K. Ishihara, and Y. Nagase, *Makromol. Chem.*, **191**, 2103 (1990).
9. D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, *Purification of Laboratory Chemicals*, 1966.
10. H. Gilman and A. H. Haubeim, *J. Am. Chem. Soc.*, **69**, 2609 (1947).
11. G. Greber and G. Engle, *Makromol. Chem.*, **54**, 122 (1962).
12. SAS: ^1H NMR (CDCl_3): δ 0.12 (9H, s, H-1), δ 1.73 (2H, $J_{2,6}=6.9 \text{ Hz}$, d, H-2), δ 5.24 (1H, $J_{3,7}=10.8 \text{ Hz}$, d, H-3), δ 5.76 (1H, $J_{4,7}=17.6 \text{ Hz}$, d, H-4), δ 6.26 (1H, $J_{5,6}=15.6 \text{ Hz}$, d, H-5), δ 6.32 (1H, $J_{6,2}=6.9 \text{ Hz}$, $J_{6,5}=15.6 \text{ Hz}$, q, H-6), δ 6.74 (1H, $J_{7,3}=10.8 \text{ Hz}$, $J_{7,4}=17.6 \text{ Hz}$, q, H-7), δ 7.32 (2H, $J_{8,9}=8.3 \text{ Hz}$, d, H-8), δ 7.38 (2H, $J_{9,8}=8.3 \text{ Hz}$, d, H-9)

SAS

BSAS: ^1H NMR (CDCl_3): δ 0.02 (9H, s, H-1),¹³ δ 0.13 (9H, s, H-2),¹³ δ 3.09 (1H, $J_{3,7}=9.3 \text{ Hz}$, d, H-3), δ 5.22 (1H, $J_{4,8}=10.7 \text{ Hz}$, d, H-4), δ 5.63 (1H, $J_{5,7}=18.5 \text{ Hz}$; d, H-5), δ 5.74 (1H, $J_{6,8}=17.6 \text{ Hz}$, d, H-6), δ 6.40 (1H, $J_{7,3}=9.3 \text{ Hz}$, $J_{7,5}=18.5 \text{ Hz}$, q, H-7), δ 6.74 (1H, $J_{8,4}=10.7 \text{ Hz}$, $J_{8,6}=17.6 \text{ Hz}$, q, H-8), δ 7.11 (2H, $J_{9,10}=6.8 \text{ Hz}$, d, H-9), δ 7.38 (2H, $J_{10,9}=6.8 \text{ Hz}$, d, H-10).

13. Assignments of the silylmethyl protons, H-1 and H-2, were carried out using trimethylvinylsilane and

4-(trimethylsilylmethyl)styrene as reference compounds.

14. F. L. Boschke, W. Fresenius, J. F. K. Huber, E. Pungor, G. A. Rochnitz, W. Simon, and Th. S. West, Ed., "Tables of Spectral Data for Structure Determination of Organic Compounds," Springer-Verlag, Berlin, 1983.
15. N. Kato, K. Takeda, Y. Nagasaki, and M. Kato, *Ind. Eng. Chem. Res.*, in press.
16. T. H. Kim, W. J. Koros, G. R. Husk, and K. C. Obrien, *J. Membrane Sci.*, **37**, 45 (1988).