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# Synthesis, Characterization, and Gas Permeation Properties of Silylated Derivatives of Ethyl Cellulose

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ABSTRACT: Silyl ethers of ethyl cellulose (**2a**−**f**) were synthesized in good yields by the reaction of various chlorosilanes with residual hydroxy groups of ethyl cellulose. $^1$H NMR and FTIR spectra of the silylated polymers furnished the evidence for complete substitution of hydroxy protons by the silyl groups. Silylated derivatives of ethyl cellulose (**2a**−**f**) were soluble in common organic solvents and displayed enhanced solubility in relatively nonpolar solvents due to the substitution of hydroxy groups. The onset temperatures of weight loss of the silylated derivatives (**2a**−**f**) in air were higher than 270 °C, indicating fair thermal stability. Free-standing membranes of **1** and **2a**−**f** were fabricated by casting their toluene solution, and all the silylated derivatives (**2a**−**f**) exhibited enhanced gas permeability ($P$) as compared to that of ethyl cellulose (**1**). An increment in the size of the silyl group led to the decrement in gas permeability of the polymers, and trimethylsilyl derivative (**2a**) exhibited the highest $P$ value. The $P_{CO_2}/P_{N_2}$ permselectivity values of the polymers (**2a**−**f**) were observed to be in the range of 15−19. The data for **2a**, **2b**, and **2c** were located above Robeson's upper bound, in the plot of permselectivity vs permeability for the CO$_2$/N$_2$ gas pair ($P_{CO_2}$ vs $P_{CO_2}/P_{N_2}$). Gas diffusion coefficients ($D$) increased upon silylation for all the six gases under study, while gas solubility coefficients ($S$) underwent a decline.

## Introduction

Polymeric gas separation membranes have engrossed substantial prominence, contributing to sustainable chemical processing in the past two decades, and are being exploited in a wide array of commercial applications.[1] At present, a variety of gas mixtures of industrial interest are being separated by the selective permeation of the components through nonporous membranes made of glassy polymers such as polyacetylenes, polyimides, and polysulfones.[2] Among them, silylated polyacetylenes are a class of highly gas-permeable glassy materials as they possess many microvoids in the polymer matrix due to their stiff main chain composed of alternating double bonds and the steric effect of the spherical pendant groups.[1b,3] One of them, poly(1-trimethylsilyl-1-propyne) [poly(TMSP)], is the most gas-permeable material, and many studies concerning the gas permeation properties of this polymer have been reported until today.[1b,4] Most of poly(1-aryl-2-phenylacetylenes) having spherical substituents on the phenyl moiety also exhibit high gas permeability.[3a,5] For instance, the oxygen permeability coefficient ($P_{O_2}$) of poly[1-phenyl-2-(*p*-trimethylsilyl)phenylacetylene] [poly(TMSDPA)] is 1500 barrers,[5a] which is quite high among all the synthetic polymers. However, there remains a strong need to develop high-flux membranes with high selectivity and fouling-resistant properties for large-scale applications. Physical or chemical modification of polymers is an attractive alternative to tailor the gas permeability and permselectivity of membrane-forming materials, as desired for specific applications.

Ethyl cellulose is derived from an inexhaustible natural polymeric material, cellulose, and possesses the fascinating structure and properties such as extensive linearity, chain stiffness, good solubility in organic solvents, adequate membrane-forming ability, moderate gas permeation/pervaporation capability, excellent durability, good flexibility, chemical resistance, mechanical strength, hydrophobicity, nontoxicity, and low cost.[6] Ethyl cellulose has been the subject of research activity for oxygen enrichment for several years;[7] however, only a few studies concerning the systematic investigation of gas/vapor transport through ethyl cellulose membranes have been reported.[8] Despite the fact that the carbon dioxide permeability exhibited by ethyl cellulose ($P_{CO_2} \sim 110$ barrers) is not as high as those of silylated polyacetylenes, the carbon dioxide/nitrogen permselectivity ($P_{CO_2}/P_{N_2} \sim 22$) is fairly high.[7f] Since silyl groups often favor high gas permeability,[1b,3−5] silylated derivatives of ethyl cellulose are expected to be interesting candidates for gas separation membranes.

The present study deals with the synthesis of various silyl ethers of ethyl cellulose (**2a**−**f**), their characterization, and elucidation of various properties. Free-standing membranes of the silylated polymers were fabricated, and their densities, fractional free volume, and gas permeability parameters were determined. Moreover, the diffusion and solubility coefficients of polymer membranes for O$_2$, N$_2$, CO$_2$, and CH$_4$ were also revealed.

## Experimental Section

**Instruments.** The number- and weight-average molecular weights ($M_n$ and $M_w$, respectively) and polydispersity indices ($M_w/M_n$) of polymers were measured by GPC at 40 °C with a Jasco PU-980/RI-930 chromatograph (eluent THF, columns KF-805 (Shodex) × 3, molecular weight range up to 4 × 10$^6$, flow rate 1 mL/min, calibrated with polystyrene standards). $^1$H NMR spectra were recorded on a JEOL EX-400 spectrometer. Infrared spectra were recorded on a Jasco FTIR-4100 spectrophotometer. Thermogravimetric analyses (TGA) were conducted in air with a Perkin-Elmer

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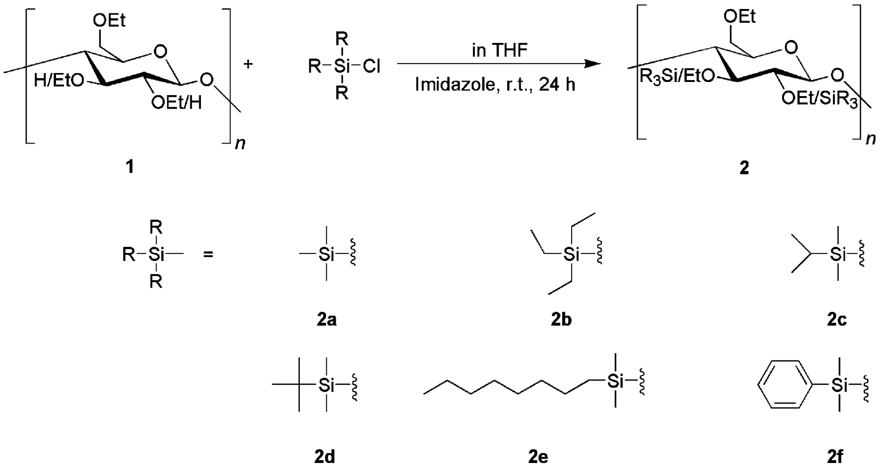
Scheme 1. Silylation of Ethyl Cellulose with Various Chlorosilanes



TGA7 thermal analyzer. Gas permeability coefficients were measured with a Rikaseiki K-315-N gas permeability apparatus at 25 °C.

**Materials.** Ethyl cellulose (ethoxy content, 48 wt %) and imidazole were purchased from Aldrich and Wako (Japan), respectively, and used as received. Chlorotrimethylsilane, chlorotriethylsilane, chlorodimethylisopropylsilane, chlorodimethyl-*n*-octylsilane, chlorodimethylphenylsilane (Tokyo Kasei, Japan), and chloro-*tert*-butyldimethylsilane (Aldrich) were obtained commercially and used without further purification. Tetrahydrofuran, used as reaction solvent, was purchased from Wako (Japan) and employed after distillation.

Silylated derivatives of ethyl cellulose (**2a**−**f**) were synthesized according to Scheme 1. The details of the synthetic procedure and analytical data are as follows:

**Trimethylsilyl Derivative of Ethyl Cellulose (2a).** A 200 mL one-necked flask was equipped with a dropping funnel, a three-way stopcock, and a magnetic stirring bar. Ethyl cellulose (1.43 g, 6.10 mmol) and imidazole (2.49 g, 36.6 mmol) were placed in the flask, evacuated for half an hour, flushed with nitrogen, and dissolved in THF (50 mL) at room temperature. Then, chlorotrimethylsilane (2.31 mL, 18.3 mmol) was added dropwise, and stirring was continued for 24 h at room temperature. Product was isolated by precipitation in methanol (1000 mL), filtered with a membrane filter, washed repeatedly with methanol and acetone successively, and dried under vacuum to constant weight to afford the desired product (89%) as white solid. IR (ATR, $cm^{-1}$): 2972, 2870, 1375, 1249, 1088, 1049, 879, 842. $^1H$ NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 4.31−3.00 (m, 12.4H, $OCH_2CH_3$, OCH, $OCH_2$), 1.12 (brs, 8.07H, $OCH_2CH_3$), 0.094 (s, 2.79H, $SiCH_3$).

**Triethylsilyl Derivative of Ethyl Cellulose (2b).** This derivative was prepared by following the same procedure as for **2a** using chlorotriethylsilane instead of chlorotrimethylsilane. Yield 92%, white solid. IR (ATR, $cm^{-1}$): 2977, 2873, 1375, 1090, 1050, 819, 738. $^1H$ NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 4.30−2.89 (m, 12.4H, $OCH_2CH_3$, OCH, $OCH_2$), 1.12 (brs, 8.07H, $OCH_2CH_3$), 0.93 (brs, 2.79H, $SiCH_2CH_3$), 0.64 (brs, 1.86H, $SiCH_2CH_3$).

**Dimethylisopropylsilyl Derivative of Ethyl Cellulose (2c).** This derivative was prepared by following the same procedure as for **2a** using chlorodimethylisopropylsilane instead of chlorotrimethylsilane. Yield 90%, white solid. IR (ATR, $cm^{-1}$): 2972, 2867, 1374, 1253, 1089, 1050, 922, 850, 829, 802, 777. $^1H$ NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 4.30−2.98 (m, 12.4H, $OCH_2CH_3$, OCH, $OCH_2$), 1.12 (brs, 8.07H, $OCH_2CH_3$), 0.92 (brs, 1.86H, $SiCH(CH_3)_2$), 0.05 (brs, 2.17H, $SiCH_3$, $SiCH(CH_3)_2$).

**Dimethyl-*tert*-butylsilyl Derivative of Ethyl Cellulose (2d).** This derivative was prepared by following the same procedure as for **2a** using chlorodimethyl-*tert*-butylsilane instead of chlorotrimethylsilane, and precipitation was carried out using water in place of methanol. Yield 88%, white solid. IR (ATR, $cm^{-1}$): 2974, 2868, 1375, 1092, 1056, 1000, 839. $^1H$ NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 4.30−3.00 (m, 12.4H, $OCH_2CH_3$, OCH, $OCH_2$), 1.13 (brs, 8.07H, $OCH_2CH_3$), 0.85 (brs, 2.79H, $SiC(CH_3)_3$), 0.05 (brs, 1.86H, $SiCH_3$).

**Dimethyl-*n*-octylsilyl Derivative of Ethyl Cellulose (2e).** This derivative was prepared by following the same procedure as for **2a** using chlorodimethyl-*n*-octylsilane instead of chlorotrimethylsilane. Yield 92%, white solid. IR (ATR, $cm^{-1}$): 2971, 2922, 1375, 1089, 1050, 922, 839. $^1H$ NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 4.31−2.89 (m, 12.4H, $OCH_2CH_3$, OCH, $OCH_2$), 1.24 (brs, 3.72H, $CH_2(CH_2)_6$), 1.12 (brs, 8.07H, $OCH_2CH_3$), 0.86 (t, 0.93H, $CH_2CH_3$), 0.6 (brs, 0.62H, $SiCH_2$), 0.08 (s, 1.86H, $SiCH_3$).

**Dimethylphenylsilyl Derivative of Ethyl Cellulose (2f).** This derivative was prepared by following the same procedure as for **2a** using chlorodimethylphenylsilane instead of chlorotrimethylsilane. Yield 87%, white solid. IR (ATR, $cm^{-1}$): 2972, 2870, 1443, 1428, 1375, 1251, 923, 855, 830, 787, 741, 700. $^1H$ NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 7.61−7.24 (m, 1.55H, $SiC_6H_5$), 4.25−2.98 (m, 12.4H, $OCH_2CH_3$, OCH, $OCH_2$), 1.12 (brs, 8.07H, $OCH_2CH_3$), 0.39 (s, 1.86H, $SiCH_3$).

**Determination of Degree of Substitution.** The degree of substitution with the ethyl group ($DS_{Et}$) of the starting material, ethyl cellulose, and the degree of substitution with the silyl group ($DS_{Si}$) of the silylated derivatives (**2a**−**f**) were determined by $^1H$ NMR (Figure 1). The total degree of substitution ($DS_{total}$) of **2a**−**f**

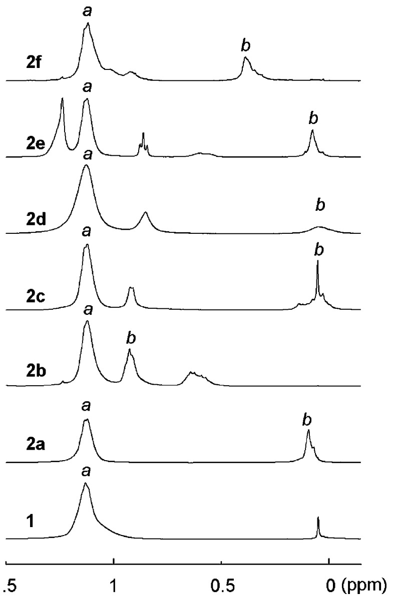


**Figure 1.** $^1H$ NMR spectra of polymers **1** and **2a**−**f** in $CDCl_3$ at 25 °C.

**Table 1. Degree of Substitution and GPC Data of Polymers 1 and 2a−f**

| polymer | $DS_{Si}$[a] | $DS_{total}$[a] | $M_n$[b] | $M_w/M_n$[b] |
|---|---|---|---|---|
| **1** | 0.00 | 2.69 | 195 000 | 3.46 |
| **2a** | 0.32 | 3.01 | 187 000 | 2.26 |
| **2b** | 0.31 | 3.00 | 237 000 | 2.90 |
| **2c** | 0.33 | 3.02 | 289 000 | 4.24 |
| **2d** | 0.31 | 3.00 | 206 000 | 3.11 |
| **2e** | 0.34 | 3.03 | 264 000 | 2.20 |
| **2f** | 0.38 | 3.07 | 168 000 | 2.59 |

[a] $DS_{Si}$ = degree of silylation; $DS_{total}$ = total degree of substitution. Calculated from $^1H$ NMR. [b] Determined by GPC (THF, PSt).

was calculated by the following equation:

$$DS_{total} = DS_{Et} + DS_{Si}$$

**Membrane Fabrication.** Membranes (thickness ca. 40−80 $\mu$m) of polymers **1** and **2a−f** were fabricated by casting their toluene solution (concentration ca. 0.50−1.0 wt %) onto a Petri dish. The dish was covered by a glass vessel to retard the rate of solvent evaporation (3−5 days).

**Membrane Density.** Membrane densities ($\rho$) were determined by hydrostatic weighing using a Mettler Toledo balance (model AG204, Switzerland) and a density determination kit.[9] This method makes use of a liquid with known density ($\rho_0$), and membrane density ($\rho$) is calculated by the following equation:

$$\rho = \rho_0 M_A/(M_A - M_L)$$

where $M_A$ is the weight of membrane in air and $M_L$ is that in the auxiliary liquid. Aqueous $NaNO_3$ solution was used as an auxiliary liquid.

**Fractional Free Volume (FFV) of Polymer Membranes.** FFV ($cm^3$ of free volume/$cm^3$ of polymer) is commonly used to estimate the efficiency of chain packing and the amount of space (free volume) available for gas permeation in the polymer matrix. FFV is calculated by the following equation:[10]

$$FFV = (\upsilon_{sp} - \upsilon_0)/\upsilon_{sp} \approx (\upsilon_{sp} - 1.3\ \upsilon_w)/\upsilon_{sp}$$

where $\upsilon_{sp}$ and $\upsilon_0$ are the specific volume and occupied volume (or zero-point volume at 0 K) of the polymer, respectively. Typically, occupied volume ($\upsilon_0$) is estimated as 3 times the van der Waals volume ($\upsilon_w$), which is calculated by the group contribution methods.[11]

**Measurement of Gas Permeation Parameters.** The $P$ values were calculated from the slopes of time−pressure curves in the steady state where Fick's law holds.[12] The $D$ values were determined by the time lag method using the following equation:

$$D = l^2/6\theta$$

Here, $l$ is the membrane thickness and $\theta$ is the time lag, which is given by the intercept of the asymptotic line of the time−pressure curve to the time axis. The membrane thickness was controlled so that the time lag would be in the range 10−300 s, preferably 30−150 s. When the time lag was <10 s, the error of measurement became relatively large. If the time lag was, on the contrary, >300 s, the error based on baseline drift became serious. The $S$ values were calculated by using the equation $S = P/D$.

## Results and Discussion

**Silylation of Ethyl Cellulose.** Silylation of ethyl cellulose was carried out by using various chlorosilanes as silylating agents, THF as a solvent, and imidazole as a base, as shown in Scheme 1, and the results are summarized in Table 1. The $DS_{Et}$ of ethyl cellulose was estimated to be 2.69, by calculating the integration ratio of methyl protons (labeled as $a$, in Figure 1) to the rest of the protons in ethyl cellulose, indicating the presence of 0.31 hydroxy groups per anhydroglucose unit of ethyl cellulose. Degrees of silylation ($DS_{Si}$) of **2a−f** were determined by calculating the integration ratio of the methyl protons of ethyl (labeled as $a$, in Figure 1) to those of silyl content (labeled as $b$, in Figure 1), and complete silylation of the residual hydroxy groups of ethyl cellulose was observed. IR spectra of polymers **2a−f** (as exemplified in Figure 2) furnished further evidence of complete substitution due to the presence of the peaks characteristic of the silyl group (1375−1425 $cm^{-1}$, 775−850 $cm^{-1}$) and the absence of the broad peak characteristic of the hydroxy group (3200−3600 $cm^{-1}$). According to GPC data of the polymers (Table 1), number-average molecular weights ($M_n$) and polydispersity indices ($M_w/M_n$) were not quite different from those of **1**. For instance, the $M_n$ and $M_w/M_n$ of **1** were observed to be 195 000 and 3.46, while those of **2a** were 187 000 and 2.26, respectively. These facts rule out any sort of polymer chain cleavage in the course of silylation.

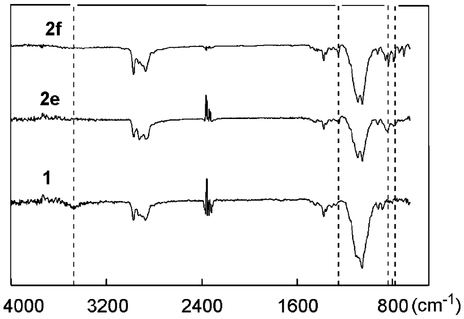


**Figure 2.** ATR-FTIR spectra of polymers **1**, **2e**, and **2f**.

**Table 2. Solubility[a] of Polymers 1 and 2a−f**

| | polymer | | | | | | |
|---|---|---|---|---|---|---|---|
| | **1** | **2a** | **2b** | **2c** | **2d** | **2e** | **2f** |
| hexane | − | + | + | + | ± | + | + |
| toluene | + | + | + | + | + | + | + |
| $CHCl_3$ | + | + | + | + | + | + | + |
| THF | + | + | + | + | + | + | + |
| acetone | − | − | − | − | + | − | + |
| methanol | + | − | − | − | ± | − | − |
| DMF | + | − | ± | ± | ± | ± | − |

[a] Symbols: +, soluble; ±, partly soluble; −, insoluble.

**Solubility and Thermal Stability of Polymers.** The solubility properties of polymers **1** and **2a−f** are summarized in Table 2. The silylated ethyl cellulose derivatives (**2a−f**) displayed enhanced solubility in nonpolar solvents. Ethyl cellulose (**1**) was soluble in DMF, while its silylated derivatives were either insoluble or partly soluble. Similarly, **1** exhibited solubility in methanol, while its silylated derivatives were insoluble except **2d** which was partly soluble. On the other hand, all of the silylated polymers were soluble (**2d** was partly soluble) in hexane, a nonpolar solvent, while ethyl cellulose was insoluble. This augmented nonpolar character of silylated derivatives of ethyl cellulose finds its explanation in the less polar character of siloxy groups as compared to the hydroxy groups present in ethyl cellulose.

The thermal stability of polymers **1** and **2a−f** was examined by thermogravimetric analysis (TGA) in air (Figure 3). The onset temperatures of weight loss ($T_0$) of **2a−d** were in the range 280−300 °C (Table 3). As the bulk of the silyl group increased, the onset temperature of weight loss became higher. The $T_0$ value of **2e** was lower than the rest owing to the presence of the silyl group having longer alkyl chain. Polymer **2f** displayed the highest thermal stability among **2a−f**, probably imparted by the phenyl moiety in the silyl group. These results imply

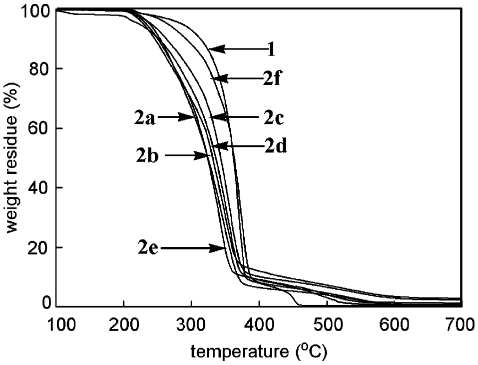


**Figure 3.** TGA curves of polymers **1** and **2a**−**f** (in air, heating rate 10 °C min$^{-1}$).

**Table 3. Physical Properties of Polymers 1 and 2a−f**

| polymer | $T_0$[a] (°C) | $\upsilon_w$[b] (cm$^3$/mol) | $\rho$[c] (g/cm$^3$) | FFV[d] |
|---|---|---|---|---|
| **1** | 338 | 135.8 | 1.095 | 0.185 |
| **2a** | 280 | 152.1 | 1.076 | 0.180 |
| **2b** | 283 | 162.1 | 1.065 | 0.177 |
| **2c** | 305 | 159.0 | 1.067 | 0.178 |
| **2d** | 298 | 162.1 | 1.083 | 0.163 |
| **2e** | 273 | 183.8 | 1.034 | 0.148 |
| **2f** | 338 | 162.6 | 1.091 | 0.173 |

[a] Onset temperature of weight loss observed from TGA measurement in air. [b] $\upsilon_w$ = van der Waals volume. [c] $\rho$ = density. Determined by hydrostatic weighing. [d] FFV = fractional free volume. Estimated from membrane density.

**Table 4. Gas Permeability Coefficients[a] ($P$) of Polymer Membranes at 25 °C**

| | *P* | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| polymer | He | $H_2$ | $O_2$ | $N_2$ | $CO_2$ | $CH_4$ | $P_{CO_2}/P_{N_2}$ | $P_{CO_2}/P_{CH_4}$ |
| **1** | 53 | 76 | 18 | 5.0 | 110 | 12 | 22 | 9.2 |
| **2a** | 98 | 160 | 45 | 14 | 250 | 35 | 18 | 7.1 |
| **2b** | 81 | 130 | 42 | 13 | 230 | 33 | 18 | 7.0 |
| **2c** | 82 | 130 | 40 | 13 | 230 | 31 | 18 | 7.4 |
| **2d** | 67 | 100 | 27 | 8.0 | 150 | 18 | 19 | 8.3 |
| **2e** | 65 | 98 | 31 | 10 | 150 | 25 | 15 | 6.0 |
| **2f** | 58 | 86 | 23 | 7.0 | 130 | 15 | 19 | 8.7 |

[a] In units of barrers (1 barrer = 1 × $10^{-10}$ cm$^3$ (STP) cm cm$^{-2}$ s$^{-1}$ cmHg$^{-1}$).

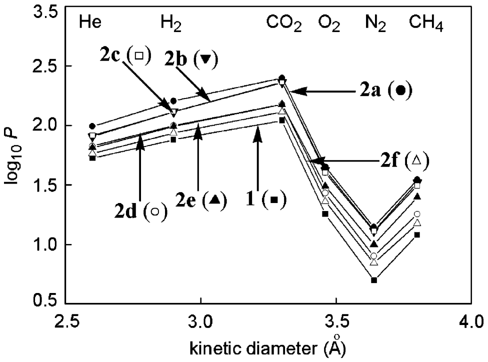


**Figure 4.** Gas permeability coefficients ($\log_{10} P$) of ethyl cellulose (**1**) and its silylated derivatives (**2a**−**f**) vs kinetic diameter of gases.

that the thermal stability increases with increase in the stiffness of the silyl substituent and undergoes a decrease as the length of the alkyl chain in the silyl group increases. Although the thermal stability of the silylated derivatives of ethyl cellulose (**2a**−**f**), except **2f**, is slightly lower than that of the starting material (**1**), it is still appreciably reasonable for practical applications as membrane-forming materials.

**Density and FFV of Polymer Membranes.** Table 3 lists the van der Waals volumes ($\upsilon_w$), densities ($\rho$), and fractional free volumes (FFV) of the polymer membranes (**1** and **2a**−**f**). All of the silylated derivatives (**2a**−**f**) exhibited lower values of membrane density as compared to ethyl cellulose (**1**); e.g., the $\rho$ value of **1** was observed to be 1.095, while those of **2a**−**f** were in the range of 1.034−1.091. It was observed that an increase in the length of the alkyl chain in the silyl group led to a decrease in the density of the polymer membranes. Although silylation of ethyl cellulose resulted in the decreased density of polymer membranes, this decrease was counterbalanced by the increased van der Waals volumes of the silylated derivatives and resulted in net decrease in the FFV values of **2a**−**f** as compared to the starting polymer membrane (**1**). For instance, **2e** exhibited the lowest value for fractional free volume (FFV is 0.148) despite its lowest density among all the silylated derivatives of ethyl cellulose ($\rho$ is 1.034), which is probably due to its highest van der Waals volume.

**Gas Permeation Properties.** The permeability coefficients of the membranes of polymers **1** and **2a**−**f** to various gases measured at 25 °C are listed in Table 4, and their plot vs kinetic diameter of the gases is shown in Figure 4. The gas permeability of the silylated derivatives was higher than that of ethyl cellulose and approximately obeys the following order: **2a** > **2b** ≈ **2c** > **2d** > **2e** > **2f** > **1**. The order of the gas permeability coefficients corresponds to the shape, size, and mobility of the silyl substituents. It has been reported that the increase in the bulk or the length of the alkyl group in the silyl moiety accompanies a decrease in the gas permeability; e.g., the $P_{O_2}$ value of poly(TMSDPA) is 1500 barrers,[5a] while those of poly[1-phenyl-2-(*p*-triisopropylsilyl)phenylacetylene] and poly[1-phenyl-2-(*p*-triphenylsilyl)phenylacetylene] are 20 and 3.8 barrers, respectively.[13]

Among all the silylated derivatives of ethyl cellulose (**2a**−**f**), **2a** exhibited the highest permeability to various gases, and this trend bears a resemblance to that observed in the case of silylated polyacetylenes. This tendency has been explained in terms of the finding that the trimethylsilyl group effectively generates many molecular-scale voids and simultaneously exhibits large local mobility.[14] For instance, the $P_{O_2}$ value of poly(TMSP) is 10 000 barrers, while that of poly(1-triethylsilyl-1-propyne) is no more than 640 barrers.[15] The lowest gas permeability has been observed in the case of polymer **2f**, and it can be explained in terms of the planar and nonflexible nature of the aryl group present in the silyl moiety, thus leading to the stacking and decreased local mobility of the substituent.

The most important feature of the gas permeability data of ethyl cellulose and its silylated derivatives is relatively high $P_{CO_2}/P_{N_2}$ selectivity (>15) of these polymers. Especially, **2a**−**c** displayed good perforamance for $CO_2$ separation, and their data were located above Robeson's upper bound[16] in the plot of permselectivity vs permeability for the $CO_2/N_2$ gas pair (Figure 5). However, as the value of gas permeability undergoes an increase, a decrease in permselectivity is observed. These results imply that spherical substituents with appropriate size are required to achieve high gas permeability rather than planar and bulky groups, and those having long alkyl chains.

**Gas Diffusivity and Solubility.** Gas permeability can be expressed as the product of gas solubility in the upstream face of the membrane and effective average gas diffusion coefficient in the membrane, strictly in rubbery polymers and approximately in glassy polymers:[1a,17]

$$P = SD$$

To carry out a detailed investigation of the gas permeability of **1** and **2a**−**f**, gas diffusion coefficients ($D$) and gas solubility

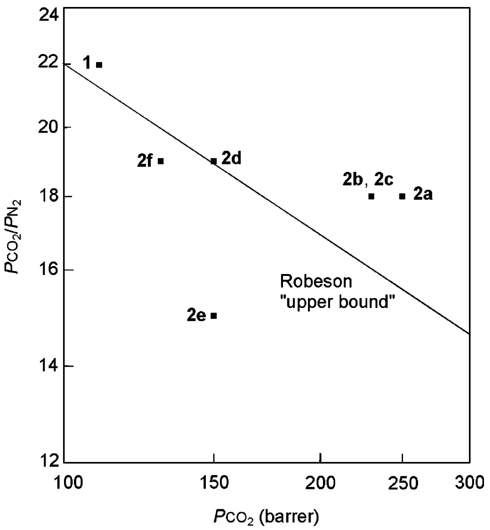


**Figure 5.** Plot of permselectivity vs permeability for the $CO_2/N_2$ gas pair.

**Table 5. Gas Diffusion Coefficients[a] (*D*) of the Polymer Membranes**

| | $10^7D$ ($cm^2\ s^{-1}$) | | | |
|---|---|---|---|---|
| | $O_2$ | $N_2$ | $CO_2$ | $CH_4$ |
| critical volume ($cm^3$/mol) | 73.4 | 89.8 | 93.9 | 99.2 |
| **1** | 8.3 | 3.8 | 2.6 | 1.8 |
| **2a** | 19 | 13 | 7.6 | 5.0 |
| **2b** | 30 | 21 | 8.5 | 5.4 |
| **2c** | 27 | 18 | 7.3 | 4.5 |
| **2d** | 16 | 8.0 | 4.7 | 3.1 |
| **2e** | 38 | 18 | 10 | 7.0 |
| **2f** | 16 | 9.5 | 5.3 | 3.0 |

[a] Determined by the "time lag" method at 25 °C.

**Table 6. Gas Solubility Coefficients[a] (*S*) of the Polymer Membranes**

| | $10^3S$ ($cm^3$ (STP) $cm^{-3}\ cmHg^{-1}$) | | | |
|---|---|---|---|---|
| | $N_2$ | $O_2$ | $CH_4$ | $CO_2$ |
| critical temp (K) | 126.2 | 154.8 | 191.0 | 304.1 |
| **1** | 1.4 | 2.2 | 6.5 | 45 |
| **2a** | 1.1 | 2.3 | 6.1 | 33 |
| **2b** | 0.64 | 1.4 | 6.2 | 27 |
| **2c** | 0.79 | 1.6 | 6.7 | 31 |
| **2d** | 0.96 | 1.6 | 5.7 | 33 |
| **2e** | 0.58 | 0.8 | 3.5 | 15 |
| **2f** | 0.68 | 1.4 | 4.7 | 24 |

[a] Calculated by using quotients, *P*/*D*.

coefficients (*S*) were determined. The *D* and *S* values of polymers **1** and **2a**−**f** for $O_2$, $N_2$, $CO_2$, and $CH_4$ are given in Tables 5 and 6, respectively. In the case of polymeric membranes, generally the *D* value undergoes a decrease with increasing critical volume of gases, while the *S* value experiences an increase with increasing critical temperature of gases. Similar tendencies were observed in the *D* and *S* values of the polymer membranes of ethyl cellulose and its silylated derivatives; e.g., in the case of **2a**, the diffusivity of $CH_4$ (5.0) was the lowest and that of $O_2$ (19) was the highest, while $CO_2$ (33) displayed the highest solubility and $N_2$ (1.1) the lowest.

As shown in Table 5, the diffusion coefficients of all the gases increased upon silylation. For instance, **1** diplayed the $D_{O_2}$ value of 8.3, while those of **2a**−**f** were in the range of 16−38. The increment of gas diffusivity can be accounted for by the increase in the local mobility of the substituents.[14]

As far as the gas solubility coefficients are concerned, a decrease in the *S* value was observed in almost all of the silylated derivatives as compared to ethyl cellulose itself, as shown in Table 6. The decrement in the *S* values finds its explanation in the decreased FFV values for all the silylated derivatives (**2a**−**f**) as compared to ethyl cellulose (**1**), as summarized in Table 3. Quite interestingly, in the case of $CO_2$, the *S* values underwent a relatively large decline, in comparison with all the other gases under study; e.g., the *S* values of $CO_2$ and $CH_4$ for **1** were discerned to be 45 and 6.5, respectively, while those for **2a** were 33 and 6.1, respectively. Such behavior can be explained in terms of the strong interaction of $CO_2$ with the hydroxy groups present in ethyl cellulose prior to silylation. A similar effect has been observed in the case of poly(diphenylacetylene) membranes bearing hydroxy group in their side chain.[18]

Among **2a**−**f**, **2e** exhibited the highest *D* value for all the gases, while its *S* value was the lowest, suggesting no increase in FFV but enhanced local mobility due to the presence of the silyl substituent with long alkyl chain, leading to the increased diffusion coefficient. Similar trends have been observed in various substituted polyacetylenes.[12] It is noteworthy that the increase in the diffusion coefficients upon silylation was more pronounced than the decrease in the solubility coefficients, thus leading to the net effect of enhanced permeability. Furthermore, these results indicate the significance of silyl groups to enhance the gas permeability by increasing the gas diffusion coefficients of the polymer membranes.

## Conclusions

The present study is concerned with the synthesis of novel silyl ethers of ethyl cellulose (**2a**−**f**). It was demonstrated that halosilanes served as excellent silylating agents, in the presence of imidazole, which accomplished the complete silylation of ethyl cellulose even at room temperature without any chain degradation of the starting material. All of the silylated polymers (**2a**−**f**) displayed good solubility in common organic solvents, fair thermal stability, and adequate membrane-forming ability. Membranes of **2a**−**f** exhibited higher gas permeability than that of **1** due to the increased diffusion coefficients resulting from the introduction of silyl moiety in ethyl cellulose. Although silylation could not affect a very large increase in gas flux, probably due to a very small extent of hydroxy groups (0.31 per anhydroglucose unit) available for derivitization yet good separation performance for $CO_2/N_2$ and $CO_2/CH_4$ was discerned.

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