Perfluoroacylated Ethyl Cellulose: Synthesis, Characterization, and Gas Permeation Properties

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ABSTRACT: Perfluoroacylated derivatives of ethyl cellulose [R = CF_3CO (**2a**), C_2F_5CO (**2b**), C_3F_7CO (**2c**), $C_7F_{15}CO$ (**2d**), C_6F_5CO (**2e**)] were synthesized in good yields by the reaction of various perfluoroacylating agents with residual hydroxy groups of ethyl cellulose (**1**; DS_{Et}, 2.69). FTIR spectra of the resulting polymers **2a**−**d** furnished the evidence for complete substitution of hydroxy protons by the perfluoroacyl groups. All the derivatives (**2a**−**e**) were soluble in common organic solvents and displayed enhanced solubility in moderately polar aprotic and nonpolar solvents. The onset temperatures of weight loss of **2a**−**d** in air were higher than 270 °C, indicating fair thermal stability. Free-standing membranes of **1** and **2a**−**e** were fabricated, and **2a**−**d** exhibited large contact angle with water and enhanced gas permeability (P) as compared to **1**. An optimum increment in the size of the perfluoroacyl group led to the largest increment in the gas permeability of the polymers; i.e., **2c** exhibited the highest P values (e.g., P_{CO_2} 284 barrers; cf. P_{CO_2} of **1** 110 barrers). The P_{CO_2}/P_{N_2} and P_{CO_2}/P_{CH_4} permselectivity values of the polymers (**2a**−**e**) were in the range of 14−22 and 8−11, respectively.

Introduction

Cellulose, an inexhaustible natural polymeric material, endowed with a polyfunctional macromolecular structure and an environmentally benign nature, suffers from the lack of solubility in most organic solvents emanating from its supramolecular architecture. However, ethyl cellulose, an organosoluble cellulosic, possesses a fascinating structure and properties such as extensive linearity, chain stiffness, excellent durability, good flexibility, chemical resistance, mechanical strength, hydrophobicity, nontoxicity, low cost, and above all remarkably good solubility in organic solvents, thus having an adequate membrane-forming ability and moderate gas permeation/pervaporation capability.[1]

Physical or chemical modification of polymers is as an attractive alternative to tailor the material properties as desired for specific applications. The incorporation of fluorine-containing groups is an apt way to alter the physical and chemical properties of polymers because of the highly electronegative nature of fluorine,[2] and is known to enhance polymer solubility (commonly referred to as the fluorine effect) and fractional free volume without forfeiture of thermal stability, and affords materials with low dielectric constants, low water absorption, excellent barrier properties, and extremely low critical surface tension.[3] Owing to their unique properties, partially fluorinated polymers have attracted considerable attention as a new class of materials, finding a variety of applications as in organic thin film transistors (OTFT),[4] organic light-emitting diodes (OLED),[5] photonic devices,[6] low energy surfaces,[7] etc. Furthermore, gases dissolve well in fluorinated compounds,[8] and high gas permeability of some fluorine-containing polymer membranes including polysulfone,[9] polyacetylene,[10] polynorbornene,[11] polycarbonate,[12] and polyphosphazene[13] has been reported.

Derivatization of polysaccharides starting from the organosoluble polymer has undoubtedly broadened the diversity of products and reaction paths. Despite many aforementioned remarkable features and organosolubility of ethyl cellulose, studies concerning the systematic investigation of chemical derivatization of ethyl cellulose are few and far between.[14] Esterification is one of the facile means to exploit the hydroxy groups present in ethyl cellulose, however, there have been a few reports regarding the synthesis of mixed esters of ethyl cellulose; and (acetyl)(ethyl) cellulose is probably the one whose properties have been studied in detail.[14j−m] Although the organofluorine compounds have engrossed substantial prominence as a new class of polymeric materials, trifluoroacetyl derivative is most likely the only fluorine-containing derivative of ethyl cellulose, reported so far.[15] Since, there have been a few reports concerning the incorporation of fluorinated substituents into ethyl cellulose and fluorine-containing groups often favor high gas permeability,[9−13] it is anticipated that the perfluoroacylated derivatives of ethyl cellulose will serve as interesting candidates for gas separation membranes.

The present study deals with the synthesis of various perfluoroacyl derivatives (**2a**−**e**) of ethyl cellulose (**1**), their characterization, and elucidation of solubility and thermal properties (Scheme 1). Free-standing membranes of the perfluoroacylated polymers were fabricated and their contact angle with water, density, 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 determined by size-exclusion chromatography (SEC) at 40 °C with a Jasco PU-980/RI-930 and Viscotek UV/LS-T60A

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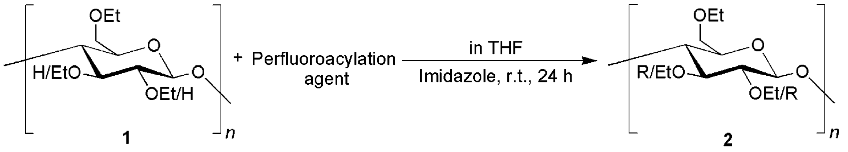
Scheme 1. Perfluoroacylation of Ethyl Cellulose with Various Perfluoroacylating Agents



R = CF_3CO (**2a**), C_2F_5CO (**2b**), C_3F_7CO (**2c**), $C_7F_{15}CO$ (**2d**), C_6F_5CO (**2e**)

chromatograph (eluent THF, column TSK-GEL GMHXL (Tosoh), molecular weight range up to 4×10^8, flow rate 1 mL/min). Infrared spectra were recorded on a Jasco FTIR-4100 spectrophotometer. Elemental analyses were performed at the Microanalytical Center of Kyoto University. Thermogravimetric analyses (TGA) were conducted in air with a Perkin-Elmer TGA7 thermal analyzer. Differential scanning calorimetric (DSC) analyses were performed using a Seiko DSC6200/EXSTAR6000 apparatus and measurements were carried out by making use of 3−5 mg samples, under a nitrogen atmosphere, after calibration with an indium standard. The samples were first heated from ambient temperature (25 °C) to +200 °C at a scanning rate of 20 °C $\min^{-1}$ (first heating scan) and then immediately quenched to −50 °C at a rate of about 80 °C $\min^{-1}$. The second heating scans were run from −50 to +200 °C at a scanning rate of 20 °C $\min^{-1}$ to record stable thermograms. The data for glass transition temperature (T_g), cold crystallization temperature (T_{cc}), and melting temperature (T_m), were all obtained from the second run and correspond to the midpoint of discontinuity in the heat flow. The static contact angle (CA) of water with polymer membranes was determined with a CA-X contact angle goniometer at 25 °C. Membrane thickness was estimated by using a Mitutoyo micrometer. Gas permeability coefficients (P) were measured with a Rikaseiki K-315-N gas permeability apparatus at 25 °C.

Materials. Ethyl cellulose (**1**; ethoxy content, 49 wt %; *DS*, 2.69) and imidazole were purchased from Aldrich and Wako (Japan), respectively, and used as received. Trifluoroacetic anhydride, heptafluorobutanoyl chloride, pentafluorobenzoyl chloride (Aldrich), pentafluoropropionic anhydride (Tokyo Kasei, Japan), and pentadecafluorooctanoyl chloride (Wako, Japan) were obtained commercially and used without further purification. Tetrahydrofuran (THF), used as reaction solvent, was purchased from Wako (Japan) and employed after distillation.

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

Trifluoroacetyl 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** (1.43 g, 6.10 mmol), and imidazole (0.83 g, 12.2 mmol) were placed in the flask, evacuated for a half hour, flushed with nitrogen, and dissolved in THF (50 mL) at room temperature. Then, trifluoroacetic anhydride (0.85 mL, 6.10 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 dried under vacuum to constant weight to afford the desired product (91%) as white solid. IR (ATR, cm^{-1}): 2974, 2870, 1794, 1375, 1220, 1090, 1050, 920, 880, 770, 736.

Pentafluoropropanoyl Derivative of Ethyl Cellulose (2b). This derivative was prepared by following the same procedure as for **2a** using pentafluoropropionic anhydride (1.21 mL) instead of trifluoroacetic anhydride. Yield: 93%, white solid. IR (ATR, cm^{-1}): 2974, 2872, 1789, 1376, 1354, 1221, 1090, 1049, 1027, 920, 883, 839, 739.

Heptafluorobutanoyl Derivative of Ethyl Cellulose (2c). This derivative was prepared by following the same procedure as for **2a** using heptafluorobutanoyl chloride (0.91 mL) instead of trifluoroacetic anhydride. Yield: 92%, white solid. IR (ATR, cm^{-1}): 2975, 2872, 1789, 1377, 1299, 1233, 1088, 1050, 928, 827, 722.

Pentadecafluorooctanoyl Derivative of Ethyl Cellulose (2d). This derivative was prepared by following the same procedure as for **2a** using pentadecafluorooctanoyl chloride (1.51 mL) instead of trifluoroacetic anhydride. Yield: 94%, white solid. IR (ATR, cm^{-1}): 2976, 2873, 1790, 1376, 1354, 1240, 1208, 1091, 1052, 920.

Pentafluorobenzoyl Derivative of Ethyl Cellulose (2e). This derivative was prepared by following the same procedure as for **2a** using pentafluorobenzoyl chloride (0.85 mL) instead of trifluoroacetic anhydride and precipitation was carried out in water rather than methanol, as **2e** was soluble in it. Yield: 90%, white solid. IR (ATR, cm^{-1}): 2974, 2869, 1693, 1502, 1374, 1055, 917, 877, 797.

Determination of Degree of Substitution. The degree of substitution with ethyl group (DS_{Et}) of the starting material, **1**, was determined by ^{1}H NMR and complete substitution of the residual hydroxy protons by the perfluoroacyl group in **2a**−**d** was confirmed by the complete disappearance of the peak characteristic of the hydroxy group (3200−3600 cm^{-1}) in the FTIR spectra of the compounds (Figure 1). The degree of substitution with pentafluorobenzoyl group in **2e** was estimated from the elemental analysis. The total degree of substitution (DS_{total}) of **2a**−**e** was calculated by the following equation:

$$DS_{\mathrm{total}} = DS_{\mathrm{Et}} + DS_{\mathrm{Ac}}$$

Membrane Fabrication. Membranes (thickness ca. 40−80 μm) of polymers **1** and **2e** were fabricated by casting their toluene solution and those of **2a**−**d** from their 1,3-bis(trifluoromethyl)benzene solution (concentration ca. 0.50−1.0 wt %) onto a Petri dish. The dish was covered with a glass vessel to retard the rate of solvent evaporation (3−5 days).

Membrane Density. Membrane densities (ρ) were determined by hydrostatic weighing using a Mettler Toledo balance (model AG204, Switzerland) and a density determination kit.[16] This method makes use of a liquid with known density (ρ_0), and membrane density (ρ) is calculated by the following equation:

$$\rho = \rho_0 M_{\mathrm{A}}/(M_{\mathrm{A}} - M_{\mathrm{L}})$$

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 to measure the density of the polymer membranes except for **2d**, whose density was determined by using aqueous NaI solution.

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:[17]

$$\mathrm{FFV} = (v_{\mathrm{sp}} - v_0)/v_{\mathrm{sp}} \approx (v_{\mathrm{sp}} - 1.3v_{\mathrm{w}})/v_{\mathrm{sp}}$$

where v_{sp} and v_0 are the specific volume and occupied volume (or zero-point volume at 0 K) of the polymer, respectively. Typically, occupied volume (v_0) is estimated as 1.3 times the van der Waals volume (v_{w}), which is calculated by the group contribution methods.[18]

Measurement of Gas Permeation Parameters. The P values were calculated from the slopes of the time−pressure curves in the steady state where Fick's law holds.[19] The gas diffusion

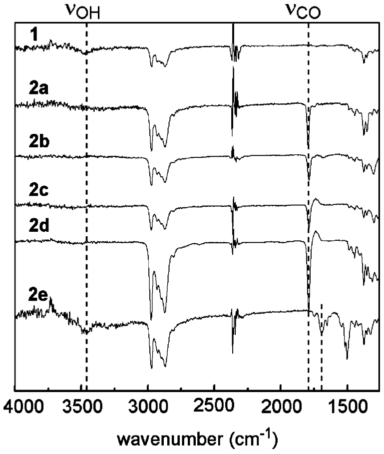


Figure 1. FTIR spectra of polymers **1** and **2a**−**e**.

Table 1. Degree of Substitution (*DS*) and SEC Data of Polymers 1 and 2a−e

polymer	DS_{total}[a]	M_n[b]	M_w[b]	M_w/M_n[b]
1	2.69	47 000	106 000	2.3
2a	3.00	68 000	103 000	1.5
2b	3.00	93 000	117 000	1.3
2c	3.00	96 000	120 000	1.2
2d	3.00	132 000	147 000	1.1
2e	2.92[c]	49 000	124 000	2.5

[a] Determined by FTIR. [b] Determined by SEC/RALLS (size-exclusion chromatography/right-angle laser light scattering). [c] Determined by elemental analysis.

coefficients (D) were determined by the time lag method using the following equation:

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

Here, l is the membrane thickness and θ 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 gas solubility coefficients (S) were calculated by using the equation, $S = P/D$.

Results and Discussion

Perfluoroacylation of Ethyl Cellulose. Perfluoroacylation of ethyl cellulose (**1**) was carried out by using various perfluorinated acid anhydrides/chlorides as perfluoroacylating 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 **1** was estimated to be 2.69, by calculating the integration ratio of methyl protons to the rest of the protons in **1**, indicating the presence of 0.31 hydroxy groups per anhydroglucose unit.[14a] The IR spectrum of **1** (Figure 1) has a broad peak characteristic of the residual hydroxy groups (3200−3600 cm^{-1}), which disappeared upon complete perfluoroacylation in polymers **2a**−**d**. Further evidence was furnished by the presence of the peaks characteristic of the carbonyl group (1690−1695 cm^{-1}) in the IR spectra of perfluoroalkanoyl derivatives (**2a**−**d**). On the other hand, complete substitution could not be achieved with pentafluorobenzoyl group, as is indicated by the presence of the broad peak for the hydroxy group (3200−3600 cm^{-1}) in the IR spectrum of **2e**; its degree of acylation (DS_{Ac}) was determined by the elemental analysis and total degree of substitution (DS_{total}) was 2.92. According to SEC data of the polymers (Table 1), the number-average molecular weight (M_n) of **1** was found to be 47 000 and a regular increase in the M_n values of perfluoroacylated polymers was observed with the increase in the bulk of perfluoroacyl group. Moreover, the polydispersity indices (M_w/M_n) of perfluoroacylated polymers (**2a**−**d**) were not quite different from those of **1**. For instance, the M_n and M_w/M_n of **1** were observed to be 47 000 and 2.3, respectively, while those of **2a** were 68 000 and 1.5. These facts rule out the possibility of polymer chain cleavage in the course of perfluoroacylation.

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

	1	2a	2b	2c	2d	2e
methanol	+	−	−	−	−	+
DMF	+	±	±	−	−	+
acetone	±	±	+	+	+	+
EtOAc	+	+	+	+	+	+
THF	+	+	+	+	+	+
CH_2Cl_2	+	+	+	+	+	+
$CHCl_3$	+	+	+	+	+	+
toluene	+	+	+	+	+	+
hexane	−	−	+	+	+	+
C_6F_6	−	+	+	+	+	−
1,3-$(CF_3)_2C_6H_4$	−	+	+	+	+	−

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

Solubility and Thermal Properties of Polymers. The solubility properties of ethyl cellulose (**1**) and **2a**−**e** are summarized in Table 2. **1** is soluble in highly polar protic solvents such as methanol, while its perfluoroacylated derivatives (**2a**−**d**) were found to be insoluble (except **2e**), which is presumably due to the loss of hydrogen bonding because of the complete substitution of hydroxy groups by the perfluoroacyl groups in **2a**−**d**. The solubility behavior of perfluoroacylated polymers in polar aprotic solvents exhibited several variations depending on the polarity of the solvent and an increased affinity toward relatively less polar solvents was discerned. For instance, **1** is soluble in DMF while its perfluoroalkanoylated derivatives exhibited a decrease in solubility with the increase in the length of the perfluoroalkanoyl chain; on the other hand, **1** is partly soluble in acetone while **2b**−**e** were completely soluble. Solubility characteristics of **1** in EtOAc, THF, $CHCl_3$, and toluene remain unchanged upon perfluoroacylation. Furthermore, **1** is insoluble in hexane, a nonpolar solvent, while its perfluoroacylated derivatives except **2a** were found to be soluble, due to the presence of long perfluorocarbon chains in **2b**−**d** and an aromatic ring in **2e**. Moreover, the solubility of perfluoroacylated polymers in perfluorinated solvents such as hexafluorobenzene and 1,3-bis(trifluoromethyl)benzene was examined and it was observed that the completely perfluoroacylated derivatives of ethyl cellulose (**2a**−**d**) were soluble in these solvents. Thus, it can be said that the perfluoroacylated ethyl cellulose derivatives (**2a**−**e**) display enhanced solubility in moderately polar aprotic solvents like acetone and nonpolar solvents like hexane.

The thermal stability of polymers **1** and **2a**−**e** was examined by thermogravimetric analysis (TGA) in air (Figure 2). The onset temperatures of weight loss (T_0) of **2a**−**d** were in the range of 270−300 °C, while that of **1** was 338 °C, thus indicating a slight decrease in T_0 values because of the loss of hydrogen bonding upon perfluoroacylation, resulting from the substitution of hydroxy groups by the perfluoroacyl moieties (Table 3). It was observed that the onset temperature of weight loss underwent a slight decrease with an increase in the length of the perfluoroalkanoyl group; for instance, T_0 of **2a** and **2b** were 293 and 288 °C, respectively. The TGA thermogram of pentafluorobenzoyl derivative (**2e**) displayed two major points of weight loss at 145 and 293 °C, respectively; the weight loss at 145 °C corresponds to that of the pentafluorobenzoyl moiety (~8%), while that at 293 °C to the rest of the polymer. The first T_0

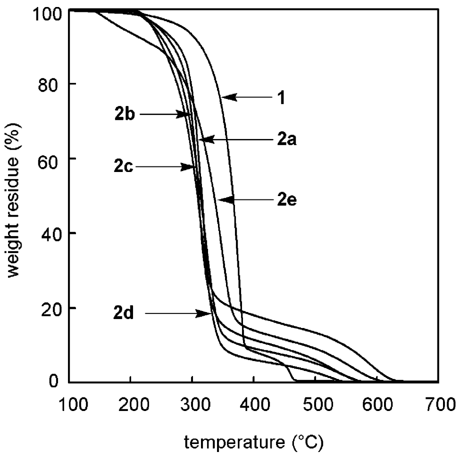


Figure 2. TGA curves of polymers **1** and **2a**−**e** (in air, heating rate 10 °C min^{-1}).

Table 3. Thermal Properties of Polymers 1 and 2a−e

polymer	T_0[a] (°C)	T_g[b] (°C)	T_{cc}[b] (°C)	T_m[b] (°C)	ΔH_{cc}[b] (mJ/mg)	ΔH_f[b] (mJ/mg)
1	338	132	*c*	190	*c*	4.2
2a	293	227	244	266	0.96	14.9
2b	288	158	211	221	1.21	7.8
2c	275	159	*c*	215	*c*	7.3
2d	273	101	131	180	0.50	6.2
2e	145, 293	*c*	*c*	*c*	*c*	*c*

[a] T_0: Onset temperature of weight loss. Observed from TGA measurement in air. [b] T_g: Glass transition temperature. T_{cc}: Cold crystallization temperature. T_m: Melting temperature. ΔH_{cc}: Enthalpy of cold crystallization. ΔH_f: Enthalpy of fusion. Determined by DSC analysis in nitrogen. [c] Could not be determined.

value of perfluorobenzoyl derivative (**2e)** was considerably lower than those of the perfluoroalkanoyl derivatives (**2a**−**d**), which is presumably due to a weaker ester linkage than those in **2a**−**d** (as C_6F_5COOH is a considerably stronger acid than perfluoroalkanoic acids). These results imply that the thermal stability undergoes a slight decrease as the length of the alkyl chain in the perfluoroalkanoyl group increases, while decreases considerably by the incorporation of relatively less stable perfluorobenzoyl moiety. Although the thermal stability of the perfluoroacylated derivatives of ethyl cellulose (**2a**−**d**) is slightly lower than that of the starting material (**1**), it is still appreciably reasonable for practical applications as membrane-forming materials.

Other thermal properties such as glass transition temperature (T_g), cold crystallization temperature (T_{cc}), and melting temperature (T_m) of polymers **1** and **2a**−**e** were determined by the differential scanning calorimetric (DSC) analysis under nitrogen (Figure 3). It was observed that the glass transition temperature (T_g) of **1** (132 °C) underwent a significant increase upon the substitution of trifluoroacetyl group (227 °C), and then followed a decline as the length of the perfluoroalkanoyl group increased; e.g., T_g values for **2c** and **2d** were 159 and 101 °C, respectively (Table 3). The increase in the polymer chain-stiffness due to the hindered rotation of the substituent, resulting from the substitution of hydroxy group by a relatively bulky, stiff, and polar trifluoroacetyl group, presumably led to the increased T_g in **2a**, which became offset due to the plasticization induced by the increased length of the perfluoroalkanoyl chain, thus leading to the decreased T_g values (**2b**−**d**). In general, the glass transition temperature (T_g) depends on the energy barriers that conformational transitions must overcome in such a way that the larger the barriers are, the fewer the conformational transitions that occur at a given temperature.[20] Substitution of the relatively small hydroxy moieties by the stiff and polar trifluoroacetyl groups appeared to increase the energy barriers associated with the conformational transitions in the chains, and as a result, the T_g of **1** underwent an increase upon perfluoroacylation/trifluoroacetylation.

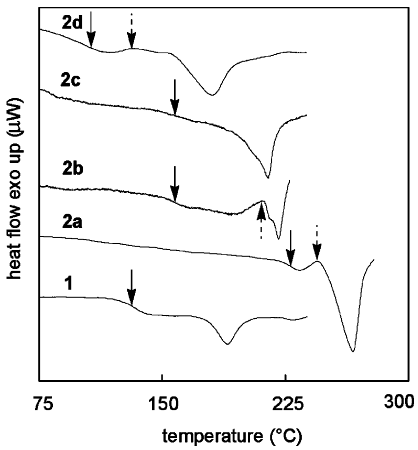


Figure 3. DSC thermograms of polymers **1** and **2a**−**d** (in N_2, second scan). Solid arrows denote the T_g, and dotted arrows denote the T_{cc} of polymers.

Table 4. Contact Angle of Water with the Surface of Polymers 1 and 2a−e

polymer	θ (deg)[a]
1	83.4 ± 0.3
2a	92.1 ± 0.2
2b	94.2 ± 0.5
2c	95.6 ± 0.2
2d	97.0 ± 0.5
2e	93.1 ± 0.3

[a] Determined at 25 °C.

Herein the term, cold crystallization temperature (T_{cc}), represents the temperature above the glass transition temperature (T_g) at which a small portion of the structurally irregular amorphous state of the polymer attains regularity and turns into crystalline state; the T_{cc} values were observed in the case of perfluoroalkanoyl derivatives of **1**, as shown in Table 3.

Similar tendencies were observed in T_m values of polymers as those in T_g, which can also be explained in terms of the increased rigidity of the polymer chains upon perfluoroacylation; and this effect was more pronounced in the case of trifluoroacetyl derivative (**2a**) in comparison with those having longer chain of carbon atoms. Increase in the melting temperature (T_m) of the polymers suggests an increase in the crystallinity as a result of perfluoroacylation; however, this effect has significantly been observed only in the case of **2a**, displaying a T_m value of 266 °C in comparison with that of **1** (190 °C), while those of **2b**−**d** were 221, 215, and 180 °C, respectively.

Contact Angle of Water with Polymer Membranes. Static contact angles (θ) of water were measured for all the polymer films, under study, to determine the relative hydrophobicity of the surface. Table 4 lists the contact angles[21] of water with the surface of polymer membranes at 25 °C and their plot as a function of % F content of polymers **1** and **2a**−**e**, is shown in Figure 4. The polymer membranes of perfluoroacylated derivatives (**2a**−**e**) displayed larger contact angle ($\theta > 90°$) with water than that of **1** ($\theta = 83°$). In other words, introduction of fluorine-containing substituents led to an increase in the hydrophobicity or nonwettability of ethyl cellulose membranes; and this trend bears a resemblance to that observed in the case of other fluorinated polymeric materials.[22] Moreover, it was revealed that

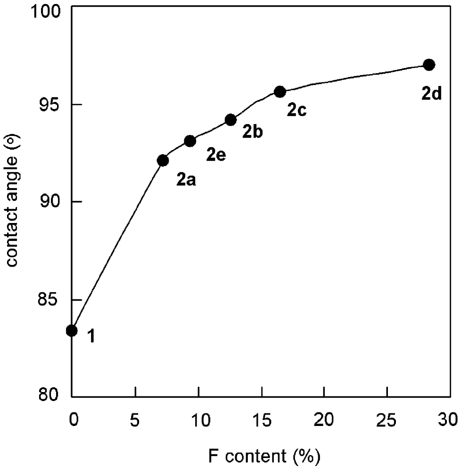


Figure 4. Contact angle of water with the surface of polymer membranes **1** and **2a**−**e** vs their % F content.

Table 5. Physical Properties of Polymers 1 and 2a−e

polymer	$\upsilon_w{}^a$ (cm^3/mol)	ρ^b (g/cm^3)	FFV^c
1	135.8	1.099	0.182
2a	145.0	1.155	0.185
2b	149.6	1.178	0.189
2c	154.2	1.194	0.197
2d	172.5	1.298	0.191
2e	150.9	1.206	0.161

[a] υ_w: van der Waals volume. [b] ρ: density. Determined by hydrostatic weighing. [c] FFV: fractional free volume. Estimated from membrane density.

an increment in the F content of the perfluoroacylated polymers accompanied an increase in the contact angle of water with the surface of the membranes, and **2d** having the highest F content displayed the highest CA value. For instance, the % F content of **2a** and **2d** were 7.2 and 28.3, while the values for the contact angle of water with their membranes were observed to be 92 and 97°, respectively.

Density and FFV of Polymer Membranes. The van der Waals volumes (υ_w), densities (ρ), and fractional free volumes (FFV) of the polymer membranes (**1** and **2a**−**e**) are summarized in Table 5. All of the perfluoroacylated derivatives (**2a**−**e**) exhibited higher values of membrane density than that of ethyl cellulose (**1**); thus, the ρ value of **1** was observed to be 1.099, while those of **2a**−**e** were in the range of 1.155−1.206. It was observed that an increase in the F content of the perfluoroacyl group accompanied an increase in the density of the polymer membranes. These findings are quite reasonable as fluorine-containing polymers generally possess larger densities than those of the corresponding hydrocarbon polymers.[10b] It is worth mentioning that perfluoroalkanoylation resulted in an enhancement in the FFV values of polymer membranes (**2a**−**d**) regardless of the simultaneous increase in density as compared to the starting material (**1**). For instance, **2c** was observed to possess the highest fractional free volume (FFV is 0.197), despite its quite high density (ρ is 1.194) among all of the perfluoroacylated derivatives of **1**, which probably indicates the formation of relatively sparse structures due to the incorporation of fluorine-containing moieties. Similar tendencies have been reported in the case of F-containing polycarbonates.[12] Furthermore, it is a general trend that the bulky substituents sterically obstruct intersegmental packing[9] and in the case of F-containing polymers, chain packing is further restrained by the intermolecular repulsive forces, resulting from the presence of fluorine atoms having high electron density.

Table 6. Gas Permeability Coefficients (*P*) of the Polymer Membranes at 25 °C

	P (barrer)^a							
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
2a	72	102	28	8.0	172	17	21	10
2b	100	140	44	16	250	30	16	9
2c	114	155	52	20	284	37	14	8
2d	110	130	48	16	251	29	16	9
2e	40	51	11	3.0	64	6.0	22	11

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

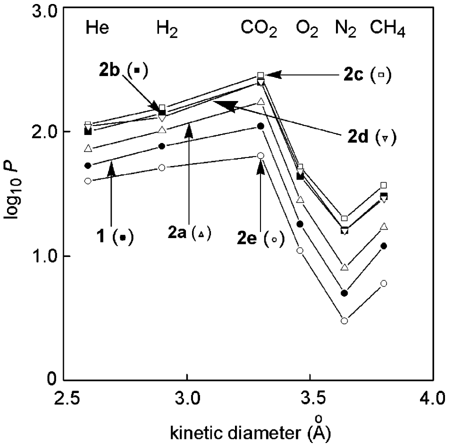


Figure 5. Gas permeability coefficients of ethyl cellulose (**1**) and its perfluoroacylated derivatives (**2a**−**e**) vs kinetic diameter of gases.

Gas Permeation Properties. The permeability coefficients of the membranes of polymers **1** and **2a**−**e** to various gases measured at 25 °C are listed in Table 6, and their plot vs kinetic diameter of the gases is shown in Figure 5. The gas permeability coefficients (*P*) of the perfluoroacylated derivatives (except **2e**) were higher than that of **1**, and approximately obey the following order: **2c** > **2b** ≈ **2d** > **2a** > **1** > **2e**, which is in accordance with the FFV of the polymer membranes. The order of the gas permeability coefficients depends on the shape, size, and mobility of the perfluoroacyl substituents.

In this study, it has been revealed that an optimum increase in the bulk or the length of the perfluoroalkanoyl group accompanies an enhancement in the gas permeability; while an excessive increase affects conversely. For instance, the carbon dioxide permeability coefficients (P_{CO_2}) for **2a**−**d** were 172, 250, 284, and 251 barrers, respectively, where **2c** displayed the highest CO_2 permeability; and similar tendencies were observed for other gases in the present study. These trends in the gas permeability suggest that an optimum increase in the bulk and length of the perfluoroalkanoyl group results in a looser chain-packing, leading to the increased free volume space inside the polymer matrix, and in turn enhanced gas permeability; while these effects are counterbalanced to some extent by an excessive increase in the bulk/length of the substituent due to the hindered chain/segmental mobility. The smallest *P* values have been observed for **2e**, which are probably due to the planar and nonflexible nature of the aryl group present in the pentafluorobenzoyl moiety, thus leading to the stacking (as indicated by the decreased FFV) and decrement in the local mobility of the substituent.

The most important feature of the gas permeability data of ethyl cellulose (**1**) and its perfluoroacylated derivatives (**2a**−**e**) is relatively high P_{CO_2}/P_{N_2} selectivity (≥14) of these polymers, and notably, **2a**−**c** displayed good perforamance for CO_2 separation. However, as the gas permeability undergoes

Table 7. Gas Diffusion Coefficients[a] (*D*) of the Polymer Membranes

	10^7 *D* ($cm^2\ s^{-1}$)			
	O_2	N_2	CO_2	CH_4
critical vol (cm^3/mol)	73.4	89.8	93.9	99.2
1	8.3	3.8	2.6	1.8
2a	9.6	5.3	3.9	2.2
2b	14.2	8.9	5.3	3.8
2c	16.7	10.8	6.0	4.9
2d	14.6	8.3	5.3	3.8
2e	5.4	2.5	1.9	1.1

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

Table 8. Gas Solubility Coefficients[a] (*S*) of the Polymer Membranes

	10^3 *S* (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	45.0
2a	1.5	2.9	7.5	43.7
2b	1.7	3.1	7.8	46.9
2c	1.8	3.1	7.6	47.0
2d	2.0	3.3	7.6	47.3
2e	1.1	2.0	5.2	33.1

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

an increase, a decrease in permselectivity is observed. Moreover, similar tendencies were displayed by the $P(CO_2)/P(CH_4)$ selectivity data of the perfluoroacylated polymers. Enhanced gas permeability without loss of permselectivity in **2a**, was probably due to the decreased chain-packing (as indicated by the slight increase in FFV) and increased chain-stiffness/hindered rotation of the pendant groups (as indicated by the increased T_g), resulting from the trifluoroacetylation of **1**. These findings are consistent with the previous results that the structural alterations, which inhibit chain packing and simultaneously constrain the rotational motion about flexible linkages on the polymer backbone, for instance, the incorporation of fluorinated substituents, tend to increase permeability while maintaining or increasing permselectivity.[20a,23]

The present results imply that the gas transport properties of membrane-forming materials can be selectively improved through a controlled modification of subtle structural features such as interchain spacing and chain stiffness.

Gas Diffusivity and Solubility. Gas permeability (*P*) can be expressed as the product of gas solubility (*S*) in the upstream face of the membrane and effective average gas diffusion coefficient (*D*) in the membrane, strictly in rubbery and approximately in glassy polymers:[24]

$$P = S \times D$$

To carry out a detailed investigation of the gas permeability of **1** and **2a**−**e**, their gas diffusion coefficients (*D*) and gas solubility coefficients (*S*) were determined. The *D* and *S* values of polymers **1** and **2a**−**e** for O_2, N_2, CO_2, and CH_4 are given in Tables 7 and 8, 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 **1** and its perfluoroacylated derivatives; e.g., in the case of **2a**, the diffusivity of CH_4 (2.2) was the lowest and that of O_2 (9.6) was the highest, while CO_2 (43.7) displayed the highest solubility and N_2 (1.5) the lowest.

As shown in Table 7, the diffusion coefficients of all the gases increased upon perfluoroalkanoylation (**2a**−**d**), while underwent a considerable decline upon perfluorobenzoylation (**2e**). For instance, **1** displayed the D_{O_2} value of 8.3, and those of **2a**−**d** were in the range of 9.6−16.7, while **2e** exhibited a D_{O_2} value of 5.4. The increment of gas diffusivity can be accounted for by the increase in the FFV of the polymer membranes (**2a**−**d**) as a result of perfluoroacylation; however, the enhanced local mobility of the substituents might also be anticipated to make a major contribution in the case of **2b**−**d**, having substituents with longer alkyl chain.[25]

As far as the gas solubility coefficients are concerned, a small increase in the *S* value was observed in almost all of the perfluoroalkanoyl derivatives as compared to **1**, as shown in Table 8. A small increment in the *S* values probably arises from the higher FFV values of the perfluoroalkanoyl derivatives (**2a**−**d**) than that of **1**, as summarized in Table 5. It was observed that the *S* values underwent a subtle increase, with the increase in the size of the perfluoroalkanoyl group (**2a**−**d**); e.g., S_{CO_2} values of **2a**−**d** were 43.7, 46.9, 47.05, and 47.35, respectively.

Among **2a**−**e**, **2c** exhibited the highest *D* value for all the gases, presumably resulting from its highest FFV (0.197) and also because of the enhanced local mobility of the perfluoroacyl substituent due to the presence of the alkyl chain of optimum length, leading to the increased diffusion coefficient. Similar tendencies have been observed in various substituted polyacetylenes.[19] It is noteworthy that the increase in the diffusion coefficients upon perfluoroacylation (**2a**−**d**) was more pronounced than that in the solubility coefficients, thus penetrant diffusivity playing the major role, leading to the net effect of enhanced gas permeability.[12a,23e] Furthermore, these results indicate the significance of perfluoroalkanoyl groups to enhance the gas permeability by mainly increasing the gas diffusion coefficients of the polymer membranes along with a slight increase in the gas solubility.

Conclusions

The present study is concerned with the synthesis of various perfluoroalkanoyl(benzoyl) esters of ethyl cellulose (**2a**−**e**). It was demonstrated that the perfluorinated acid anhydrides/chlorides served as excellent acylating agents, in the presence of imidazole, which accomplished the complete perfluoroalkanoylation of ethyl cellulose (**1**) even at room temperature without any chain degradation. All of the perfluoroalkanoyl derivatives of ethyl cellulose (**2a**−**d**) displayed good solubility in common organic and perfluorinated solvents, fair thermal stability, increased chain-stiffness, enhanced hydrophobicity, and adequate membrane-forming ability. Membranes of **2a**−**d** exhibited higher gas permeability than that of **1**, primarily due to the increased diffusion coefficients resulting from the introduction of fluorine-containing acyl moiety in **1**. Although perfluoroacylation could not induce 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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