Synthesis and Properties of Amidoimide Dendrons and Dendronized Cellulose Derivatives

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ABSTRACT: First and second generation amidoimide dendrons (**G1-a-II**−**G1-c-II** and **G2-a-II**−**G2-c-II**) having branched alkyl periphery and focal carboxyl functionality were synthesized via a convergent pathway and incorporated into ethyl cellulose. Dendronized ethyl cellulose derivatives (**2a**−**c**, **3a**−**c**) were synthesized in good yield by the reaction of the terminal carboxyl moiety of various dendrons with residual hydroxy groups of ethyl cellulose (**1**; degree of substitution with ethyl group (DS_{Et}), 2.69). ^{1}H NMR spectra and elemental analysis were employed to determine the degree of esterification (DS_{Est}) of the resulting polymers. The presence of the peak characteristic of the C═O group in the FTIR spectra accomplished further evidence for the incorporation of dendritic moieties into ethyl cellulose. All of the derivatives (**2a**−**c**, **3a**−**c**) were soluble in chloroform and methanol, and the solubility window narrowed in going from G1- to G2-derivatized polymers. The onset temperatures of weight loss of **2a**−**c** (295−325 °C) and **3a**−**c** (312−320 °C) in air were slightly higher than 294 °C, indicating that the thermal stability was retained upon dendron functionalization. Free-standing membranes of **1** and **2a**−**c** were fabricated, and **2a**−**c** exhibited enhanced permselectivity for He/N$_2$, H$_2$/N$_2$, CO$_2$/N$_2$, and CO$_2$/CH$_4$ gas pairs as compared to **1**.

Introduction

Dendrimers, a class of precisely branched, highly symmetrical, treelike macromolecules capable of furnishing the most exquisitely tailored forms and functions ever realized outside the realms of nature, have evolved from little more than a curiosity into new horizons of macromolecular architecture finding potential applications in pharmaceutical, biotechnological, and polymer sciences and are expected to reign as the flagship building blocks of nanotechnology.[1] Because of the unique architectural and functional control achieved during their synthesis, dendrimers possess characteristic structural features and properties quite different from those of their linear counterparts and have extensively been studied in the past three decades.[2] Despite such an enormous activity enriching the structural diversities of dendrimers, research has almost exclusively been focused on dendrimers with small cores, except for a U.S. patent filed by Tomalia and Kirchhoff in 1987[3] followed by a few reports[4] until a breakthrough in the synthesis of dendronized polymers was reported by Schlüter in the mid 90s,[5] recognizing the significance of dendron functionalization for the backbone conformation and the overall shape of the resulting macromolecules.

Dendronized polymers are characterized by the presence of dendritic fragments attached to a polymeric backbone, and the past few years have witnessed a variety of dendritic substituents and polymeric backbones to which they are appended to.[6] Recently, there is an increasing interest to exploit the dendritic macromolecules or dendron appendages for the chemical and surface modification of silica,[7] agarose,[8] carbon,[9] chitosan,[10] and DNA;[11] however, the reports concerning the dendronization of cellulose or its organosoluble derivatives are few and far between.[12]

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 the fascinating features of extensive linearity, chain stiffness, excellent durability, chemical resistance, mechanical strength, hydrophobicity, nontoxicity, low cost, and above all appreciably good solubility in organic solvents, thus adequate membrane-forming ability, good film-flexibility, and moderate gas permeation/pervaporation capability.[13]

Considering the many aforementioned remarkable features of dendritic structures and organosolubility of ethyl cellulose carrying hydroxy (anchor) groups available for derivatization, it would be interesting to synthesize novel dendron-functionalized macromolecular architectures based on cellulose and to investigate the structural characteristics and functions of this new emerging class of “hybrid architectures” derived from dendrimers and the most sustainable linear polymers.

The present contribution reports the synthesis and characterization of **G1** and **G2** of various amidoimide dendrons and dendronized derivatives (**2a**−**c**, **3a**−**c**) of ethyl cellulose (**1**) (Schemes 1 and 2). The solubility characteristics and thermal properties of the resulting polymers were elucidated. Free-standing membranes of the dendronized polymers (**2a**−**c**) were fabricated, and their density, fractional free volume, and gas permeation 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

Measurements. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL EX-400 spectrometer, and the residual proton or carbon signal of the deutrated solvent was used as an internal standard. The samples for the NMR measurements were prepared at a concentration of approximately 10 mg/mL, and chemical shifts are reported

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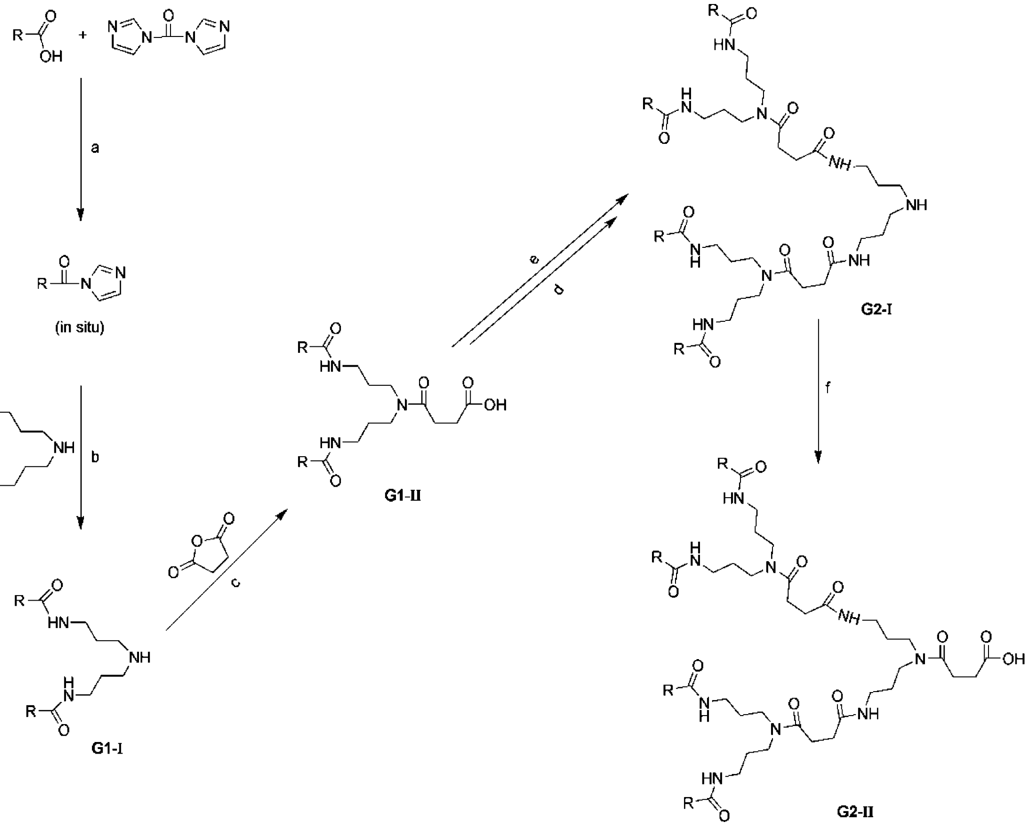
Scheme 1. Synthesis of G1 and G2 Amidoimide Dendrons[a]



[a] Conditions: (a) toluene, 80 °C, 1 h; (b) toluene, 80 °C, 3 h; (c) toluene, 80 °C, 3 h; (d) 1,1′-Carbonyldiimidazole, as in reaction a; (e) *N*-(3-Aminopropyl)propane-1,3-diamine, as in reaction b; (f) Succinic anhydride, as in reaction c.

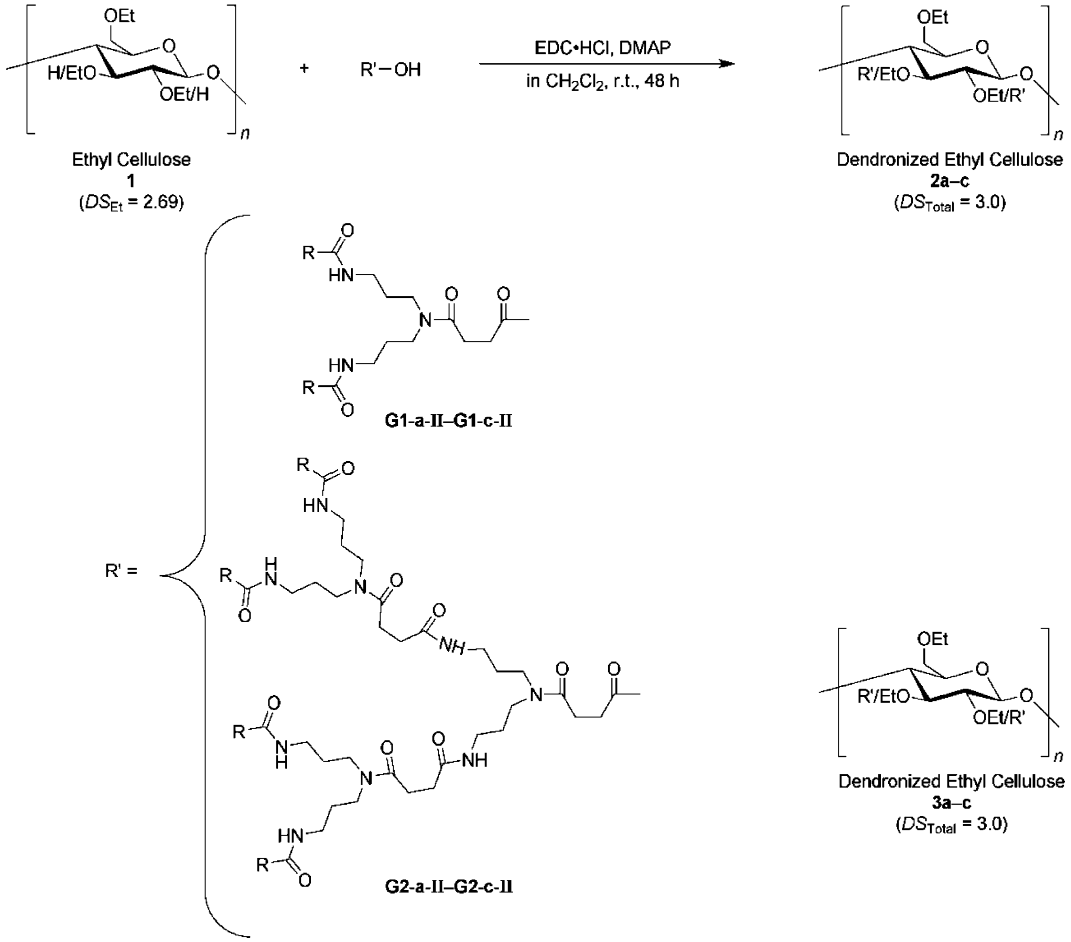
in parts per million (ppm). The ^{1}H NMR spectra of ethyl cellulose and dendronized polymers were recorded for 192 scans with a pulse delay of 37 s in order to obtain reliable integrations. Infrared spectra were recorded on a Jasco FTIR-4100 spectrophotometer, and 68 spectra were accumulated at a resolution of 4 cm^{-1}, for each measurement. The FAB-MS analyses were conducted using the JEOL JMS-HX110A and JMS-SX102A spectrometers while 3-nitrobenzyl alcohol (MNBA) was used as a matrix. Melting points (mp) were determined with a Yanaco micromelting point apparatus, and elemental analyses were conducted with a Yanaco-CHN corder at the Microanalytical Center of Kyoto University. 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 gel permeation chromatography (GPC) on a JASCO Gulliver system (PU-980, CO-965, RI-930, and UV-2075). All of the measurements were carried out at 40 °C using two TSK-Gel columns [α-M (bead size, 13 μm; molecular weight range $> 1 \times 10^7$) and GMH$_{XL}$ (bead size 9 μm; molecular weight range up to 4×10^8)] in series and LiBr solution (0.01 M) in *N*,*N*-dimethylformamide as an eluent at a flow rate of 1.0 mL/min. The elution times were converted into molecular weights using a calibration curve based on polystyrene standards, in combination with the information obtained from the refractive index detector. Thermogravimetric analyses (TGA) were conducted in the air with a Shimadzu TGA-50 thermal analyzer by heating the samples (3−5 mg) from 100−700 °C at a scanning rate of 10 °C min^{-1}. 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 260 °C at a scanning rate of 20 °C min^{-1} (first heating scan) and then immediately quenched to −100 °C at a rate of 100 °C min^{-1}. The second heating scans were run from −100 to 260 °C at a scanning rate of 20 °C min^{-1} to record stable thermograms. The data for glass transition temperature (T_g) were obtained from the second run and correspond to the midpoint of discontinuity in the heat flow. Membrane thickness was estimated by using a Mitutoyo micrometer. The gas permeability coefficients (P) were measured with a Rikaseiki K-315-N gas permeability apparatus using a constant volume/variable-pressure system.[14] All of the measurements were carried out at 25 °C and a feed pressure of 0.1 MPa (1 atm), while the pressure difference across the membrane was ∼107 kPa as the system used vacuum on the downstream side of the membrane.

Materials. Ethyl cellulose (**1**; ethoxy content, 49 wt %; DS, 2.69) and *N*-(3-aminopropyl)propane-1,3-diamine (98%) were purchased from Aldrich and used as received. 1,1′-Carbonyldiimidazole (Sigma-Aldrich), 2-ethylbutanoic acid (97%, Wako, Japan), 2-propylpentanoic acid (Sigma-Aldrich), 2-ethylhexanoic acid (Tokyo Kasei, Japan), succinic anhydride (≥99%, Tokyo Kasei, Japan), 4-(dimethylamino)pyridine (99%, Wako, Japan), *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC·HCl; Eiweiss Chemical Corporation), and distilled water (Wako, Japan) were obtained commercially and used without further purification. Toluene and dichloromethane (CH_2Cl_2), used as reaction solvents, were purchased from Wako (Japan) and purified by distillation prior to use.

The first and second generation amidoimide dendrons (**G1-a-II**−**G1-c-II, G2-a-II**−**G2-c-II**) and dendronized ethyl cellulose derivatives (**2a**−**c**, **3a**−**c**) were synthesized according to the Schemes 1 and 2, respectively. The details of the synthetic procedure and analytical data are as follows.

Dendron Synthesis. ***N*,*N*′-(3,3′-Azanediylbis(propane-3,1-diyl))bis(2-ethylbutanamide) (G1-a-I).** A 200 mL three-necked flask was equipped with a dropping funnel, a reflux condenser, a three-way stopcock, and a magnetic stirring bar and evacuated and flushed with argon three times. 2-Ethylbutanoic acid (40.6 mL, 0.312 mol) was charged into the flask, toluene (100 mL) was added, and the system was heated to 60 °C and stirred. 1,1′-Carbonyldiimidazole, CDI, (50.6 g, 0.312 mol) was added slowly along with constant stirring until CO_2 evolution had ceased. The solution was

Scheme 2. Esterification of Ethyl Cellulose with G1 and G2 Dendrons[a]



[a] Abbreviations: EDC•HCl, *N*-(3-Dimethylaminopropyl)-*N*′-ethylcarbodiimide Hydrochloride; DMAP, 4-(Dimethylamino)pyridine.

further heated for an hour at 80 °C and purged with argon. *N*-(3-aminopropyl)propane-1,3-diamine (22.5 mL, 0.156 mol) was added dropwise to the solution, and stirring was continued for 3 h at 80 °C. The reaction mixture was allowed to cool to room temperature, concentrated in vacuo, and the remaining clear liquid was dissolved in CH_2Cl_2 and washed three times with water. The washed CH_2Cl_2 solution was dried with anhydrous $MgSO_4$, filtered, concentrated, and dried under vacuum to constant weight to afford the desired product as a white solid. Yield 67%, white solid, mp 95−96 °C, ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C, ppm): 0.97 (t, J = 7.2 Hz, 12H, CH_3CH_2), 1.51−1.72 (m, 8H, CH_3CH_2), 1.74−1.79 (m, 4H, C(=O)NHCH$_2$CH$_2$CH$_2$), 1.99−2.07 (m, 2H, (CH$_3$CH$_2$)$_2$CH)), 2.43 (brs, 1H, CH$_2$NHCH$_2$), 2.68−2.77 (m, 4H, C(=O)NHCH$_2$CH$_2$CH$_2$), 3.41−3.51 (m, 4H, C(=O)NHCH$_2$CH$_2$CH$_2$), 7.7 (brs, 2H, C(=O)NH). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C, ppm): 11.8, 25.5, 29.2, 36.9, 46.8, 50.8, 175.8. MS(FAB): [MH]$^+$, calcd for $C_{18}H_{37}N_3O_2$ 328.2959, found 328.2931. Anal. Calcd for $C_{18}H_{37}N_3O_2$: C, 66.01; H, 11.39; N, 12.83; O, 9.77. Found: C, 66.00; H, 11.09; N, 12.81; O, 10.10.

4-(Bis(3-(2-ethylbutanamido)propyl)amino)-4-oxobutanoic Acid (G1-a-II). **G1-a-I** (25 g, 0.076 mol) and succinic anhydride (11.46 g, 0.1146 mol) were charged into a 200 mL three-necked flask equipped with a reflux condenser, a three-way stopcock, and a magnetic stirring bar, and argon exchange was carried out three times. Toluene (50 mL) was added and after stirring for 3 h at 80 °C, the reaction mixture was allowed to cool to room temperature and concentrated in vacuo. After being concentrated in vacuo (in order to remove toluene), $CHCl_3$ (50 mL) was added to the reaction mixture and purification was carried out by washing three times with water followed by the drying under vacuum to constant weight. Yield 85%, white solid, mp 136 °C, ^{1}H NMR (CD_3OD, 400 MHz, 25 °C, ppm): 0.80 (t, J = 6.8 Hz, 12H, CH_3CH_2), 1.32−1.51 (m, 8H, CH_3CH_2), 1.60−1.78 (m, 4H, C(=O)NHCH$_2$CH$_2$CH$_2$), 1.89−1.94 (m, 2H, (CH$_3$CH$_2$)$_2$CH)), 2.51−2.58 (m, 4H, CH$_2$CH$_2$C(=O)OH), 3.07−3.18 (m, 4H, C(=O)NHCH$_2$CH$_2$CH$_2$), 3.22−3.28 (m, 4H, C(=O)NHCH$_2$CH$_2$CH$_2$), 7.81 (brs, 1H, C(=O)NH), 7.99 (brs, 1H, C(=O)NH), 12.18 (brs, 1H, C(=O)OH). ^{13}C NMR (CD_3OD, 100 MHz, 25 °C, ppm): 12.5, 26.8, 28.7, 29.9, 37.6, 44.6, 46.8, 52.0, 173.9, 176.4, 178.5, 178.8. MS(FAB): [MH]$^+$, calcd for $C_{22}H_{41}N_3O_5$ 428.3119, found 428.3130. Anal. Calcd for $C_{22}H_{41}N_3O_5$: C, 61.80; H, 9.67; N, 9.83; O, 18.71. Found: C, 61.61; H, 9.78; N, 9.72; O, 18.89.

***N,N*′-(3,3′-Azanediylbis(propane-3,1-diyl))bis(2-propylpentanamide) (G1-b-I).** It was synthesized by using 2-propylpentanoic acid (44.9 mL, 0.312 mol) rather than 2-ethylbutanoic acid while the rest of the conditions and procedure were the same as those for the synthesis of **G1-a-I**. Yield 84%, white solid, mp 92 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C, ppm): 0.84 (t, J = 7.2 Hz, 12H, CH_3CH_2), 1.18−1.34 (m, 8H, CH_3CH_2), 1.49−1.55 (m, 8H, CH$_3$CH$_2$CH$_2$), 1.62−1.68 (m, 4H, C(=O)NHCH$_2$CH$_2$CH$_2$), 1.99−2.06 (m, 2H, (CH$_3$CH$_2$CH$_2$)$_2$CH)), 2.15 (brs, 1H, CH$_2$NHCH$_2$), 2.56−2.64 (m, 4H, C(=O)NHCH$_2$CH$_2$CH$_2$), 3.29−3.34 (m, 4H, C(=O)NHCH$_2$CH$_2$CH$_2$), 6.63 (brs, 2H, C(=O)NH). ^{13}C NMR ($CDCl_3$, 100 MHz, 25 °C, ppm): 14.0, 20.8, 29.1, 35.2, 37.0, 46.7, 47.5, 176.4. MS(FAB): [MH]$^+$, calcd for $C_{22}H_{45}N_3O_2$ 384.3585, found 384.3588. Anal. Calcd for $C_{22}H_{45}N_3O_2$: C, 68.88; H, 11.82; N, 10.95; O, 8.35. Found: C, 68.69; H, 11.68; N, 10.98; O, 8.65.

4-(Bis(3-(2-propylpentanamido)propyl)amino)-4-oxobutanoic Acid (G1-b-II). The reaction of **G1-b-I** (25 g, 0.065 mol) with succinic anhydride (9.79 g, 0.097 mol) and the purification of the product were carried out in the same way as that for the synthesis of **G1-a-II**. Yield 95%, white solid, mp 151 °C. ^{1}H NMR (CD_3OD, 400 MHz, 25 °C, ppm): 0.84 (t, J = 6.8 Hz, 12H, CH_3CH_2), 1.18−1.28 (m, 8H, CH_3CH_2), 1.42−1.53 (m, 8H, CH$_3$CH$_2$CH$_2$), 1.60−1.79 (m, 4H, C(═O)NHCH$_2$C*H*$_2$CH$_2$), 2.09−2.17 (m, 2H, (CH$_3$CH$_2$CH$_2$)$_2$C*H*)), 2.53−2.58 (m, 4H, C*H*$_2$C*H*$_2$C(═O)OH), 3.06−3.17 (m, 4H, C(═O)NHCH$_2$CH$_2$C*H*$_2$), 3.22−3.34/3.28 (m, 4H, C(═O)NHC*H*$_2$CH$_2$CH$_2$), 7.87 (brs, 1H, C(═O)N*H*), 8.05 (brs, 1H, C(═O)N*H*). ^{13}C NMR (CD$_3$OD, 100 MHz, 25 °C, ppm): 14.4, 21.8, 28.8, 30.1, 36.4, 37.6, 44.6, 46.8, 47.9, 173.9, 176.4, 178.7, 179.1. MS(FAB): [MH]$^+$, calcd for $C_{26}H_{49}N_3O_5$ 484.3745, found 484.3749. Anal. Calcd for $C_{26}H_{49}N_3O_5$: C, 64.56; H, 10.21; N, 8.69; O, 16.54, Found: C, 64.59; H, 9.98; N, 8.62; O, 16.81.

_N_,_N_′-(3,3′-Azanediylbis(propane-3,1-diyl))bis(2-ethylhexanamide) (G1-c-I). It was synthesized by using 2-ethylhexanoic acid (44.9 mL, 0.312 mol) rather than 2-ethylbutanoic acid whereas the rest of the conditions and procedure were the same as those for the synthesis of **G1-a-I**. Yield 89%, white solid, mp 50 °C. ^{1}H NMR (CDCl$_3$, 400 MHz, 25 °C, ppm): 0.81−0.85 (m, 12H, C*H*$_3$CH$_2$), 1.16−1.28 (m, 8H, CH$_3$C*H*$_2$C*H*$_2$CH$_2$), 1.31−1.44 (m, 4H, CH$_3$CH$_2$CH$_2$C*H*$_2$), 1.50−1.67 (m, 8H, CH$_3$C*H*$_2$, C(═O)NHCH$_2$C*H*$_2$CH$_2$), 1.85−1.94 (m, 2H, (CH$_3$CH$_2$CH$_2$CH$_2$)(CH$_3$CH$_2$)C*H*), 2.28 (brs, 1H, CH$_2$N*H*CH$_2$), 2.55−2.63 (m, 4H, C(═O)NHCH$_2$CH$_2$C*H*$_2$), 3.27−3.37 (m, 4H, C(═O)NHC*H*$_2$CH$_2$CH$_2$), 6.57 (brs, 2H, C(═O)N*H*). ^{13}C NMR (CDCl$_3$, 100 MHz, 25 °C, ppm): 11.9, 13.8, 22.6, 25.9, 29.1, 29.8, 32.4, 37.0, 46.8, 49.4, 176.1. MS(FAB): [MH]$^+$, calcd for $C_{22}H_{45}N_3O_2$ 384.3585, found 384.3593. Anal. Calcd for $C_{22}H_{45}N_3O_2$: C, 68.88; H, 11.82; N, 10.95; O, 8.35. Found: C, 68.66; H, 11.91; N, 10.71; O, 8.72.

4-(Bis(3-(2-ethylhexanamido)propyl)amino)-4-oxobutanoic Acid (G1-c-II). The reaction of **G1-c-I** (25 g, 0.065 mol) with succinic anhydride (9.79 g, 0.097 mol) and the purification of the product were carried out in the same way as that for the synthesis of **G1-a-II**. Yield 96%, white solid, mp 115 °C, ^{1}H NMR (CD$_3$OD, 400 MHz, 25 °C, ppm): 0.85−0.90 (m, 12H, C*H*$_3$CH$_2$), 1.22−1.47 (m, 8H, CH$_3$C*H*$_2$C*H*$_2$CH$_2$), 1.51−1.59 (m, 4H, CH$_3$CH$_2$CH$_2$C*H*$_2$), 1.68−1.75 (m, 4H, CH$_3$C*H*$_2$), 1.79−1.87 (m, 4H, C(═O)NHCH$_2$C*H*$_2$CH$_2$), 2.03−2.12 (m, 2H, (CH$_3$CH$_2$CH$_2$CH$_2$)(CH$_3$CH$_2$)C*H*), 2.59−2.65 (m, 4H, C*H*$_2$C*H*$_2$C(═O)OH), 3.14−3.25 (m, 4H, C(═O)NHCH$_2$CH$_2$C*H*$_2$), 3.36−3.41 (m, 4H, C(═O)NHC*H*$_2$CH$_2$CH$_2$), 7.89 (brs, 1H, C(═O)N*H*), 8.10 (brs, 1H, C(═O)N*H*). ^{13}C NMR (CD$_3$OD, 100 MHz, 25 °C, ppm): 12.4, 14.4, 23.7, 27.2, 28.9, 29.7, 30.1, 33.6, 37.6, 44.7, 46.9, 50.2, 174.0, 176.5, 178.7, 179.0. MS(FAB): [MH]$^+$, calcd for $C_{26}H_{49}N_3O_5$ 484.3745, found 484.3750. Anal. Calcd for $C_{26}H_{49}N_3O_5$: C, 64.56; H, 10.21; N, 8.69; O, 16.54. Found: C, 64.58; H, 10.23; N, 8.62; O, 16.57.

_N_^{1},_N_$^{1\prime}$-(3,3′-Azanediylbis(propane-3,1-diyl))bis(_N_^{4},_N_^{4}-bis(3-(2-ethylbutanamido)propyl)succinamide) (G2-a-I). The synthesis of **G2-a-I** was accomplished in the same way as that of **G1-a-I** by making use of **G1-a-II** instead of 2-ethylbutanoic acid and the product was purified by washing with water. Yield 55%, white solid, mp 148−149 °C, ^{1}H NMR (CD$_3$OD, 400 MHz, 25 °C, ppm): 0.85−0.90 (m, 24H, C*H*$_3$CH$_2$), 1.43−1.58 (m, 16H, CH$_3$C*H*$_2$), 1.66−1.72 (m, 4H, C(═O)NHCH$_2$C*H*$_2$CH$_2$NH), 1.79−1.86 (m, 8H, C(═O)NHCH$_2$C*H*$_2$CH$_2$), 1.95−2.05 (m, 4H, (CH$_3$CH$_2$)$_2$C*H*)), 2.21 (brs, 1H, CH$_2$N*H*CH$_2$), 2.47−2.67 (m, 12H, C(═O)NHCH$_2$CH$_2$C*H*$_2$NH, C(═O)C*H*$_2$C*H*$_2$C(═O)), 3.14−3.25 (m, 12H, C(═O)NHCH$_2$CH$_2$C*H*$_2$NC(═O), C(═O)NHC*H*$_2$CH$_2$CH$_2$NH), 3.34−3.40 (m, 8H, C(═O)NHC*H*$_2$CH$_2$CH$_2$), 7.94 (brs, 2H, C(═O)N*H*), 8.15 (brs, 4H, C(═O)N*H*). ^{13}C NMR (CD$_3$OD, 100 MHz, 25 °C, ppm): 12.5, 26.8, 28.6, 29.2, 30.1, 31.8, 37.7, 38.3, 44.7, 46.8, 52.0, 174.0, 174.8, 178.5, 178.8. MS(FAB): [MH]$^+$, calcd for $C_{50}H_{95}N_9O_8$ 950.7376, found 950.7383. Anal. Calcd for $C_{50}H_{95}N_9O_8$: C, 63.19; H, 10.08; N, 13.26; O, 13.47. Found: C, 62.94; H, 10.13; N, 13.18; O, 13.75.

G2-a-II. It was synthesized by the reaction of **G2-a-I** (10 g, 0.010 mol) with succinic anhydride (1.58 g, 0.016 mol) under the same conditions as those for the synthesis of **G1-a-II** and the product was purified by washing with water. Yield 68%, white solid, mp 156 °C, ^{1}H NMR (CD$_3$OD, 400 MHz, 25 °C, ppm): 0.78−0.83 (m, 24H, C*H*$_3$CH$_2$), 1.35−1.51 (m, 16H, CH$_3$C*H*$_2$), 1.62−1.81 (m, 12H, C(═O)NHCH$_2$C*H*$_2$CH$_2$), 1.90−1.96 (m, 4H, (CH$_3$CH$_2$)$_2$C*H*)), 2.41−2.63 (m, 12H, C(═O)C*H*$_2$C*H*$_2$C(═O)), 3.07−3.24 (m, 16H, C(═O)NHCH$_2$CH$_2$C*H*$_2$, C(═O)NHC*H*$_2$CH$_2$CH$_2$), 3.32−3.36 (m, 8H, C(═O)NHC*H*$_2$CH$_2$CH$_2$), 7.89 (brs, 2H, C(═O)N*H*), 8.07 (brs, 4H, C(═O)N*H*). ^{13}C NMR (CD$_3$OD, 100 MHz, 25 °C, ppm): 12.5, 26.8, 28.4, 28.7, 29.1, 29.7, 31.8, 37.8, 44.7, 46.7, 51.9, 173.9, 174.2, 174.3, 178.5, 178.8. MS(FAB): [MH]$^+$, calcd for $C_{54}H_{99}N_9O_{11}$ 1050.7537, found 1050.7543. Anal. Calcd for $C_{54}H_{99}N_9O_{11}$: C, 61.74; H, 9.50; N, 12.00; O, 16.76. Found: C, 61.90; H, 9.51; N, 11.95; O, 16.64.

_N_^{1},_N_$^{1\prime}$-(3,3′-Azanediylbis(propane-3,1-diyl))bis(_N_^{4},_N_^{4}-bis(3-(2-propylpentanamido)propyl)succinamide) (G2-b-I). The synthesis of **G2-b-I** was carried out in the same way as that of **G1-a-I** by making use of **G1-b-II** instead of 2-ethylbutanoic acid, and the product was isolated by washing with water. Yield 73%, white solid, mp 146−147 °C, ^{1}H NMR (CD$_3$OD, 400 MHz, 25 °C, ppm): 0.90 (t, J = 7.0 Hz, 24H, C*H*$_3$CH$_2$), 1.24−1.37 (m, 16H, CH$_3$C*H*$_2$), 1.51−1.58 (m, 16H, CH$_3$CH$_2$C*H*$_2$), 1.67−1.73 (m, 4H, C(═O)NHCH$_2$C*H*$_2$CH$_2$NH), 1.78−1.85 (m, 8H, (C(═O)NHCH$_2$C*H*$_2$CH$_2$), 2.03 (brs, 1H, CH$_2$N*H*CH$_2$), 2.15−2.25 (m, 4H, (CH$_3$CH$_2$CH$_2$)$_2$C*H*), 2.47−2.51 (m, 4H, C(═O)NHCH$_2$CH$_2$C*H*$_2$NH), 2.62−2.67 (m, 8H, C(═O)C*H*$_2$C*H*$_2$C(═O)), 3.12−3.24 (m, 12H, C(═O)NHCH$_2$CH$_2$C*H*$_2$NC(═O), C(═O)NHC*H*$_2$CH$_2$CH$_2$NH), 3.33−3.39 (m, 8H, C(═O)NHC*H*$_2$CH$_2$CH$_2$), 7.95 (brs, 2H, C(═O)N*H*), 8.11 (brs, 4H, C(═O)N*H*). ^{13}C NMR (CD$_3$OD, 100 MHz, 25 °C, ppm): 14.4, 21.8, 28.6, 29.2, 29.8, 31.8, 36.4, 37.7, 38.1, 44.7, 46.8, 47.9, 174.0, 174.9, 178.7, 179.0. MS(FAB): [MH]$^+$, calcd for $C_{58}H_{111}N_9O_8$ 1062.8628, found 1062.8636. Anal. Calcd for $C_{58}H_{111}N_9O_8$: C, 65.56; H, 10.53; N, 11.86; O, 12.05. Found: C, 65.49; H, 10.67; N, 11.99; O, 11.85.

G2-b-II. It was synthesized by the reaction of **G2-b-I** (10 g, 0.009 mol) with succinic anhydride (1.41 g, 0.014 mol) under the same conditions as those for the synthesis of **G1-a-II** and the product was purified by washing with water. Yield 88%, white solid, mp 141 °C, ^{1}H NMR (CD$_3$OD, 400 MHz, 25 °C, ppm): 0.89 (t, J = 6.8 Hz, 24H, C*H*$_3$CH$_2$), 1.22−1.39 (m, 16H, CH$_3$C*H*$_2$), 1.49−1.59 (m, 16H, CH$_3$CH$_2$C*H*$_2$), 1.66−1.86 (m, 12H, C(═O)NHCH$_2$C*H*$_2$CH$_2$), 2.16−2.23 (m, 4H, (CH$_3$CH$_2$CH$_2$)$_2$C*H*), 2.49−2.68 (m, 12H, C(═O)C*H*$_2$C*H*$_2$C(═O)), 3.12−3.23 (m, 12H, C(═O)NHCH$_2$CH$_2$C*H*$_2$), 3.33−3.41 (m, 12H, C(═O)NHC*H*$_2$CH$_2$CH$_2$), 7.96 (brs, 2H, C(═O)N*H*), 8.12 (brs, 4H, C(═O)N*H*). ^{13}C NMR (CD$_3$OD, 100 MHz, 25 °C, ppm): 14.4, 21.9, 28.4, 28.6, 28.9, 29.1, 29.2, 29.6, 31.7, 36.4, 37.8, 44.7, 46.7, 48.0, 174.0, 174.7, 174.9, 178.8, 179.1. MS(FAB): [MH]$^+$, calcd for $C_{62}H_{115}N_9O_{11}$ 1162.8789, found 1162.8795. Anal. Calcd for $C_{62}H_{115}N_9O_{11}$: C, 64.05; H, 9.97; N, 10.84; O, 15.14. Found: C, 63.88; H, 9.75; N, 11.08; O, 15.29.

_N_^{1},_N_$^{1\prime}$-(3,3′-Azanediylbis(propane-3,1-diyl))bis(_N_^{4},_N_^{4}-bis(3-(2-ethylhexanamido)propyl)succinamide) (G2-c-I). The synthesis of **G2-c-I** was carried out in the same way as that of **G1-a-I** by making use of **G1-c-II** instead of 2-ethylbutanoic acid and the product was isolated by washing with water. Yield 91%, white solid, mp 99 °C, ^{1}H NMR (CD$_3$OD, 400 MHz, 25 °C, ppm): 0.85−0.90 (m, 24H, C*H*$_3$CH$_2$), 1.21−1.45 (m, 24H, CH$_3$C*H*$_2$C*H*$_2$C*H*$_2$), 1.50−1.59 (m, 8H, CH$_3$C*H*$_2$), 1.64−1.74 (m, 4H, C(═O)NHCH$_2$C*H*$_2$CH$_2$NH), 1.79−1.84 (m, 8H, (C(═O)NHCH$_2$C*H*$_2$CH$_2$), 2.04−2.11 (m, 4H, (CH$_3$CH$_2$CH$_2$CH$_2$)(CH$_3$ CH$_2$)C*H*), 2.23 (brs, 1H, CH$_2$N*H*CH$_2$), 2.47−2.67 (m, 12H, C(═O)NHCH$_2$CH$_2$C*H*$_2$NH, C(═O)C*H*$_2$C*H*$_2$C(═O)), 3.13−3.24 (m, 12H, C(═O)NHCH$_2$CH$_2$C*H*$_2$NC(═O), C(═O)NHC*H*$_2$CH$_2$CH$_2$NH), 3.34−3.41 (m, 8H, C(═O)NHC*H*$_2$CH$_2$CH$_2$), 7.91 (brs, 2H, C(═O)N*H*), 8.08 (brs, 4H, C(═O)N*H*). ^{13}C NMR (CD$_3$OD, 100 MHz, 25 °C, ppm): 12.5, 14.4, 23.7, 27.2, 28.6, 29.2, 29.7, 30.1, 30.9, 31.8, 33.6, 37.7, 38.2, 44.7, 46.8, 174.0, 174.8, 178.7, 179.0. MS(FAB): [MH]$^+$, calcd for $C_{58}H_{111}N_9O_8$ 1062.8628, found 1062.8620. Anal. Calcd for $C_{58}H_{111}N_9O_8$: C, 65.56; H, 10.53; N, 11.86; O, 12.05. Found: C, 65.61; H, 10.50; N, 11.77; O, 12.12.

G2-c-II. It was synthesized by the reaction of **G2-c-I** (10 g, 0.009 mol) with succinic anhydride (1.41 g, 0.014 mol) under the same conditions as those for the synthesis of **G1-a-II**, and the product was purified by washing with water. Yield 94%, white solid, mp 118−119 °C, ^{1}H NMR (CD$_3$OD, 400 MHz, 25 °C, ppm): 0.85−0.90 (m, 24H, C*H*$_3$CH$_2$), 1.21−1.45 (m, 24H, CH$_3$C*H*$_2$C*H*$_2$C*H*$_2$), 1.51−1.57 (m, 8H, CH$_3$C*H*$_2$), 1.69−1.85 (m, 12H, C(═O)NHCH$_2$C*H*$_2$CH$_2$), 2.01−2.10 (m, 4H, (CH$_3$CH$_2$CH$_2$CH$_2$)(CH$_3$CH$_2$)C*H*), 2.48−2.67 (m, 12H, C(═O)C*H*$_2$C*H*$_2$C(═O)), 3.13−3.25 (m, 12H, $C(=O)NHCH_2CH_2CH_2$), 3.34−3.41 (m, 12H, $C(=O)NHCH_2CH_2CH_2$), 7.93 (brs, 2H, $C(=O)NH$), 8.10 (brs, 4H, $C(=O)NH$). ^{13}C NMR (CD_3OD, 100 MHz, 25 °C, ppm): 12.5, 14.4, 23.7, 27.2, 28.7, 29.2, 29.7, 30.3, 31.0, 31.7, 31.9, 33.6, 37.7, 37.8, 44.7, 46.9, 50.2, 173.9, 174.7, 174.9, 178.7, 178.9. MS(FAB): $[MH]^+$, calcd for $C_{62}H_{115}N_9O_{11}$ 1162.8789, found 1162.8779. Anal. Calcd for $C_{62}H_{115}N_9O_{11}$: C, 64.05; H, 9.97; N, 10.84; O, 15.14. Found: C, 63.76; H, 9.85; N, 11.03; O, 15.36.

Synthesis of Dendronized Ethyl Cellulose. 2a. A 200 mL one-necked flask was equipped with a stopper and a magnetic stirring bar. Ethyl cellulose, **1**, (1.43 g, 6.10 mmol) and 4-(dimethylamino)pyridine (0.75 g, 6.10 mmol) were added to the flask and dissolved in CH_2Cl_2 (50 mL) at room temperature, followed by the addition of **G1-a-II** (2.61 g, 6.10 mmol) and EDC·HCl (1.17 g, 6.10 mmol), respectively, and stirring was continued for 48 h at room temperature. The product was isolated by the precipitation in aqueous $NaHCO_3$ solution (1000 mL), filtered with a membrane filter, washed with water several times to ensure the complete removal of $NaHCO_3$, and dried under vacuum to constant weight to afford the desired product as a beige solid. Yield 95%, ^1H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 0.85 (brs, 3.72H, CH_3CH_2), 1.13 (brs, 8.07H, OCH_2CH_3), 1.44 (brs, 2.48H, CH_3CH_2), 1.57 (brs, 1.24H, $C(=O)NHCH_2CH_2CH_2$), 1.86 (brs, 0.62H, $(CH_3CH_2)_2CH$), 2.07 (brs, 1.86H, $CH_2CH_2C(=O)O$), 2.50−4.51 (m, (12.4H, OCH_2CH_3, OCH, OCH_2) and (2.48H, $C(=O)NHCH_2CH_2CH_2$)), 6.26 (brs, 0.31H, $C(=O)NH$), 6.68 (brs, 0.31H, $C(=O)NH$). IR (attenuated total reflection (ATR), cm^{-1}): 3310 (ν_{NH}), 2970, 2873, 1746 (ν_{CO}), 1645, 1539, 1443, 1375, 1277, 1228, 1088, 1052, 921, 883, 798, 674. Anal. Calcd for $(C_{18.2}H_{32.85}N_{0.93}O_{6.24})_n$ $(364.57)_n$: C, 59.96; H, 9.08; N, 3.57; O, 27.39. Found: C, 59.36; H, 8.56; N, 3.99; O, 28.09.

2b. This derivative was prepared by following the same procedure as for **2a** using **G1-b-II** (2.95 g, 6.10 mmol) instead of **G1-a-II**. Yield 93%, peach-colored solid, ^1H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 0.86 (brs, 3.72H, CH_3CH_2), 1.13 (brs, 8.07H, OCH_2CH_3), 1.24 (brs, 4.96H, $CH_3CH_2CH_2$), 1.55 (brs, 1.24H, $C(=O)NHCH_2CH_2CH_2$), 1.82 (brs, 0.62H, $(CH_3CH_2CH_2)_2CH$), 2.04 (brs, 1.24H, $CH_2CH_2C(=O)O$), 2.51−4.60 (m, (12.4H, OCH_2CH_3, OCH, OCH_2) and (2.48H, $C(=O)NHCH_2CH_2CH_2$)), 6.03 (brs, 0.31H, $C(=O)NH$), 6.64 (brs, 0.31H, $C(=O)NH$). IR (ATR, cm^{-1}): 3308 (ν_{NH}), 2973, 2930, 2872, 1743 (ν_{CO}), 1646, 1539, 1443, 1375, 1309, 1265, 1091, 1053, 920, 882, 794, 656. Anal. Calcd for $(C_{19.4}H_{35.3}N_{0.93}O_{6.24})_n$ $(381.96)_n$: C, 61.13; H, 9.32; N, 3.41; O, 26.14. Found: C, 60.56; H, 9.26; N, 3.49; O, 26.69.

2c. This derivative was prepared by following the same procedure as for **2a** using **G1-c-II** (2.95 g, 6.10 mmol) instead of **G1-a-II**. Yield 98%, off-white solid, ^1H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 0.84 (brs, 3.72H, CH_3CH_2), 1.13 (brs, 8.07H, OCH_2CH_3), 1.23 (brs, 2.48H, $CH_3CH_2CH_2CH_2$), 1.39 (brs, 1.24H, $CH_3CH_2CH_2CH_2$), 1.56 (brs, 1.24H, CH_3CH_2), 1.82 (brs, 1.24H, $C(=O)NHCH_2CH_2CH_2$), 1.92 (brs, 0.62H $(CH_3CH_2CH_2CH_2)(CH_3CH_2)CH$), 2.11 (brs, 1.24H, $CH_2CH_2C(=O)O$), 2.49−4.45 (m, (12.4H, OCH_2CH_3, OCH, OCH_2) and (2.48H, $C(=O)NHCH_2CH_2CH_2$)), 6.14 (brs, 0.31H, $C(=O)NH$), 6.63 (brs, 0.31H, $C(=O)NH$). IR (ATR, cm^{-1}): 3299 (ν_{NH}), 2970, 2930, 2871, 1744 (ν_{CO}), 1645, 1541, 1458, 1376, 1300, 1272, 1232, 1091, 1053, 920, 855, 798. Anal. Calcd for $(C_{19.4}H_{35.3}N_{0.93}O_{6.24})_n$ $(381.96)_n$: C, 61.13; H, 9.32; N, 3.41; O, 26.14. Found: C, 60.74; H, 9.37; N, 3.88; O, 26.01.

3a. This derivative was prepared by following the same procedure as for **2a** using **G2-a-II** (6.41 g, 6.10 mmol) instead of **G1-a-II**. Yield 92%, peach-colored solid, ^1H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 0.845 (brs, 7.44H, CH_3CH_2), 1.12 (brs, 8.07H, OCH_2CH_3), 1.43 (brs, 4.96H, CH_3CH_2), 1.55−1.64 (m, 3.72H, $C(=O)NHCH_2CH_2CH_2$), 1.86 (brs, 1.24H, $(CH_3CH_2)_2CH$), 2.15 (brs, 1.24H, $C(=O)CH_2CH_2C(=O)$), 2.47−4.59 (m, (12.4H, OCH_2CH_3, OCH, OCH_2) and (9.92H, $C(=O)CH_2CH_2C(=O)$, $C(=O)NHCH_2CH_2CH_2$)), 6.55 (brs, 0.62H, $C(=O)NH$), 6.65 (brs, 1.24H, $C(=O)NH$). IR (ATR, cm^{-1}): 3300 (ν_{NH}), 3090, 2960, 2928, 2873, 1744 (ν_{CO}), 1638, 1540, 1455, 1378, 1276, 1231, 1091, 1058, 920, 856, 804. Anal. Calcd for $(C_{28.12}H_{50.8}N_{2.8}O_{8.1})_n$ $(557.65)_n$: C, 60.57; H, 9.19; N, 7.01; O, 23.23. Found: C, 60.02; H, 9.28; N, 7.59; O, 23.11.

3b. This derivative was prepared by following the same procedure as for **2a** using **G2-b-II** (7.1 g, 6.10 mmol) instead of **G1-a-II**. Yield 96%, light peach-colored solid, ^1H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 0.85 (brs, 7.44H, CH_3CH_2), 1.11−1.36 (m, (8.07H, OCH_2CH_3) and (9.92H, $CH_3CH_2CH_2$)), 1.51−1.65 (m, 3.72H, $C(=O)NHCH_2CH_2CH_2$), 1.82 (brs, 1.24H, $(CH_3CH_2CH_2)_2CH$), 2.07 (brs, 1.24H, $C(=O)CH_2CH_2C(=O)$), 2.47−4.59 (m, (12.4H, OCH_2CH_3, OCH, OCH_2) and (9.92H, $C(=O)CH_2CH_2C(=Om)$, $C(=O)NHCH_2CH_2CH_2$)), 6.73 (brs, 0.62H, $C(=O)NH$), 6.99 (brs, 1.24H, $C(=O)NH$). IR (ATR, cm^{-1}): 3292 (ν_{NH}), 3075, 2972, 2929, 2871, 1739 (ν_{CO}), 1635, 1542, 1441, 1378, 1257, 1221, 1091, 1053, 879, 802, 710. Anal. Calcd for $(C_{30.6}H_{55.8}N_{2.8}O_{8.1})_n$ $(592.43)_n$: C, 62.04; H, 9.49; N, 6.60; O, 21.87. Found: C, 62.58; H, 9.11; N, 7.09; O, 21.22.

3c. This derivative was prepared by following the same procedure as for **2a** using **G2-c-II** (7.1 g, 6.10 mmol) instead of **G1-a-II**. Yield 90%, light yellow solid, ^1H NMR (400 MHz, $CDCl_3$, 25 °C, ppm): 0.83 (brs, 7.44H, CH_3CH_2), 1.12 (brs, 8.07H, OCH_2CH_3), 1.22 (brs, 4.96H, $CH_3CH_2CH_2CH_2$), 1.38 (brs, 2.48H, $CH_3CH_2CH_2CH_2$), 1.55 (brs, 2.48H, CH_3CH_2), 1.63 (brs, 3.72H, $C(=O)NHCH_2CH_2CH_2$), 1.83 (brs, 1.24H, $(CH_3CH_2CH_2CH_2)(CH_3CH_2)CH$), 1.95 (brs, 1.24H, $C(=O)CH_2CH_2C(=O)$), 2.44−4.61 (m, (12.4H, OCH_2CH_3, OCH, OCH_2) and (9.92H, $C(=O)NHCH_2CH_2CH_2$)), 6.60 (brs, 0.62H, $C(=O)NH$), 6.95 (brs, 1.24H, $C(=O)NH$). IR (ATR, cm^{-1}): 3294 (ν_{NH}), 3080, 2958, 2929, 2872, 1732 (ν_{CO}), 1636, 1545, 1456, 1379, 1232, 1123, 1091, 1053, 853, 806, 707. Anal. Calcd for $(C_{30.6}H_{55.8}N_{2.8}O_{8.1})_n$ $(592.43)_n$: C, 62.04; H, 9.49; N, 6.60; O, 21.87. Found: C, 61.45; H, 9.16; N, 7.13; O, 22.26.

Determination of the Degree of Substitution. The degree of substitution with ethyl group (DS_{Et}) of the starting material, **1**, was determined by ^1H NMR measurement, which also provided a clear indication of the incorporation of the dendritic moieties into ethyl cellulose. However, the overlapping of the peaks arising due to the methyl protons of the dendritic moiety and those of ethyl cellulose did not allow the exact estimation of the degree of esterification (DS_{Est}) which was determined by the elemental analysis (%N content) of the polymers (**2a**−**c**, **3a**−**c**). The total degree of substitution (DS_{total}) of **2a**−**c** and **3a**−**c** was calculated by the following equation:

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

Membrane Fabrication. Membranes (thickness approximately 40−80 μm) of polymers **1** and **2a**−**c** were fabricated by casting their chloroform solution (concentration approximately 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.[15] This method makes use of a liquid with known density (ρ_0), and membrane density (ρ) is calculated by the following equation:

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

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 to measure the density of the polymer membranes.

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 thus the amount of space (free volume) available for gas permeation in the polymer matrix. FFV is calculated by the following equation:[16]

$$FFV = \frac{(v_{sp} - v_0)}{v_{sp}} \approx \frac{(v_{sp} - 1.3\, v_w)}{v_{sp}}$$

Chart 1. Structure of G1 and G2 Amidoimide Dendrons

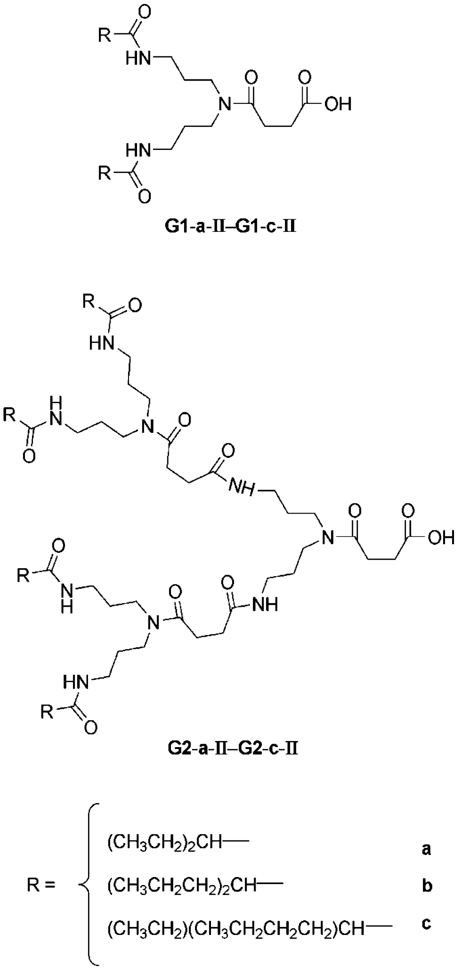


Table 1. Degree of Substitution (*DS*) and Molecular Weight of Polymers 1, 2a−c, and 3a−c

polymer	DS_{total}	$M_n{}^c$	$M_w{}^c$	$M_w/M_n{}^c$
1	2.69^a	71 000	237 000	3.3
2a	≈3.00^b	222 000	750 000	3.4
2b	≈3.00^b	225 000	677 000	3.0
2c	≈3.00^b	226 000	739 000	3.3
3a	≈3.00^b	—^{d}	—^{d}	—^{d}
3b	≈3.00^b	—^{d}	—^{d}	—^{d}
3c	≈3.00^b	—^{d}	—^{d}	—^{d}

[a] Determined by ^{1}H NMR. [b] Determined by elemental analysis. [c] Determined by GPC (0.01 M LiBr in DMF as eluent). [d] Could not be determined.

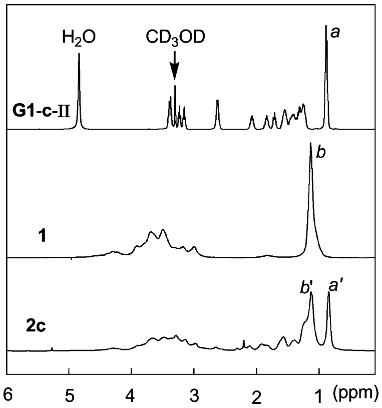


Figure 1. ^{1}H NMR spectra of **G1-c-II**, **1**, and **2c**. Labels: *a*, terminal methyl protons of dendron; *b*, terminal methyl protons of ethyl cellulose; *a′*, terminal methyl protons derived from the dendron; *b′*, terminal methyl protons derived from ethyl cellulose.

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 method.[17]

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.[18] The gas diffusion coefficients (*D*) were determined by the time lag method using the following equation:

$$D = \frac{l^2}{6\theta}$$

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 of 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 arising due to the baseline drift became serious. The gas solubility coefficients (*S*) were calculated by using the equation, $S = P/D$.

Results and Discussion

Dendron Synthesis. A series of G1 and G2 amidoimide dendrons with branched alkyl periphery and focal carboxyl moiety (Chart 1) were prepared via a convergent pathway[19] as shown in Scheme 1. The first generation amidoimide dendrons (**G1-a-II−G1-c-II**) were prepared by the reaction of branched aliphatic acids with 1,1′-carbonyldiimidazole and subsequently with *N*-(3-aminopropyl)propane-1,3-diamine generating a secondary amine at the focal point (**G1-a-I−G1-c-I**), which upon further treatment with succinic anhydride afforded a carboxyl moiety at the dendron termini. The second generation dendrons (**G2-a-II−G2-c-II**) were prepared by the iteration of the same three-step reaction sequence.[20] The presence of the branched alkyl periphery helps prevent the dendrons from being insoluble in common organic solvents thus making the otherwise cumbersome purification quite practicable, and the presence of carboxyl functionality at the dendron termini renders them capable to be engineered for various applications. All of the synthetic procedures were carried out several times and can be considered optimized. The characterization of the first and second generation amidoimide dendrons was accomplished by ^{1}H and ^{13}C NMR spectroscopy, mass spectrometry, and elemental analysis.

Synthesis of Dendronized Ethyl Cellulose. The incorporation of dendritic moieties (**G1-a-II−G1-c-II** and **G2-a-II−G2-c-II**) into ethyl cellulose (**1**) was carried out by coupling the carboxyl termini of dendrons to the hydroxy functionalities of ethyl cellulose; *N*-(3-dimethylaminopropyl)-*N′*-ethylcarbodiimide hydrochloride (EDC·HCl) was employed as a condensating agent and 4-(dimethylamino)pyridine (DMAP) as a base, as shown in Scheme 2, and the results are summarized in Table 1. The dendronized ethyl cellulose derivatives (**2a−c** and **3a−c**) were characterized by the ^{1}H NMR and IR spectroscopy and elemental analysis. 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.[21] The ^{1}H NMR spectra of one of the G1 dendrons (**G1-c-II**), ethyl cellulose (**1**), and the corresponding dendronized ethyl cellulose (**2c**) are shown in Figure 1, and similar information for a G2-derivatized ethyl cellulose (**3c**) is depicted in Figure 2. Although the ^{1}H NMR spectra of the dendronized polymers provide a clear indication of the substitu-

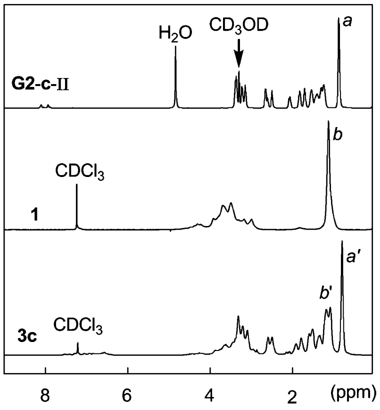


Figure 2. ^{1}H NMR spectra of **G2-c-II**, **1**, and **3c**. Labels: *a*, terminal methyl protons of dendron; *b*, terminal methyl protons of ethyl cellulose; *a′*, terminal methyl protons derived from the dendron; *b′*, terminal methyl protons derived from ethyl cellulose.

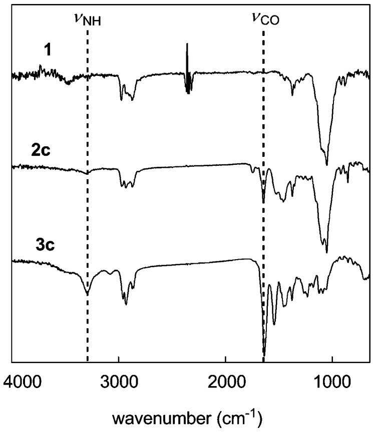


Figure 3. FTIR spectra of **1**, **2c**, and **3c**.

tion of hydroxy protons by the dendritic moieties, the calculation of the exact degree of esterification could not be carried out due to the overlapping of the peaks arising from the methyl protons of the ethyl group of ethyl cellulose and those of the dendrons' periphery. Further evidence was furnished by the presence of the peaks characteristic of the carbonyl group of an ester (1732−1746 cm^{-1}) in the IR spectra of the dendronized derivatives (**2a**−**c** and **3a**−**c**). The IR spectrum of **1** (Figure 3) has a broad band due to the residual hydroxy groups (3200−3600 cm^{-1}), which did not disappear completely upon dendronization as the NH groups of the dendritic moiety also absorb IR radiation in the same wavenumber region.

Despite the fact that the starting as well as the dendronized polymers are soluble in chloroform, the attempts to carry out molecular weight determination by GPC, using chloroform as an eluent, were unsuccessful to yield satisfactory and reproducible results probably due to the aggregation of the polymers. Therefore, molecular weights of the polymers were determined by making use of the LiBr solution in DMF (10 mM), and reproducible results were obtained for G1-derivatized ethyl cellulose (**2a**−**c**). According to GPC data of the polymers (Table 1), the number-average molecular weight (M_n) of **1** was found to be 71 000 and a significant increase in the M_n values ($\geq$222 000) was observed as a consequence of the substitution of small hydroxy groups with fairly bulky G1 dendritic moieties. Meanwhile, the polydispersity indices (M_w/M_n) of the dendronized polymers (**2a**−**c**) were not quite different from those of **1**. For instance, the M_n and M_w/M_n of **1** were observed to be 71 000 and 3.3, respectively, while those of **2a** were 222 000 and 3.4. These facts rule out the possibility of polymer chain cleavage in the course of esterification. However, observed M_n values were twice those of the theoretical ones for G1-functionalized polymers (**2a**−**c**) which might have resulted either due to the aggregation of dendronized polymers in DMF or relatively nonpolar and quite different morphological nature of the polystyrene standards which have been used to construct the calibration curve employed for the estimation of the molecular weight. With G2-derivatized polymers (**3a**−**c**), very broad GPC elution curves and irreproducibility of the results did not allow the correct molecular weight determination. This might be due to the low solubility (Table 2) and/or anomalous elution, which is known to occur in very large polymers or aggregated systems.[22]

Table 2. Solubility[a] of Polymers 1, 2a−c, and 3a−c

polymer	1	2a	2b	2c	3a	3b	3c
methanol	+	+	+	+	+	+	+
DMF	+	+	+	+	+	±	±
DMSO	+	±	−	−	+	−	−
acetone	±	+	+	+	−	−	−
THF	+	+	+	+	−	−	±
$CHCl_3$	+	+	+	+	+	+	+
toluene	+	±	+	+	−	−	−
hexane	−	−	−	−	−	−	−

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

Solubility and Thermal Properties of Polymers. The solubility properties of ethyl cellulose (**1**) and its G1- and G2-functionalized (**2a**−**c** and **3a**−**c**) derivatives are summarized in Table 2. **1** is soluble in polar protic solvents such as methanol and the same tendency was retained after dendronization. The solubility behavior of dendronized polymers in polar aprotic solvents exhibited several variations depending on the polarity of the solvent and the length of the peripheral alkyl groups of the dendritic moieties. For instance, **1**, **2a**−**c**, and **3a** were soluble in DMF whereas **3b** and **3c** were almost soluble (cannot be described as completely soluble); on the other hand, **1** is soluble in DMSO but all of the dendronized derivatives were insoluble except **2a** (partly soluble) and **3a** (soluble). Ethyl cellulose is partly soluble in acetone and switched to being soluble (**2a**−**c**) when derivatized with first generation amidoimide dendrons and turned insoluble (**3a**−**c**) upon the incorporation of second generation dendritic moieties. **1** and **2a**−**c** were soluble in the moderately polar cyclic ether, THF, while **3a**−**c** were insoluble. The solubility characteristics of **1** in $CHCl_3$ were unchanged upon dendronization, and all of the dendronized derivatives of ethyl cellulose were soluble in $CHCl_3$. The appreciably good solubility of G1-derivatized polymers (**2a**−**c**) in $CHCl_3$ was exploited for membrane fabrication. Furthermore, **1** and **2a**−**c** are soluble (**2a** is almost soluble) in toluene, a less polar solvent, while the higher polarity of **3a**−**c** due to the presence of six amide and three imide linkages renders them insoluble. Thus it can be inferred that the dendronized ethyl cellulose derivatives tend to be soluble in polar protic solvents like methanol, highly polar aprotic solvents like DMF, and moderately polar halogenated solvents like $CHCl_3$. Moreover, the solubility window narrows in going from the G1- to G2-derivatized polymers.

The thermal stability of polymers **1**, **2a**−**c**, and **3a**−**c** was examined by thermogravimetric analysis (TGA) in air (Figure 4). The onset temperatures of weight loss (T_0) of **2a**−**c** and **3a**−**c** were in the ranges of 295−325 °C and 312−320 °C, respectively, while that of **1** was 297 °C (Table 3) thus indicating no decrement in thermal stability. The retained thermal stability, despite the substitution of small hydroxy groups by the bulky dendritic moieties, is most likely to arise from the polarity of

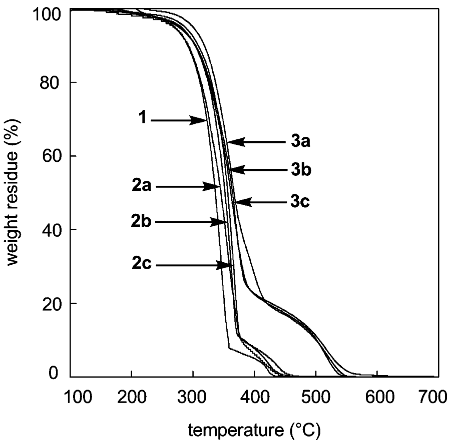


Figure 4. TGA curves of polymers **1**, **2a**−**c**, and **3a**−**c** (in air, heating rate 10 °C min^{-1}).

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

polymer	T_0^{a} (°C)	T_g^{b}(°C)
1	297	132
2a	295	69
2b	317	57
2c	325	53
3a	320	52
3b	312	40
3c	313	28

[a] T_0: onset temperature of weight loss. Determined from TGA measurement in air. [b] T_g: glass transition temperature. Determined by DSC analysis under nitrogen.

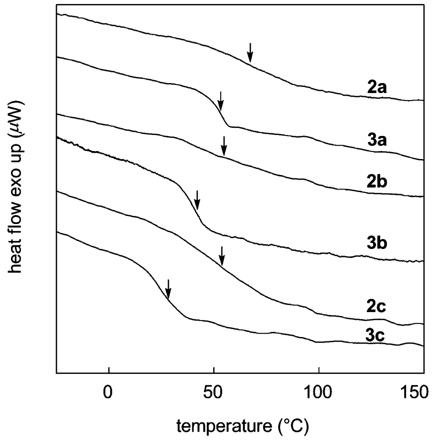


Figure 5. DSC thermograms of polymers **1**, **2a**−**c**, and **3a**−**c** (under N_2, second scan).

the dendritic substituents and the conjunctional ester linkage. The incorporated dendritic structures are also capable of hydrogen bond formation as the parent polymeric material (**1**) is; but it is probably the retainment of the individual bond strengths in the polymer structure which is responsible for the retained thermal stability upon dendron-functionalization.

The glass transition temperature (T_g) of polymers **1**, **2a**−**c**, and **3a**−**c** were determined by the differential scanning calorimetric (DSC) analysis under nitrogen (Figure 5). It was observed that the glass transition temperature (T_g) of **1** (132 °C) underwent a significant decrease as a result of the substitution by dendritic appendages; for instance, the T_g of **2a**−**c** and **3a**−**c** were 53−69 °C and 28−52 °C, respectively (Table 3). The variation in the glass transition temperature of the dendritic macromolecules is dramatically affected by the nature of chain ends and the increased polarity of the peripheral groups (convergent pathway) entails enhanced T_g values and vice versa.[23] The amidoimide dendritic moieties have fairly bulky nonpolar peripheral alkyl groups which are responsible for such a significant decrease in the glass transition temperature when incorporated into the ethyl cellulose. Furthermore, the T_g of dendron functionalized ethyl cellulosics underwent a decrement in going from the G1- to G2-derivatized ones perhaps due to the increment in the number of the peripheral alkyl groups.

Table 4. Physical Properties of Polymers 1 and 2a−c

polymer	υ_w^{a} (cm^3/mol)	ρ^{b} (g/cm^3)	FFV^{c}
1	135.8	1.099	0.182
2a	210.6	1.133	0.148
2b	223.3	1.104	0.159
2c	223.3	1.105	0.159

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

Density and FFV of Polymer Membranes. An appreciably good solubility of the G1-functionalized polymers (**2a**−**c**) in $CHCl_3$ rendered the fabrication of free-standing membranes attainable. The van der Waals volume (υ_w), density (ρ), and fractional free volume (FFV) of the polymer membranes (**1** and **2a**−**c**) are summarized in Table 4. All of the dendronized derivatives (**2a**−**c**) 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**−**c** were in the range of 1.104−1.133. The increased density can be ascribed to the increased mass of the substituents and enhanced interactions inside the polymer matrix due to the presence of polar amide and imide linkages. These findings are quite reasonable as polymers bearing polar functionalities generally possess higher densities than those of the corresponding hydrocarbon polymers.[24] It is worth mentioning that the incorporation of dendritic moieties led to the reduction in the FFV of the polymer membranes (**1**, 0.182; **2a**−**c**, 0.148−0.159). For instance, **2a** was observed to possess the lowest fractional free volume (FFV is 0.148), which indicates the reduction in the size of free volume cavities due to the introduction of polar dendritic substituents. However, it is a general trend that the presence of the polar substituents favors the intersegmental packing as has been reported in amino- and hydroxy-functionalized polymers.[24,25] Hence, the polarity of the dendron appendages, inducing the favorable interactions inside the polymer network, contributes to enhance the intersegmental packing which might have led to the decrease in the size of free volume elements in the polymer matrix. As another possible explanation, it can be assumed that the introduction of dendritic substituents with bulky alkyl periphery into ethyl cellulose has resulted in the more flexible polymeric structures (as indicated by the lowering of T_g) which often pack more tightly in the noncrystalline regions than their semirigid parent polymers with longer persistence length, thus exhibiting reduction in the fractional free volume.

Gas Permeation Properties. The permeability coefficients of the membranes of **1** and **2a**−**c** to various gases measured at 25 °C are listed in Table 5, and their plot versus kinetic diameter of gases is presented in Figure 6. The gas permeability coefficients (P) of the dendronized polymers were lower than that of **1** and approximately obey the following order: $\mathbf{1} > \mathbf{2b} > \mathbf{2a} \approx \mathbf{2c}$. Although the P values of the dendron-functionalized polymers show a little disparity from each other, the general order of the gas permeability coefficients seems to be determined by the shape, size, chemical nature, and mobility of the dendritic substituents.

The present study reveals the effect of the incorporation of amidoimide dendritic appendages on the gas permeation char-

Table 5. Gas Permeability Coefficients (*P*) of the Polymer Membranes at 25 °C

polymer	*P* (barrer)[a]						P_{He}/P_{N_2}	P_{H_2}/P_{N_2}	P_{CO_2}/P_{N_2}	P_{CO_2}/P_{CH_4}
	He	H_2	O_2	N_2	CO_2	CH_4				
1	47	68	15	4.5	91	9.2	10.4	15.1	20.2	9.9
2a	26	33	5.2	1.2	27	2.4	21.7	27.5	22.5	11
2b	28	37	7.0	1.7	38	3.8	16.5	21.8	22.2	10
2c	27	31	5.6	1.3	29	2.8	20.8	23.8	22.3	10

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

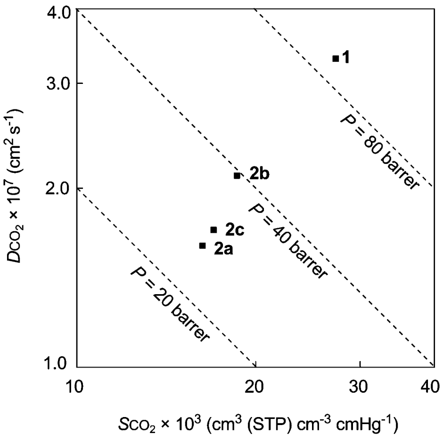


Figure 6. A plot of S_{CO_2} vs D_{CO_2} of ethyl cellulose (**1**) and its dendronized derivatives (**2a**−**c**).

acteristics of ethyl cellulose. There have been no systematic reports concerning the dendron functionalization of ethyl cellulose and outcomes of this successful conjunction as a membrane-forming material, until today. It has been discerned that the substitution of small hydroxy groups of ethyl cellulose with bulky and polar dendritic substituents results in the decreased permeability coefficients for all the gases. For instance, the P_{O_2} and P_{N_2} of **1** are 15 and 4.5 barrers and those observed for **2a**−**c** were 5.2−7.0 and 1.2−1.7 barrers, respectively. The gas permeability did not vary significantly with the change in the dendritic substituents as they possess great similarity in the composition and shape; however, subtle variations in the gas permeability emanating from the slight structural modification did not go unnoticed. For instance, the carbon dioxide permeability coefficients (P_{CO_2}) for **2a**−**c** were 27, 38, and 29 barrers, respectively, where **2b** displayed the highest CO_2 permeability; and similar tendencies were observed for other gases in the present study. The *P* values for **2b** were higher than those for **2a** which stem probably from the relatively bulky alkyl periphery slightly overruling the effect of the polarity of amidoimide linkages. In the case of **2c**, the number of carbon atoms is the same as that for **2b** but the shape/size might have played its role as the branching of alkyl groups at the peripheral amide linkages does not exhibit the same uniformity as that in **2b**. These results are quite in compliance with the previous ones describing the effect of the shape and the length of the alkyl groups, present in the side chains, on the gas permeability of polymeric membranes.[21,26] These trends in the gas permeability of dendronized polymers can reasonably be attributed to the presence of polar (amide, imide, and ester) groups resulting in a denser chain-packing, leading to the reduced free volume space inside the polymer matrix, and in turn lower gas permeability; moreover, the bulk of the dendritic substituents might have influenced in the same way due to the hindered local mobility.

The most worth mentioning of the gas permeation characteristics of ethyl cellulose (**1**) and its dendronized derivatives (**2a**−**c**) is the increased permselectivity for various gas pairs (Table 5). The P_{CO_2}/P_{N_2} selectivity of ethyl cellulose (**1**) is 20.2 which increased up to 22.5 (**2a**) after the substitution of dendron appendages. Similarly, the P_{He}/P_{N_2}, P_{H_2}/P_{N_2}, P_{CO_2}/P_{CH_4} selectivity values of **1** (10.4, 15.1, and 9.9, respectively) experienced an increase upon derivatization, and **2a** displayed the highest permselectivity (21.7, 27.5, and 11) for the corresponding gas pairs. The decrease in the gas permeability with a concomitant increase in the permselectivity for various gas pairs is in accordance with the well-known "tradeoff" relation.[27] Furthermore, the decrease in gas permeability became more pronounced as the molecular size of the penetrant gases increased as is evident from the augmented selectivity of small gases such as He and H_2 over N_2 with a larger kinetic diameter. These findings are consistent with the previous results that the structural alterations, which enhance chain packing and simultaneously hinder the segmental motion in the polymer matrix, tend to decrease permeability while increasing permselectivity.[24] The permselectivity enhancement in the present series of polymers might not appear quite significant at first glance; however, these results should be dealt with great care keeping in mind the two plausible reasons: (i) the dendronization across the polymer chain could not be effected at each monomer unit as there was one hydroxy group available for derivatization per three anhydroglucose units and (ii) the polar amidoimide and ester groups are not peripheral (due to the presence of bulky alkyl moieties) and might not be exposed enough to get involved in effective interactions with CO_2 molecules. The present results imply the sensitivity of the gas transport properties of membrane-forming materials toward the modification of subtle structural features such as interchain spacing and segmental mobility.

Gas Diffusivity and Solubility. Gas permeability (*P*), which is the steady-state, pressure- and thickness-normalized gas flux through a membrane, can be expressed as the product of gas solubility (*S*) in the upstream face of the membrane and effective average gas diffusion (*D*) through the membrane, strictly in rubbery and approximately in glassy polymers:[28]

$$P = S \times D$$

A detailed investigation of the gas permeation characteristics was carried out by determining the gas diffusion coefficients (*D*) and gas solubility coefficients (*S*) of the polymers. The plots of *D* and *S* values of polymers **1** and **2a**−**c** for CO_2 and CH_4 are illustrated in Figures 6 and 7, respectively. A distinct lowering of the gas permeability of ethyl cellulose as a consequence of the incorporation of fairly bulky and polar dendritic moieties has been revealed to stem from the subsidence of both the gas diffusion and gas solubility coefficients.

The *D* values of all the gases were observed to follow a decline upon dendronization (**2a**−**c**); for instance, **1** displayed the D_{O_2} value of 9.1, and those of **2a**−**c** were in the range of 4.8−5.9, in the units of 10^7 cm^2 s^{-1}. The gas diffusion coefficients, delineated as a complex interplay between fractional free volume and local/torsional mobility, tend to decrease if accompanied by a loss in either of these factors. The decrement in the gas diffusion coefficients finds its explanation in the

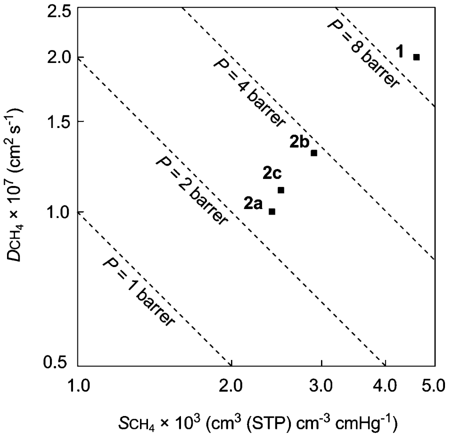


Figure 7. A plot of S_{CH_4} vs D_{CH_4} of ethyl cellulose (**1**) and its dendronized derivatives (**2a**−**c**).

reduced FFV and hindered segmental mobility of the dendronized ethyl cellulose derivatives.[24−26,29]

On the other hand, the dendron functionalization of ethyl cellulose accompanied a decrease in the gas solubility coefficients as well; e.g., the S_{CO_2} of **1** and **2a**−**c** were 27.3 and 16.3−18.6, while the S_{N_2} values being 1.1 and 0.5−0.6, respectively, in the units of $\times 10^3$ cm^3 (STP) cm^{-3} cmHg^{-1}. The reduction in the S values can be accounted for by the attenuated fractional free volume of the dendronized polymers (**2a**−**c**), as summarized in Table 4.

In the glassy polymeric membranes, generally the D value undergoes a decrease with increasing critical volume of gases, whereas the S value experiences an increase with increasing critical temperature of gases.[28a] Similar tendencies were observed in the D and S values of the polymer membranes of **1** and its dendronized derivatives; e.g., in the case of **2a**, the diffusivity of CH_4 was the lowest and that of O_2 was the highest ((1.0 and 4.8) $\times 10^7$ cm^2 s^{-1}, respectively), while CO_2 displayed the highest solubility and N_2 the lowest ((16.3 and 0.5) $\times 10^3$ cm^3 (STP) cm^{-3} cmHg^{-1}, respectively). The diffusion coefficients of this new family of dendron-functionalized cellulosics (**2a**−**c**) were in the order $D_{O_2} > D_{N_2} > D_{CO_2} > D_{CH_4}$, the same as for the starting polymer, ethyl cellulose. Similarly, the S values of **1** and **2a**−**c** were observed to follow the same trend ($S_{CO_2} > S_{CH_4} > S_{O_2} > S_{N_2}$).

It has already been mentioned that the dendronized polymers displayed better separation performance for various gas pairs, and as far as the CO_2/N_2 separation is concerned, the increase in solubility selectivity is responsible for the enhanced P_{CO_2}/P_{N_2} selectivity. Despite the D_{CO_2}/D_{N_2} of **1** being almost unaffected by the dendron incorporation, the S_{CO_2}/S_{N_2} experienced an augmentation probably due to the interaction of quadrupolar CO_2 molecules with the polar dendron appendages.

Conclusions

The present study is concerned with the synthesis of a series of first and second generation novel amidoimide dendrons (**G1-a-II**−**G1-c-II** and **G2-a-II**−**G2-c-II**) and describes an approach to design new dendritic macromolecules based on ethyl cellulose. The complete substitution of the residual hydroxy protons of ethyl cellulose (**1**; DS_{Et}, 2.69) by the dendritic moieties has been demonstrated by ^{1}H NMR and is evidenced by the elemental analysis. The G1-derivatized polymers (**2a**−**c**) displayed better organosolubility than that of G2-derivatized ones (**3a**−**c**); however, all of the dendron-functionalized polymers were soluble in chloroform and methanol. The dendronization of ethyl cellulose accompanied the retention of thermal stability and the lowering of glass transition temperature. G1-appended polymers (**2a**−**c**) afforded free-standing membranes, exhibiting decrement in density and FFV, hence low gas permeability as compared to **1**. The decrease in the gas permeability was investigated to arise from the attenuation in the gas diffusion and solubility coefficients, presumably ensuing from the decreased FFV and hindered local mobility in the polymer matrix. The improved separation performance was discerned for He/N_2, H_2/N_2, CO_2/N_2, and CO_2/CH_4 gas pairs.

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