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Micropatterned Thin Film Honeycomb Materials from Regiospecifically Modified Cellulose

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Thin film honeycomb materials were prepared from regioselectively modified celluloses. The method uses water condensation at the surface of a cellulosic solution as an ordered template to form honeycomb structures. Pore size and distribution is controlled by several factors, one of which is the hydrophilicity of the cellulosic used. The amphiphilic nature of the celluloses was modified with varying lengths of ethylene glycol side chains using 2,6-thexyldimethylsilyl cellulose. It was found that the side chains do affect the honeycomb formation, with longer ethylene glycol chains leading to increased pore uniformity but having little influence on the pore size.

Introduction

Microporous materials are of interest as they have a wide range of applications,[1] including photonic crystals,[2] microreactors or microarray chips,[3] scaffolds for tissue growth,[4] and as catalyst supports for fuel cells.[5] Of particular interest is the ability to create microporous biomaterials for both medical and non-medical use.

The reported process by which these materials are formed involves the condensation of the water on a cold surface of a polymer solution and creating an ordered hexagonal template in which the polymer then deposits between the water droplets thereby forming a honeycomb structure.[1,6,7] The process was reported by Francois et al. and further studied by several researchers.[8−12] The underlying process by which these polymeric honeycomb structures form is that of Bérnard−Marangoni convection where, in thin films, pattern formation is governed by a balance of the surface-tension-driven forces and dissipation due to the thermal diffusion and the frictional action of viscosity.[13,14] Humidity and polymer concentration do affect the pore size and distribution; however, it is unclear if the amphiphilic nature of the polymer affects the process or not.

Microporous films have been reported for cellulosics. Stenzel et al.[15,16] recently reported the production of polystyrene comb polymers built on hydroxyisopropyl cellulose. It was found that the regularity of the porous films increased with the density of branches and with the increasing length of each branch; however, poor quality low regularity films were obtained. Likewise Kondo et al.[17] and Uraki et al.[18] reported the formation of honeycomb-shaped films based on cellulose acetate. In both studies the acetate films were extremely irregular, having macroporous sizes ranging from 1 to 100 μm.

If the surface tension of the organic polymer solution is a function of the amphiphilic nature of the polymer, then a small modification of the polymer should affect the honeycomb formation. An increase in the hydrophilic character of the polymer could correspond to smaller pore sizes within the honeycomb.[1] Furthermore, regioselective allocation of the hydrophilic moieties may enhance microporous regularity. Of the available hydroxyl groups within the anhydroglucopyranose unit of cellulose, derivatives of C_6-OR versus C_3-OR cellulosic polymers will exhibit different properties, the C_6-OH being involved in interchain hydrogen bonding, while the C_3-OH participates in only intrachain hydrogen bonding.[19] We look to determine how these differences affect the formation of honeycomb structures and their pore sizes and distribution. As part of our ongoing research into new materials based on modified cellulose, we report the synthesis and characterization of a series of substituted 2,6-thexyldimethylsilyl (TDMS) cellulosics with varying lengths of ethylene glycol side chains. This report also discusses the effect of increasing the length of oligo(ethylene glycol) side chains at the C_3-OH position on the formation of cellulosic honeycomb structures.

Experimental Section

Materials. Dimethylthexylsilyl chloride (TDMSCl), imidazole, lithium chloride, dimethyl acetamide (DMA), tetrahydrofuran (THF), and acetic anhydride were purchased from Aldrich and used as received. Cellulose was obtained from the deacetylation of cellulose acetate 30K (Aldrich) using sodium hydroxide in methanol and thoroughly dried prior to use.

Characterization. ^{1}H, ^{13}C, and heteronuclear multiple bond correlation (HMBC) NMR spectra were measured using a Bruker AVANCE-300 spectrometer at 40 °C. Chemical shifts were referenced to tetramethyl silane (TMS; 0.0 ppm). Infrared spectra were obtained with a Perkin-Elmer Spectrum One FTIR spectrometer as potassium bromide pellets in a 1:3 (v/v) sample to salt ratio. Differential scanning calorimetry (DSC) measurements were run using 10 mg of sample under nitrogen at a heating rate of 20 °C min^{-1} using a TA Instruments Q1000 calibrated with indium. High resolution thermogravimetric analysis (Hi-Res TGA) measurements were run under nitrogen using a TA Instruments Q500. Sample mass was ~2 mg, and an initial heating rate of 30 °C min^{-1} was used with a sensitivity value of 1.00 and a resolution of 4.00. Elemental analysis was measured using a Perkin-Elmer Series II CHNS/O analyzer.

Synthesis. Monomethylene glycol tosylates were synthesized from tris(ethylene glycol) monomethyl ether, poly(ethylene glycol) 350 monomethyl ether, and poly(ethylene glycol) 750 monomethyl ether (Aldrich). Monoethylene glycol (0.014 mol) dissolved in 20 mL of pyridine was added dropwise (over 30 min) to a solution of 0.0157 mol of *p*-tosyl chloride in 20 mL of pyridine at 5 °C. The reaction mixture was held at 5 °C with stirring for 2 h and then warmed to room temperature and stirred for an additional 8 h, following which it

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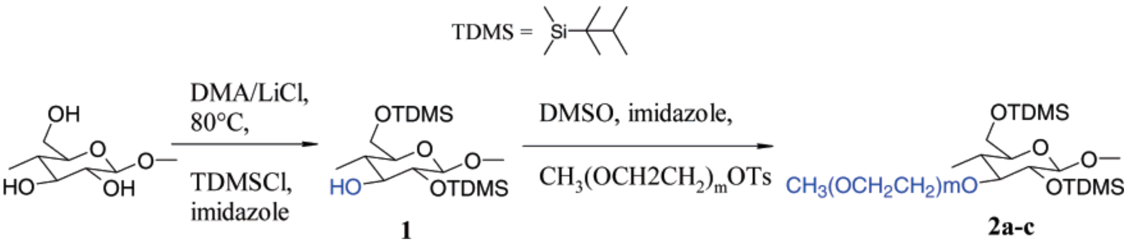
Scheme 1. Synthetic Scheme for the Production of 2,6-TDMS Cellulose (**1**) and 3-EG$_m$-2,6-TDMS Cellulose ($m = 3$ for **2a**, $m = 7$ for **2b**, $m = 16$ for **2c**)



was added to 100 mL of cold water. The water layer was extracted with two 75-mL portions of dichloromethane, which were combined and extracted with three 75-mL portions of 6 N HCl. The organic layer was dried over sodium sulfate and 4 Å molecular sieves, and the dichloromethane was removed by evaporation in vacuo. ^{1}H NMR (10% in acetone-d_6): δ (ppm) 2.35 (s, 3H), 3.25 (s, 3H), 3.4−3.6 (multiplet, 8/24/60H), 3.68 (t, 2H), 4.08 (t, 2H), 7.25 (d, 2H), 7.67 (d, 2H).

2,6-Di-*O*-(thexyldimethylsilyl) Cellulose (**1**) was prepared according to the procedure of Koschella et al.[20] Cellulose (162 g/mol, 2.0 g, 12.3 mmol) was suspended in 50 mL of DMA and stirred at 125 °C for 2 h. The slurry was then cooled to 100 °C, and lithium chloride (8.0 g, 180 mmol) was added and stirred for 15 min. The mixture was then cooled to room temperature and stirred overnight to afford a colorless viscous solution. Imidazole (4.2 g, 61.5 mmol) was dissolved in 15 mL of DMA and added to the solution. After 30 min of stirring, TDMSCl (8.8 g, 49.2 mmol) was added dropwise. The solution was stirred for an additional 15 min, heated to 100 °C, and stirred for 48 h under a nitrogen blanket. The reaction mixture was allowed to cool to room temperature, and the polymer was isolated by pouring slowly into 500 mL of pH 7 aqueous buffer solution and filtered. Further purification was done by redissolving the crude polymer in chloroform and precipitating in methanol to afford a white powder. Yield: 4.86 g (88%), DS 1.9; Elemental analysis: calc: 58.57 C%, 10.38 H%; measured: 58.37 C%, 10.58 H%. FTIR (KBr): 3502.4 (ν_{OH}), 2959.6, 2860.0 (ν_{CH}), 1467.6 ($\delta_{as\ CH2,\ CH3}$), 1379.2 ($\delta_{sym\ CH3}$), 1253.1 (δ_{Si}−C), 1119.6 (ν_{Si}−O−C), 1079.5, 1038.2 (ν_C−O−C$_{AGU}$), 834.2, 778.4 (ν_{Si}−C/Si−O−C). ^{13}C NMR (10% in C6D6, 313 K, 75.4 MHz): $\delta = -3.4-35.0$ (TDMS group), 60.6 (C-6), 71.9, 72.1, 75.6, 76.9, 102.5 (C-1).

Polymers 2a−c. General Procedure. Compound **1** (2.2 mmol) and imidazole (11.0 mmol) were dissolved in dry THF (25 mL) under nitrogen. After refluxing for 1 h, the appropriate tosylated monomethylene glycol (11.0 mmol) was added dropwise, and the reaction was allowed to reflux for 48 h. The solvent was then removed under reduced pressure, redissolved in benzene, filtered, and precipitated into methanol.

3-*O*-(3,6,9-Trioxydecyl)-2,6-di-*O*-(dimethylthexylsilyl) cellulose (2a) was prepared using the tosylate of tris(ethylene glycol) monomethyl ether. Yield: 52%. Elemental analysis: 58.81 C%, 11.58 H%. FTIR (KBr): 3502.4 (ν_{OH}), 2959.8, 2871.0 (ν_{CH}), 1467.2 ($\delta_{as\ CH2,\ CH3}$), 1379.2 ($\delta_{sym\ CH3}$), 1253.1 (δ_{Si}−C), 1119.6 (ν_{Si}−O−C), 1079.5, 1037.5 (ν_C−O-C$_{AGU}$), 833.6, 778.3 (ν_{Si}−C/Si−O−C). ^{13}C NMR (10% in C6D6, 313 K, 75.4 MHz): $\delta = -3.4-34.5$ (methyl of TDMS), 58.5 (OMe), 61.5 (C-6), 68.8 (CH$_2$-OCell), 70.5, 70.7, 70.8, 72.1 (EG), 75.3, 75.4, 76.9, 102.5 (C-1).

3-*O*-(3,6,9,12,15,18,21-Heptaoxyicosyl (average))-2,6-di-*O*-(dimethylthexylsilyl) cellulose (2b) was prepared using the tosylate of poly(ethylene glycol) monomethyl ether (MW 350 g/mol). Yield: 48%. Elemental analysis: 58.60 C%, 10.54 H%

3-*O*-(3,6,9,12,15,18,21,24,27,30,33,36,39,42,45,48-Hexadecaoxynonatetracon tyl (average))-2,6-di-*O*-(dimethylthexylsilyl) cellulose (2c) was prepared using the tosylate of poly(ethylene glycol) monomethyl ether (MW 750 g/mol). Yield: 38%. Elemental analysis: 58.09 C%, 10.66 H%.

Film Preparation. Microporous films were prepared by applying 10 μL of (i) neat cellulosic solution (solvent: chloroform for polymer **1** and toluene for polymers **2a**−**c**; concentration: 0.5−1.5 mg/mL) or (ii) sonicated (power: 300 W; time: 10 min) 10% v/v water emulsion, onto a glass slide in a humid environment (flow rate: 700 mL min^{-1}; relative humidity: 70−80%; temperature: 20 ± 1 °C). The surface morphology of the cast films was observed by transmission optical microscopy (BX41, Olympus) and scanning electron microscopy (SEM; JEOL JSM-5900LV, 8.0 kV accelerating voltage, 9000× magnification).

Results and Discussion

Synthesis and Characterization of Cellulose Derivatives. It has been shown that chemical modification of cellulose with bulky silyl groups can lead to regioselective substitution.[20] Using thexyldimethylsilyl chloride (TDMSCl) in DMA/LiCl with imidazole, the completely 2,6-di-*O*-silylated cellulose ether **1** is formed (Scheme 1). The degree of substitution (DS) was analyzed to be 1.9 by means of elemental analysis. The regioselectivity was confirmed by two-dimensional NMR techniques of the 3-*O*-allyl-substituted 2,6-(dimethylthexylsilyl) cellulose derivative (data not shown).[20]

2,6-TDMS cellulose **1** was reacted with various tosylated ethylene glycol monomethyl ethers (EG$_3$, EG$_7$, EG$_{16}$) according to Scheme 1. The C$_3$-O substituted polymers (**2a**−**c**) were obtained in moderate yield (38−52%) that decreased with increasing ethylene glycol chain length. Treating compound **1** with an excess of tosylated ethylene glycol monomethyl ether and imidazole in THF for 2 days produced the corresponding 3-O-functionalized TDMS-cellulose with relatively low DS, ∼0.2.

FTIR spectra of compounds **1** and **2b** are shown in Figure 1. The thexyldimethylsilyl groups in **1** and **2b** are evident in the Si−CH$_3$ rocking and stretching vibrations at 778 and 2960 cm^{-1}, respectively, the Si−C stretching vibration at 834 cm^{-1}, and the symmetrical Si−CH$_3$ deformation vibration at 1252 cm^{-1}.[20] As expected there is a decrease in the intensity of the OH stretching band between 3000 and 3600 cm^{-1}. The spectrum of compound **1** reveals two distinct bands in the OH region, one at 3500 cm^{-1} assigned to free-OH stretching and one around 3350 cm^{-1} corresponding to the stretching mode of the intramolecular O(3)H−O(5) hydrogen bond.[21] The latter absorption band confirms the regioselectivity and lower reactivity of the O(3)H with respect to both O(2)H and O(6)H.[22] This is further confirmed from the FTIR spectrum of **2b**, wherein there is a clear decrease in the absorption band associated with the C(3)−O(3)H stretching vibration at 1057 cm^{-1} and the disappearance of the O(3)H−O(5) intramolecular hydrogen bonding absorption band around 3350 cm^{-1}.

Thermal analysis clearly demonstrates the effect of ethylene glycol incorporation on the glass transition (T_g) and decomposition temperatures of the respective polymers. The first heating scan of the 2,6-TDMS cellulose, **1**, exhibited, aside from a step change in specific heat at 200 °C, a broad melting transition with peak temperature at 90 °C (data not shown). Cooling the sample, whether rapidly (50 °C min^{-1}) or slowly (2 °C min^{-1}),

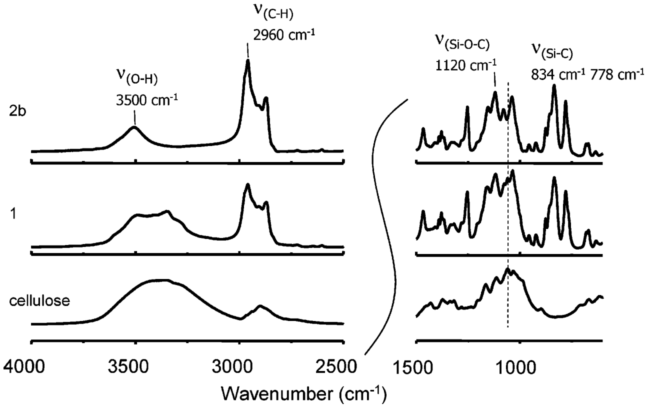


Figure 1. FTIR analysis of cellulose, 2,6-TDMS cellulose (**1**), and 3-EG$_7$-2,6-TDMS cellulose (**2b**). Included are the assignments of the various functional groups associated with the respective polymers.

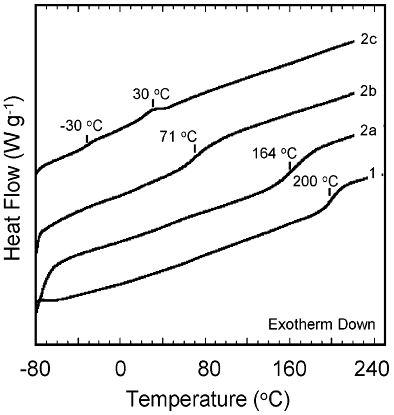


Figure 2. Differential scanning calorimetric analysis of 2,6-TDMS cellulose (**1**), 3-EG$_3$-2,6-TDMS cellulose (**2a**), 3-EG$_7$-2,6-TDMS cellulose (**2b**), and 3-EG$_{16}$-2,6-TDMS cellulose (**2c**). (sample mass = 10 mg, heating rate = 20 °C min^{-1}). Included are T_g values for each polymer and T_m (**2c**) determined from the second heating scan.

resulted in the disappearance of the broad melt peak and no change in the observed glass transition temperature at 200 °C (Figure 2). High resolution thermogravimetric analysis (Hi-Res TGA) of compound **1** revealed an increase in thermal stability as compared to cellulose (Figure 3). The peak maximum in the DTGA (derivative TGA) curve for compound **1** (340 °C) was approximately 25 °C higher than that of the original cellulose.

As anticipated, incorporation of the ethylene glycol side chains led to a decrease in the glass transition temperature of the polymers. The T_g of the tris(ethylene glycol) monomethyl ether TDMS cellulose (3-EG$_3$-2,6-TDMS cellulose), compound **2a**, decreased to 164 °C and was significantly broader (Figure 2) than that of compound **1**. Further reductions in T_g were observed for the 3-*O*-poly(ethylene glycol) monomethyl ether derivatives **2b** (3-EG$_7$-2,6-TDMS cellulose) and **2c** (3-EG$_{16}$-2,6-TDMS cellulose). Increasing the poly(ethylene glycol) size to an average M$_n$ ~350 (compound **2b**) and ~ 750 (compound **2c**) reduced the T_g to 71 and −30 °C, respectively. The decrease in T_g was accompanied with a substantial decrease in the heat capacity at the T_g. The DSC trace of compound **2c** also revealed a weak melting transition at 30 °C, likely arising from the crystallization of the longer ethylene glycol side chains.

The Hi-Res TGA/DTGA profiles of the ethylene glycol modified TDMS cellulose preparations **2a-c** were identical. All of the compounds exhibited a further increase in decomposition temperature as compared to both compound **1** and cellulose. The peak maximum in the DTGA curve for compounds **2a-c** is 370 °C (a representative profile is shown in Figure 3), 30 °C higher than compound **1**, 55 °C higher than cellulose. Although the T_g decreased substantially with increasing poly(ethylene glycol) size (**2a**−**c**) the thermal stability did not change in terms of decomposition temperature. This is likely the result of the low DS (~0.2) and relatively low DP (3−16; 350−750 amu) of the ethylene glycol segments. The increase in ethylene glycol chain length is sufficient to affect molecular mobility in the amorphous phase, but not the bulk weight loss during thermal decomposition, as evident by the single step decomposition profile.

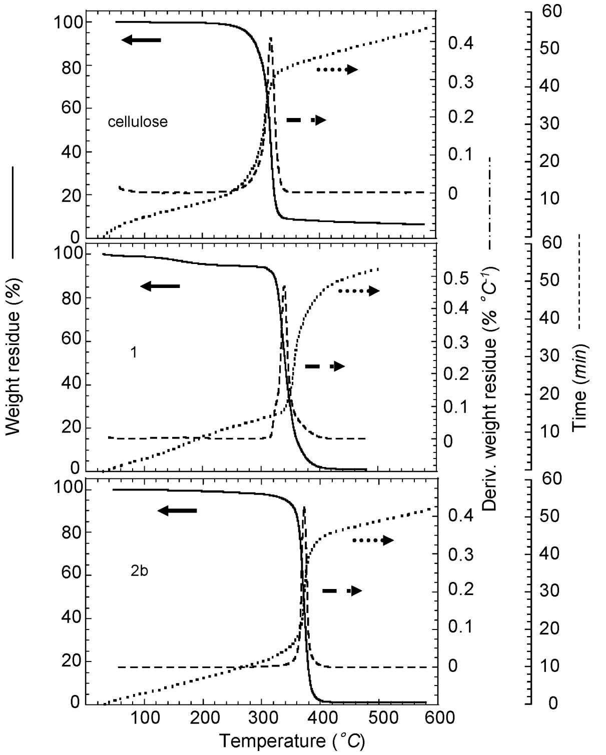


Figure 3. Hi-Res TGA analysis of cellulose, 2,6-TDMS cellulose (**1**), and 3-EG$_7$-2,6-TDMS cellulose (**2b**). (sample mass ~ 2 mg, heating rate = 30 °C min^{-1}, resolution = 4.00, sensitivity = 1.00).

Honeycomb Formation. The formation of microporous ‘honeycomb’ structured polymer films was first reported by Francois et al. in 1994,[10] although observations of such structures date back to the early 1900s.[23,24] Cellulose-based microporous honeycomb films have been produced using both neat[18] and emulsion-based[17] processes. Figure 4 shows optical micrograph images of honeycomb films made from the 3-*O*-poly(ethylene glycol) monomethyl ether derivative **2b** (3-EG$_7$-2,6-TDMS cellulose) using both water emulsion and neat organic polymer solution techniques. It was speculated that the poly(ethylene glycol) side chains may stabilize the emulsions and lead to improved honeycomb uniformity. However, it can be seen from Figure 4(i) that the cellulosic films are not uniform, exhibiting the typical array of pore sizes found in previous cellulosic films.[17,18] The films had various microporous sizes ranging from ~2 to >50 μm in diameter. Changing the sonication time, polymer concentration, or atmospheric humidity did not improve film uniformity. It may be that the degree of substitution of ethylene glycol chains was too low to fully stabilize the emulsion; we are currently investigating this.

By contrast, films produced from neat polymer solutions (Figure 4(ii)) were significantly more uniform and of a much smaller length scale pattern. The honeycomb patterned film pore size was on the order of ~2 μm. As reported by others, polymer concentration, solvent, atmospheric humidity, and flow rate all

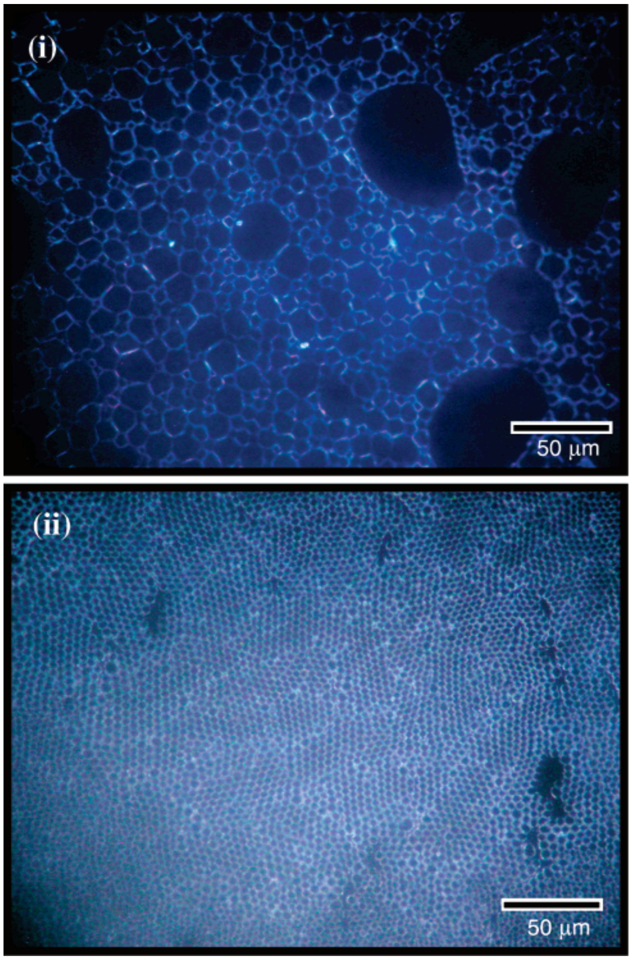


Figure 4. Optical micrograph images of honeycomb films made from 3-EG$_7$-2,6-TDMS cellulose (**2b**) (solvent: benzene; concentration: 1.0 mg/mL) using (i) 10 min sonication of a 10% v/v water emulsion and (ii) neat organic polymer solution.

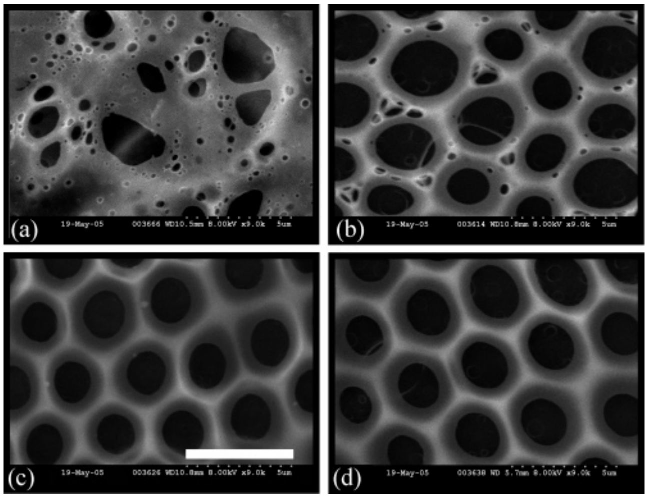


Figure 5. SEM images of honeycomb films made from (a) 2,6-TDMS cellulose (**1**), (b) 3-EG$_3$-2,6-TDMS cellulose (**2a**), (c) 3-EG$_7$-2,6-TDMS cellulose (**2b**), and (d) 3-EG$_{16}$-2,6-TDMS cellulose (**2c**). Scale bar 5 μm.

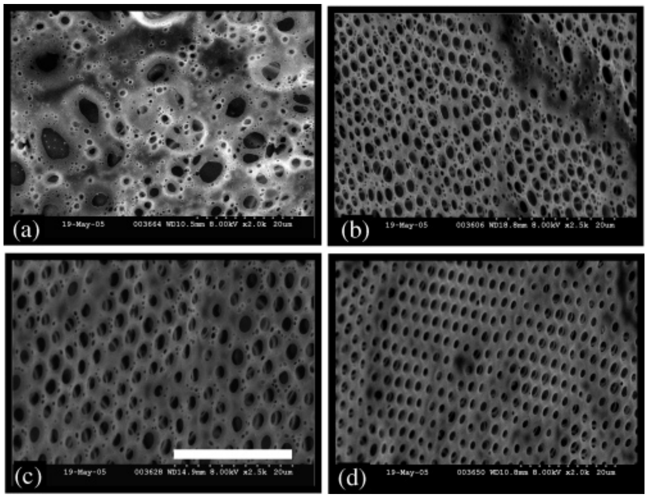


Figure 6. SEM images of honeycomb films made from (a) 2,6-TDMS cellulose (**1**), (b) 3-EG$_3$-2,6-TDMS cellulose (**2a**), (c) 3-EG$_7$-2,6-TDMS cellulose (**2b**), and (d) 3-EG$_{16}$-2,6-TDMS cellulose (**2c**). Scale bar 20 μm.

effected film formation and pattern regularity. As with most cellulose derivatives there are very few solvent choices for the compounds of interest, especially when they must also be immiscible with water. For the polymers studied it was found that 1 mg mL^{-1} in toluene was the optimal polymer concentration. Increasing polymer concentration led to poor honeycomb formation, as did using chloroform as a solvent. As compared to toluene, the rate of evaporation of chloroform was too quick to form stable honeycombs. It is thought that the fast rate of evaporation changes the marangoni conditions, i.e., surface tension-driven convection,[13,14] such that inhibition of coalescence does not prevail which leads to the lack of stabilization of the hexagonal packing of the water spheres and a very fast rate of viscosity increase.[1] The increase in viscosity combined with the high density of chloroform precludes the condensed water droplets from sinking into the forming honeycomb film. The result was thick poorly formed films. Increasing flow rate or relative humidity led to increased solvent evaporation and condensation of water droplets onto the solution surface. At flow rates beyond 700 mL min^{-1} and 70 %RH (20 °C) a decrease in the stability of the system occurred with water coalescence/polymer precipitation and the formation of irregularly structured films.

Figures 5 and 6 show scanning electron microscope (SEM) images of honeycomb films produced from compounds **1**, **2a**–**c**. Microporous honeycomb patterned films could not be produced from hydrophobic compound **1**. However, changing the amphiphilicity of the cellulosic dramatically affected the microporous polymer films. Increasing the poly(ethylene glycol) size from **2a** to **2c** resulted in uniform microporous honeycomb structures. It is apparent that the ethylene glycol chains sufficiently modify the surface tension of the organic cellulosic solution to favor the formation of such structures. The tris(ethylene glycol) monomethyl ether TDMS cellulose, compound **2a**, produced irregular honeycomb pores ranging in size from 0.5 to 3 μm in diameter with porous walls. Honeycomb structure uniformity increased in compound **2b** (Figure 5c), but still suffered from porous walls (Figure 6c), while the microporous honeycomb film produced from compound **2c** was much more uniform (Figures 5d and 6d).

The difference in microporous honeycomb film morphology and uniformity between compounds **2a**–**c** is likely the result of the molecular shape of the respective cellulosic in solution. According to Francois et al.[10] an important parameter for honeycomb formation is precipitation of the polymer at the polymer solution:water droplet interface. This is very much dependent on the shape of the polymer in the solvent used; spherical-shaped polymers, such as star-shaped and block copolymers, instantaneously precipitate, while linear polymers tend not to precipitate. Increasing the amphiphilicity of the cellulosic polymers through increasing ethylene glycol chain length must enhance the polymers propensity to associate into a spherical shape, resulting in improved polymer precipitation and creation of regular structures.

Unlike the observations of Stenzel et al.[16] wherein increasing arm length in comb polymers led to an increase in pore size, the average size distribution of our honeycomb pores was about 2 μm. This may be a result of (i) the low DS of our polymers, (ii) the nature of the pendent groups, which are hydrophilic and of relatively low molecular weight, and/or (iii) the regiospecificity of substitution. This is currently under investigation.

Conclusion

Regular microporous honeycomb structured films were prepared from regioselectively modified 2,6-(dimethylthexylsilyl) cellulose. Film formation was very dependent on casting conditions and polymer amphiphilicity. Polymer amphiphilicity was modified using ethylene glycol tosylates of varying molecular weight (degree of polymerization). Increasing ethylene glycol molecular weight led to increased pore uniformity, but did not dramatically affect pore size. Honeycomb films produced from 3-EG$_{16}$-2,6-TDMS cellulose were extremely uniform with an approximately 2 μm diameter pore size.

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Supporting Information Available. NMR spectra and elemental analysis results. This material is available free of charge via the Internet at http://pubs.acs.org.

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