Synthesis and Characterization of Nanosheet Polymer Gelling Agents

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The synthesis and characterization of nine organosilicon sheet polymers from the sheet silicate apophyllite ($KCa_4Si_8O_{20}(F,OH)\cdot 8H_2O$) and a series of chlorosilanes are described. Five of the polymers have a single pendent group of the type $OSi(CH_3)_2(n\text{-}C_nH_{2n+1})$, where $n = 1$, 4, 8, 10, or 18, and are members of the homologous series $[((n\text{-}C_nH_{2n+1})(CH_3)_2SiO)_x(OH)_{1-x}SiO_{1.5}]_n$. The other four have pendent groups of the type $OSi(CH_3)_2R$, where R = CH_3, $n\text{-}C_4H_9$, $n\text{-}C_3H_7CN$, or $n\text{-}C_4H_8Cl$, interspersed among pendent groups of type $OSi(CH_3)_2(n\text{-}C_{18}H_{37})$. These latter polymers belong to the series $[((n\text{-}C_{18}H_{37})(CH_3)_2SiO)_x((R)(CH_3)_2SiO)_y(OH)_{1-x-y}SiO_{1.5}]_n$. The five homologous polymers have interplanar spacings that vary predictably with the size of their pendent groups. All but two of the nine polymers form good gels with both *n*-decane and 10 cSt trimethylsiloxy-capped poly(dimethylsiloxane).

Introduction

In the 1960s, work on monomeric and oligomeric silicates showed that the silicate frameworks in selected silicates can be excised and substituted with organosilicon groups to give monomeric and oligomeric organosilicon compounds.[2] Efforts building on this showed that the silicate sheet in the rolled-sheet (scroll) silicate chrysotile can be excised and substituted with organosilicon groups to give organosilicon polymers.[3−7] Further efforts showed that not only the silicate sheet in chrysotile but also the silicate sheets in apophyllite,[8,9] halloysite,[10] kanemite,[11] kenyaite,[12,13] magadiite,[12,14,15] and octosilicate[16] can be excised and substituted. Studies with apophyllite-derived polymers have shown that the groups grafted on the apophyllite sheet can be short[5,8,9,17−22] or long[8,9,19−28] and their R groups unfunctionalized[5,8,9,17−24,28] or functionalized.[8,9,20−27] In addition, the grafted groups can be of more than one type,[22,24,26] and if their R groups are functionalized, they can be elaborated through the use of suitable reactions.[8,18,19,22] Furthermore, the Si atoms of the grafted groups can be unfunctionalized[5,8,9,17−26,28] or functionalized.[8,17,19,20,27] The sheets of the polymers are stacked parallel to one another in random registry (that is, with an atom of a given type in one sheet in random position with respect to a like atom in a neighboring sheet). The spacing

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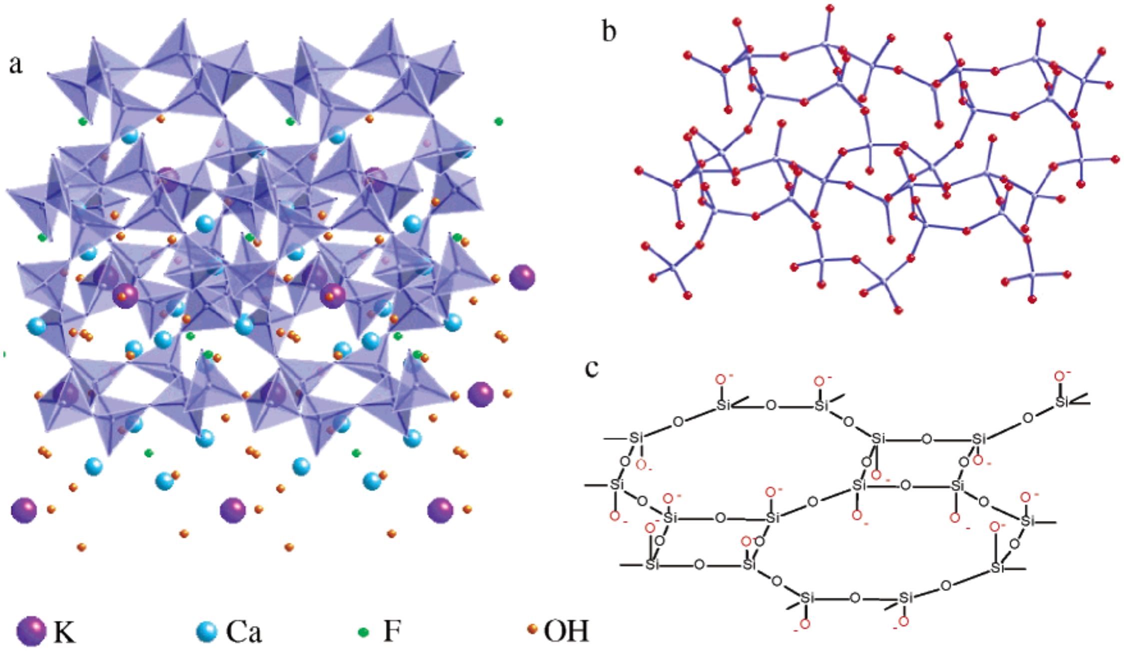

Figure 1. Structure of (a) apophyllite, (b) apophyllite sheet, and (c) idealized apophyllite sheet.

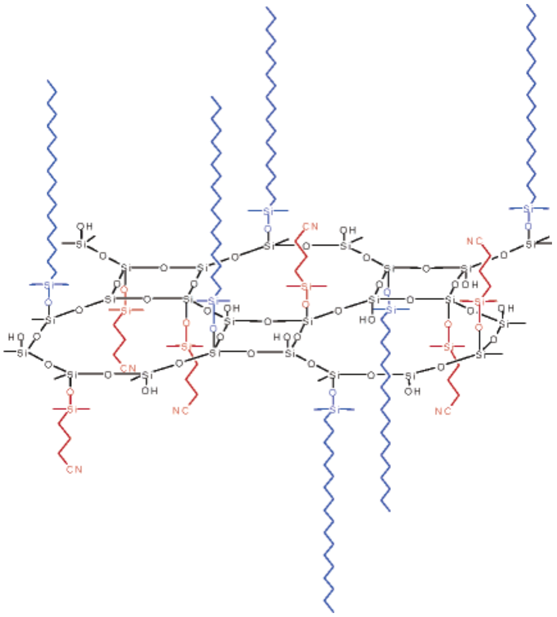

Figure 2. Structure of *n*-octadecyldimethylsiloxy-3-cyanopropyldimethylsiloxy sheet polymer, $[((n\text{-}C_{18}H_{37})(CH_3)_2SiO)_x((R)(CH_3)_2SiO)_y(OH)_{1-x-y}SiO_{1.5}]_n$, A−ODM$_2$−CM$_2$, **p-8**.

of the sheets is governed by the size of the pendent groups. Although none of the polymers are soluble in the solvents tried, some of them form gels with organic solvents.

In this study, nine sheet polymers derived from the sheet silicate apophyllite $KCa_4Si_8O_{20}(F,OH)\cdot 8H_2O$, Figure 1, have been prepared or re-prepared. Five of these have a single pendent group of the type $OSi(CH_3)_2(n\text{-}C_nH_{2n+1})$, where $n = 1$, 4, 8, 10, or 18, and are members of the homologous series $[((n\text{-}C_nH_{2n+1})(CH_3)_2SiO)_x(OH)_{1-x}SiO_{1.5}]_n$. The remaining four have pendent groups of the type $OSi(CH_3)_2R$, where $R = CH_3$, $n\text{-}C_4H_9$, $n\text{-}C_3H_7CN$, or $n\text{-}C_4H_8Cl$, interspersed among groups of the type $OSi(CH_3)_2(n\text{-}C_{18}H_{37})$, Figure 2. These latter polymers belong to the series $[((n\text{-}C_{18}H_{37})(CH_3)_2SiO)_x((R)(CH_3)_2SiO)_y(OH)_{1-x-y}SiO_{1.5}]_n$. Both the interplanar spacings and the gel-forming abilities of these two sets have been studied. These nanosheet polymer gels are models for solid nanocomposites. Composites of this type have much promise as materials.[29−31]

Experimental Section

Instrumental Measurements. In the infrared studies, the polymers were mixed with KBr and the mixtures were packed in one of the spectrophotometer sample holders. The spectrophotometer used was a Spectra One (Perkin-Elmer, Norwalk, CT) equipped with a diffuse reflectance attachment (Perkin-Elmer). For the solid-state ^{29}Si NMR studies, we packed the polymer as obtained in one of the sample rotors. The spectrometer employed was an ACP 300 NMR (Bruker, Rheinstetten, Germany). For data collection, we used a spinning rate of 4 kHz, a pulse width of 6.80 μs ($\theta = 90°$), and a recycle delay time of 300 s. For the X-ray studies of the polymers and the gels made from low-volatility solvents, we placed the polymers and gels in one of the diffractometer sample holders. The gels made from high-volatility solvents were loaded in the holder; the loaded holder was placed in a small polyethylene bag, and the bag was sealed. The diffractometer used was a Scintag model X1 diffractometer (Scintag, Cupertino, CA). In the X-ray photoelectron studies, we spread acetone gels of the polymers on pieces of glass microscope slides and dried them. The spectrometer used was a model PHI-5600 (Perkin-Elmer) equipped with an Al anode X-ray source.

Apophyllite. Apophyllite was obtained from Gelest (Tullytown, PA), and was ground to pass 120 mesh.

Trimethylsiloxy Sheet Polymer $[((CH_3)_3SiO)_x(OH)_{1-x}SiO_{1.5}]_n$, A−M$_3$, p-1. Apophyllite (0.50 g, 0.54 mmol) was treated with a procedure similar to that used by Chao[9] (0.44 g, 97% assuming $x = 0.50$). IR (diffuse reflectance, KBr, cm^{-1}): 3664 (w, free OH str), 3423 (m, H-bonded OH str), 2961 (s, CH str), 2903 (s, CH str), 1462 (m, CH def), 1254 (s, SiCH$_3$ def), 1060 (s, SiOSi str),

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842 (m, $SiCH_3$), 757 (m), 728 (w), 574 (m). XRD *d*, Å (I/I_o): 15 (100).

***n*-Butyldimethylsiloxy Sheet Polymer $[((n\text{-}C_4H_9)(CH_3)_2SiO)_x(OH)_{1-x}SiO_{1.5}]_n$, A−BM₂, p-2.** Apophyllite (0.51 g, 0.55 mmol), *n*-butyldimethylchlorosilane (2.2 g, 15 mmol), and dimethylformamide (20 mL) was heated (125 °C) for 5 h and filtered. The solid was washed (hexanes, a 1:1 water−acetone solution, acetone), vacuum-dried (50 °C), and weighed (0.44 g, 60% assuming $x = 0.50$). IR (diffuse reflectance, KBr, cm^{-1}): 3650 (m, free OH str), 3450 (m, H-bonded OH str), 2958 (s, CH str), 2924 (s, CH str), 2873 (m, CH str), 1465 (m, CH def), 1254 (s, $SiCH_3$ def), 1060 (s, SiOSi str), 845 (m, $SiCH_3$), 791 (m), 751 (w), 572 (m). XRD *d*, Å (I/I_o): 19 (100).

***n*-Octyldimethylsiloxy Sheet Polymer $[((n\text{-}C_8H_{19})(CH_3)_2SiO)_x(OH)_{1-x}SiO_{1.5}]_n$, A−OM₂, p-3.**[9] Apophyllite (0.50 g, 0.54 mmol) was treated with a procedure similar to that used to make **p-8** (0.35 g, 52% assuming $x = 0.50$). IR (diffuse reflectance, KBr, cm^{-1}): 3667 (w, free OH str), 3337 (m, H-bonded OH str), 2957 (s, CH str), 2924 (s, CH str), 2854 (m, CH str), 1467 (m, CH def), 1254 (s, $SiCH_3$ def), 1062 (s, SiOSi str), 843 (m, $SiCH_3$), 722 (w), 575 (m). XRD *d*, Å (I/I_o): 24 (100), 12 (5).

***n*-Decyldimethylsiloxy Sheet Polymer $[((n\text{-}C_{10}H_{21})(CH_3)_2SiO)_x(OH)_{1-x}SiO_{1.5}]_n$, A−DM₂, p-4.**[9] Apophyllite (0.50 g, 0.54 mmol) was treated with a procedure similar to that used to make **p-8** (0.40 g, 60% assuming $x = 0.50$). IR (diffuse reflectance, KBr, cm^{-1}): 3662 (w, free OH str), 3336 (m, H-bonded OH str), 2957 (s, CH str), 2923 (s, CH str), 2854 (m, CH str), 1466 (m, CH def), 1254 (s, $SiCH_3$ def), 1060 (s, SiOSi str), 845 (m, $SiCH_3$), 721 (w), 584 (m). XRD *d*, Å (I/I_o): 27 (100), 13 (6).

***n*-Octadecyldimethylsiloxy Sheet Polymer $[((n\text{-}C_{18}H_{37})(CH_3)_2SiO)_x(OH)_{1-x}SiO_{1.5}]_n$, A−ODM₂, p-5.** Apophyllite (0.25 g, 0.28 mmol) was treated with a procedure similar to that used to make **p-8** (0.31 g, 62% assuming $x = 0.50$). IR (diffuse reflectance, KBr, cm^{-1}): 3661 (w, free OH str), 3448 (m, H-bonded OH str), 2956 (s, CH str), 2918 (s, CH str), 2850 (s, CH str), 1467 (w, CH def), 1377 (w, CH def) 1255 (m, $SiCH_3$ def), 1063 (s, SiOSi str), 845 (m, $SiCH_3$), 722 (m), 432 (s). XRD *d*, Å (I/I_o): 34 (100), 18 (26), 12 (6).

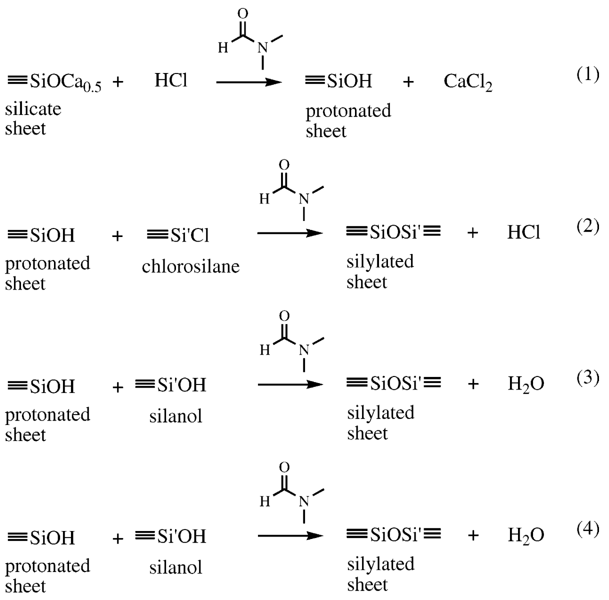
***n*-Octadecyldimethylsiloxy-trimethylsiloxy Sheet Polymer $[((n\text{-}C_{18}H_{37})(CH_3)_2SiO)_x((CH_3)_3SiO)_y(OH)_{1-x-y}SiO_{1.5}]_n$, A−ODM₂−M₃, p-6.** Apophyllite (0.25 g, 0.28 mmol) was treated with a procedure similar to that used to synthesize **p-8** (0.30 g, 71% assuming $x = 0.35$, $y = 0.15$). IR (diffuse reflectance, KBr, cm^{-1}): 3461 (m, H-bonded OH str), 2957 (s, CH str), 2922 (s, CH str), 2852 (s, CH str), 1467 (w, CH def), 1377 (w, CH def), 1254 (m, $SiCH_3$ def), 1063 (s, SiOSi str), 845 (m, $SiCH_3$), 722 (s), 432 (s). XRD *d*, Å (I/I_o): 28 (100), 15 (18).

XPS data suggested the presence of a fluorine-containing impurity in the polymer. This was probably Teflon abraded from the stir bar.

***n*-Octadecyldimethylsiloxy-*n*-butyldimethylsiloxy Sheet Polymer $[((n\text{-}C_{18}H_{37})(CH_3)_2SiO)_x((n\text{-}C_4H_9)(CH_3)_2SiO)_y(OH)_{1-x-y}SiO_{1.5}]_n$, A−ODM₂−BM₂, p-7.** Apophyllite (1.0 g, 1.1 mmol) was treated with a procedure similar to that used to synthesize **p-8** (1.31 g, 70% yield assuming $x = 0.40$, $y = 0.10$). IR (diffuse reflectance, KBr, cm^{-1}): 3652 (w, free OH str), 3464 (m, H-bonded OH str), 2956 (s, CH str), 2924 (s, CH str), 2853 (s, CH str), 1467 (m, CH def), 1378 (m, CH def), 1255 (m, $SiCH_3$ def), 1066 (s, SiOSi str), 845 (m, $SiCH_3$), 791 (m), 722 (s), 436 (s). XRD *d*, Å (I/I_o): 32 (100), 16 (17).

***n*-Octadecyldimethylsiloxy-3-cyanopropyldimethylsiloxy Sheet Polymer $[((n\text{-}C_{18}H_{37})(CH_3)_2SiO)_x((NCC_3H_6)(CH_3)_2SiO)_y(OH)_{1-x-y}SiO_{1.5}]_n$, A−ODM₂−CM₂, p-8.** Apophyllite (4.1 g, 4.4 mmol), *n*-octadecyldimethylchlorosilane (30 g, 85 mmol), 3-cyanopropyldimethylchlorosilane (5.4 g, 30 mmol), dimethylformamide (180 mL), and toluene (17 g) was heated (130 °C) for 4 h and filtered. The solid was washed (toluene, hexanes, a 1:1 water−acetone solution, acetone, a 1:1 water−acetone solution), vacuum-dried (50 °C), and weighed (5.2 g, 88% assuming $x = 0.25$, $y = 0.25$). IR (diffuse reflectance KBr, cm^{-1}): 3414 (m, H-bonded OH str), 2957 (m, CH str), 2915 (s, CH str), 2850 (s, CH str), 2248 (m, CN str), 1467 (m, CH def), 1375 (w, CH def) 1253 (m $SiCH_3$ str), 1066 (s, SiOSi str), 842 (m, $SiCH_3$), 722 (s), 433 (s). XRD *d*, Å (I/I_o): 26 (100), 13 (2). ^{29}Si NMR: δ 15.95 (s, $O_3SiO\boldsymbol{Si}(CH_3)_2(C_3H_6CN)$, $O_3SiO\boldsymbol{Si}(CH_3)_2(n\text{-}C_{18}H_{37})$), −98.02 (s, $O_3\boldsymbol{Si}OH$), −106.7 (s, $O_3\boldsymbol{Si}OSi(CH_3)_2(C_3H_6CN)$, $O_3\boldsymbol{Si}OSi(CH_3)_2(n\text{-}C_{18}H_{37})$).

Scheme 1. Synthesis of Sheet Polymers



XPS data showed the presence of a small fluorine-containing impurity in the polymer. Again, this was probably Teflon from the stir bar.

***n*-Octadecyldimethylsiloxy-4-chlorobutyldimethylsiloxy Sheet Polymer $[((n\text{-}C_{18}H_{37})(CH_3)_2SiO)_x((ClC_4H_8)(CH_3)_2SiO)_y(OH)_{1-x-y}SiO_{1.5}]_n$, A−ODM₂−CBM₂, p-9.** Apophyllite (0.49 g, 0.55 mmol) was treated with a procedure similar to that used to synthesize **p-8** (0.46 g, 57% assuming $x = 0.25$, $y = 0.25$). IR (diffuse reflectance, KBr, cm^{-1}): 3630 (w, free OH str), 3330 (m, H-bonded OH str), 2959 (m, CH str), 2923 (s, CH str), 2853 (s, CH str), 1456 (m, CH def), 1378 (w, CH def), 1255 (s, $SiCH_3$ def), 1063 (s, SiOSi str), 959 (w), 845 (m, $SiCH_3$), 653 (w), 578 (m), 432 (m). XRD *d*, Å (I/I_o): 28 (100), 15 (13).

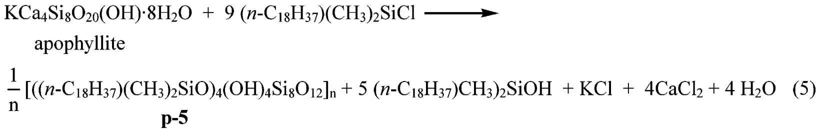
Polymer Properties. All the polymers are white solids. They are insoluble in dimethylformamide, acetone, and hexanes.

Gel Formation. Nanosheet polymer gels were made by both simple mixing and low-power sonication. The following are representative examples of the procedures used.

p-8−*n*-Decane Gel by Mixing. A mixture of **p-8** (0.1 g) and *n*-decane (0.9 g) was allowed to stand at room temperature for 12 h;it was then weighed (1.0 g).

p-8−*n*-Decane Gel by Sonication. A mixture of **p-8** (0.1 g) and *n*-decane (0.9 g) was sonicated with an ultrasonic cleaner (8991, Cole-Palmer, Chicago, IL) for 30 min and was weighed (1.0 g). The mixing procedure was suitable for those polymer−solvent pairs that gave uniform, stiff gels, e.g., **p-6** and acetone, **p-8** and *n*-decane, and **p-9** and CCl_4. All the gels described in the Results and Discussion were made by the sonication procedure (to ensure that the gellation was complete). Drying of the gels yielded the polymers as free-flowing powders.

Scheme 2. Synthesis of A−ODM$_2$, p-5



$$\underset{\text{apophyllite}}{KCa_4Si_8O_{20}(OH)\cdot 8H_2O} + 9\,(n\text{-}C_{18}H_{37})(CH_3)_2SiCl \longrightarrow$$

$$\underset{\textbf{p-5}}{\frac{1}{n}[((n\text{-}C_{18}H_{37})(CH_3)_2SiO)_4(OH)_4Si_8O_{12}]_n} + 5\,(n\text{-}C_{18}H_{37})CH_3)_2SiOH + KCl + 4CaCl_2 + 4\,H_2O \quad (5)$$

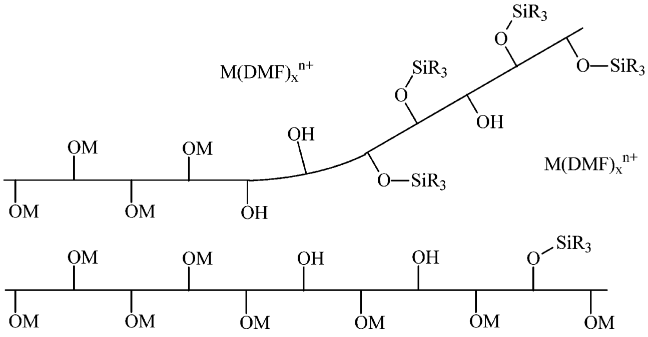


Figure 3. Schematic representation of the excision, protonation, and silylation of the apophyllite sheet.

Table 1. Infrared Bands of Apophyllite-Derived Sheet Polymers p-1−p-9 (cm^{-1})

p-1	p-2	p-3	p-4	p-5	p-6	p-7	p-8	p-9	assignment
3664	3650	3667	3662	3661		3652		3630	free OH str
3423	3450	3337	3336	3448	3461	3464	3414	3330	H-bonded OH str
2961	2958	2957	2957	2956	2957	2956	2957	2959	CH str
2903	2924	2924	2923	2918	2922	2924	2915	2923	CH str
	2873	2854	2854	2850	2852	2853	2850	2853	CH str
							2248		CN str
1462	1465	1467	1466	1467	1467	1467	1467	1456	CH def
				1377	1377	1378	1375	1378	CH def
1254	1254	1254	1254	1255	1254	1255	1253	1255	SiCH$_3$ def
1060	1060	1062	1060	1063	1063	1066	1066	1063	SiOSi str
842	845	843	845	845	845	845	842	845	SiCH$_3$

Results and Discussion

Synthesis. The main reactions yielding the sheet polymers can be represented as shown in Scheme 1. The water for the chlorosilane hydrolysis reaction is provided initially by adventitious water, and later by byproduct water. The success of the silicate protonation reaction depends on the relative ease with which apophyllite is protonated.[32] It is probable that the sheet protonation and sheet silylation reactions take place simultaneously on different portions of the same sheet, Figure 3. The ease with which these two reactions proceed is attributed in part to solvation of the protonated sheet and the byproduct K$^+$ and Ca^{2+} ions by the dimethylformamide. It is not known whether the chlorosilane or the silanol is the dominating silylation agent.

In the case of A−ODM$_2$, **p-5**, the overall reaction can be approximated as shown in Scheme 2. Under the reaction conditions used (that is, excess chlorosilane), the reaction product almost certainly contains both $[(n\text{-}C_{18}H_{37})(CH_3)_2Si]_2O$ and $(n\text{-}C_{18}H_{37})(CH_3)_2SiCl$ as well as $(n\text{-}C_{18}H_{37})(CH_3)_2SiOH$.

Infrared Spectra. The assignments of the infrared bands of **p-1**, Table 4, are based on those made earlier.[9] Those of **p-2**−**p-9** are based largely on the assignments for **p-1** and those made previously for other apophyllite-derived sheet polymers.[8,9,19,23−28]

Table 2. ^{29}Si NMR Data for A−ODM$_2$−CM$_2$, p-8

shift (ppm)	area[a]	assignment
15.95	2617	$O_3SiO\textbf{\textit{Si}}(CH_3)_2(C_3H_6CN)$ $O_3SiO\textbf{\textit{Si}}(CH_3)_2(n\text{-}C_{18}H_{37})$
−98.02	3132	$O_3\textbf{\textit{Si}}OH$
−106.7	3532	$O_3\textbf{\textit{Si}}OSi(CH_3)_2(C_3H_6CN)$ $O_3\textbf{\textit{Si}}OSi(CH_3)_2(n\text{-}C_{18}H_{37})$ $O_4\textbf{\textit{Si}}$

[a] From deconvolution.

Table 3. X-ray Powder Patterns of Polymers with C$_n$H$_{2n+1}$ R Groups

	chain length[a] (no. of atoms)	line (Å)	intensity (cts/s)	refln order (Å)	sheet spacing (Å)
p-1	3	15	800	1	15
p-2	6	19	1400	1	19
p-3	10	24	2000	1	24
		12	100	2	
p-4	12	27	1330	1	27
		13	76	2	
p-5	20	34	3700	1	34
		18	950	2	
		12	220	3	

[a] Number of atoms in the OSiR chain.

Table 4. X-ray Powder Patterns of Polymers with both Short and Long Groups

	chain length[a]					
	short (no. of atoms)	long (no. of atoms)	line (Å)	intensity (cts/s)	refln order (Å)	sheet spacing (Å)
p-5		20	34	3700	1	34
			18	950	2	
			12	220	3	
p-6	3	20	28	620	1	28
			15	110	2	
p-7	6	20	32	2100	1	32
			16	360	2	
p-8	7	20	26	2900	1	26
			13	50	2	
p-9	7	20	28	770	1	28
			15	100	2	

[a] Number of atoms in the OSiR chain.

The C−H and Si−CH$_3$ stretches of the polymers were useful for monitoring the progress of the syntheses as they are in an unencumbered region, relatively strong, present in all cases, and absent in apophyllite. Also useful was the C−N stretch of **p-8** as it too is in an unencumbered region and strong. Although the Si−O−Si stretches of all the polymers were of some value as well, this was reduced by the presence of relatively similar Si−O−Si stretches in apophyllite, Figure 4.

On the basis of the relative strengths of the C−H and Si−O−Si bands, the level of substitution of the polymers was estimated to be about 50%. This is consistent with levels reported earlier for **p-1** and other apophyllite-derived sheet polymers.[8,9,23,25]

^{29}Si NMR Spectra. Prior work was used in assigning the resonances in the ^{29}Si NMR spectrum of **p-8**, Figure 5 and Table 2, and in calculating its level of substitution as being equal to the area of the $O_3\textbf{\textit{Si}}OSi(CH_3)_2R$ resonance divided

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(32) Aldushin, K.; Jordan, G.; Fechtelkord, M.; Schmahl, W. W.; Becker, H.-W.; Rammensee, W. *Clays Clay Miner.* **2004**, *52*, 432−442.

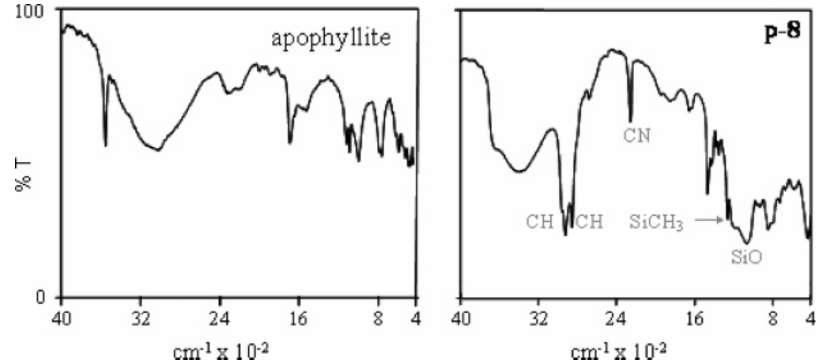


Figure 4. Infrared spectra of apophyllite and **p-8**.

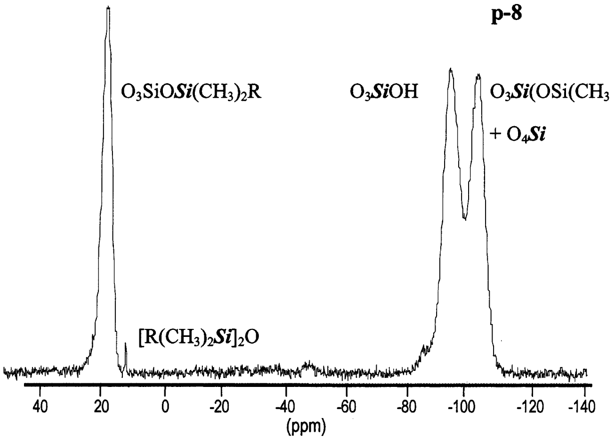


Figure 5. ^{29}Si NMR of **p-8**.

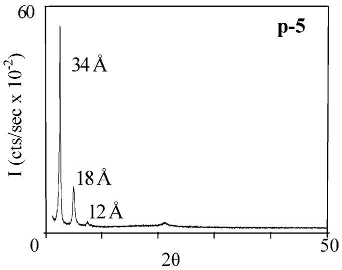


Figure 6. X-ray powder pattern of **p-5**.

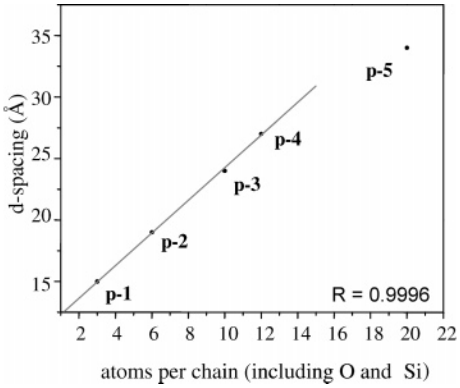


Figure 7. Atoms per chain vs *d* spacing for the $SiOSi(CH_3)_2(C_nH_{2n+1})$ series of polymers.

by the sum of the areas of the two $O_3\mathbf{Si}OSi(CH_3)_2R$ resonances plus the area of the $O_3\mathbf{Si}OH$ resonance.[9] As before, the contribution of the O_4Si resonance (the resonance from silicon atoms in the sheet that are oxygen-bridged only to other silicon atoms in the same sheet) to the area of the line at −107 ppm was assumed to be small, and the area of the line was assigned solely to the two $O_3\mathbf{Si}OSi(CH_3)_2R$ resonances. The level of substitution thus obtained, 53%, is consistent with levels reported earlier for similar apophyllite polymers.[8,9,23,25]

X-ray Data. The assignment of the major line in the X-ray powder pattern of **p-1** to a first-order reflection from the polymer sheets, and the determination of the intersheet spacing on the basis of the use of this assignment, find precedents in earlier work on this polymer, Figure 6 and Tables 3 and 4.[5,8,9,17,21] For **p-2**−**p-9**, the major-line assignments and the intersheet-spacing determinations are consistent with the work on **p-1** and have support from work on other apophyllite-derived sheet polymers.[8,9,19,21,23−28] The assignment of the smaller lines near the first-order lines in **p-3**−**p-9** to higher-order reflections is in accord with previous work.[9]

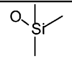
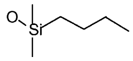
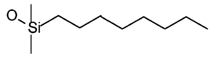
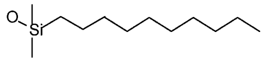
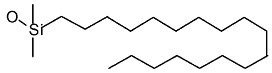
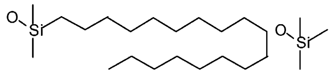
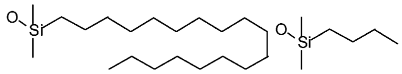
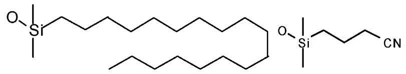
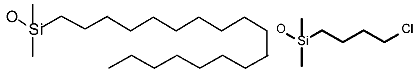
As expected, the spacings of **p-1**−**p-4** vary with the length of the OSiOSiR chain, Figure 7. Because the values for the spacings and the origin lie on a straight line, it is probable that the OSiR chains in these four polymers have the same conformation and that they are linear. The long OSiR chain of **p-5**, in contrast, is probably somewhat folded, again as expected.

The intensity data for **p-1**−**p-5**, although not fully comparable in part because of the data-collection method used, suggest that the intensities increase as the length of the OSiR chain increases. This is attributed to the greater softness of the layer formed by the OSiR groups with increasing chain length, and hence the greater ability of this layer to allow the sheet backbone to relax to a nearly planar arrangement. The presence of a third-order reflection in the powder pattern of **p-5** supports this conclusion. The smaller interplanar spacings of **p-6**−**p-9** compared to **p-5**, Table 4, are due to the intermixing of short OSiR groups with their common, long $OSi(CH_3)_2(n\text{-}C_{18}H_{37})$ groups.

Nanosheet Polymer Gels. All of the polymers except **p-1** give gels with two or more members of a list of solvents composed of *n*-decane, CCl_4, trimethylsiloxy-capped 10 cSt poly(dimethylsiloxane), 2-nonanone, and acetone, Table 5. These gels give no powder patterns in the 14−90 Å range, Figure 8. For **p-6**−**p-9**, the gels are viscous when the polymer loading is greater than 10%, Figure 9.

From the data in Table 5, it is apparent that the gel-forming ability of the polymers conforms with expectations based on the polarity of the solvent, the polarity of R in the OSi-

Table 5. Gel Data for Polymers p-1−p-9

pendent group		solvent				
		n-$C_{10}H_{22}$	PDMS[a]	CCl_4	$C_9H_{18}O$[b]	C_3H_6O[c]
p-1						
p-2		1[d]	1			
p-3		2	1	2		
p-4		2	2	2	1	
p-5		2	2	2	1	
p-6		3	3	2	3	2
p-7		3	3	2	3	1
p-8		3	3	2	3	2
p-9		3	3	2	2	1

[a] PDMS, 100 cSt poly(dimethylsiloxane). [b] 2-Nonanone. [c] Acetone. [d] (1) Grainy, (2) uniform and stiff at 15% loading, and (3) uniform and stiff at ~9% loading.

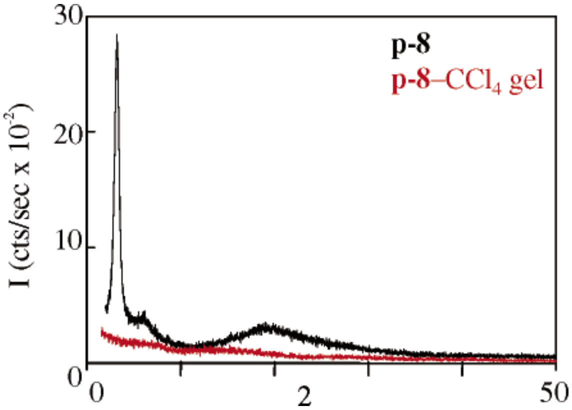


Figure 8. X-ray powder patterns of an exfoliated **p-8**−CCl_4 gel and, for reference, **p-8**.

Figure 9. Exfoliated **p-8**−CCl_4 gel containing 10% **p-8**.

$(CH_3)_2R$ group, and the length of R.[26] Thus, **p-1**, with its nonpolar, short methyl R group, forms no gels, whereas **p-2**, with its nonpolar but longer butyl R group, forms grainy gels with the nonpolar solvents n-decane and CCl_4 but not with the polar solvents 2-nonanone and acetone; **p-5**, with its nonpolar, long octadecyl R group, forms thick and uniform gels with the two nonpolar solvents but a grainy gel with 2-nonanone and no gel with acetone. Interestingly, **p-6** and **p-7**, with both nonpolar short and nonpolar long R groups, are better gel formers than **p-5**. This is attributed to a reduction in their sheet-to-sheet packing efficiency. Similarly, **p-8** and **p-9**, with both polar short and nonpolar long R groups, are better gel formers than **p-5**. Both their reduced packing efficiency and the polarity of their short R groups probably contribute to this.

The formation of these disaggregated nanosheet polymer gels suggests that similar gels can be made in which the solvent is a monomer that can serve as a resin former in composites. Gels of this type could be polymerized to give nanosheet polymer composites in which the sheets are highly disaggregated. The high degree of disaggregation of the sheets would result in a high degree of expression of the valuable properties that the sheets have the potential to confer on composites. This approach to nanosheet polymer composites is preferable to that depending on mechanical mixing because of its simplicity.

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