

# Synthesis and Characterization of Organosilicon Sheet and Tube Polymers<sup>†</sup>

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The synthesis and characterization of some organosilicon sheet and tube polymers derived from silicates are described. The sheet silicates used are apophyllite ( $\text{KC}_4\text{Si}_8\text{O}_{20}(\text{F},\text{OH})\cdot 8\text{H}_2\text{O}$ ), kenyaite ( $\text{Na}_2\text{Si}_{22}\text{O}_{45}\cdot 9\text{H}_2\text{O}$ ), magadiite ( $\text{Na}_2\text{Si}_{14}\text{O}_{29}\cdot 7\text{H}_2\text{O}$ ), and silinaite ( $\text{NaLiSi}_2\text{O}_5\cdot 2\text{H}_2\text{O}$ ). The tube silicate used is  $\text{K}_2\text{CuSi}_4\text{O}_{10}$ . The organosilicon sheet and tube polymers are made by silylation of sheet or tube silicates using a variety of nonfunctional and functional silylating agents. The formula of representative sheet and tube polymers made by silylation with trimethylchlorosilane is  $[\text{((CH}_3)_3\text{SiO)}_x(\text{HO})_{1-x}\text{SiO}_{1.5}]_n$ . The alkenyl-functional sheet and tube polymers are further elaborated by using hydrosilylation. The formula of representative sheet and tube polymers made by hydrosilylation of vinyl dimethylsiloxy polymers with pentamethyldisiloxane is  $[\text{((CH}_3)_3\text{SiO(CH}_3)_2\text{Si(CH}_2)_2(\text{CH}_3)_2\text{SiO)}_x(\text{HO})_{1-x}\text{SiO}_{1.5}]_n$ . The polymers are characterized by FTIR, XRD, XPS, SEM, and solid state <sup>29</sup>Si NMR. The characterization data demonstrate that  $\approx 60\%$  of the polymer surface silicon atoms carry pendent organosilicon groups, and the remaining silicon atoms carry silanol groups. These polymers are hydrophobic and they maintain the sheet or tube morphology both before and after the silylation and hydrosilylation reactions.

## Introduction

Organosilicon oligomers and polymers are made and used on a large scale. Typically, they are made by the polymerization of organosilicon monomers.<sup>1</sup> An alternative route to them involves the silylation of silicates.<sup>2</sup> The first report of the silylation of silicates was made by Lentz in 1964.<sup>3</sup> This alternative route is attractive because it makes the synthesis of new and interesting oligomers and polymers feasible. Lentz reported that monomeric and oligomeric silicates can be silylated with a mixture of  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ , HCl, 2-propanol, and water. Later, Gotz and Masson reported that low molecular weight silicates can be silylated with a mixture of  $(\text{CH}_3)_3\text{SiCl}$ ,  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$  and 2-propanol,<sup>4</sup> and Hoebbel and co-workers reported that such silicates can be silylated with a mixture of  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ , HCl, acetone, and bis(trimethylsilyl)acetamide (BSA).<sup>5</sup> Likewise, Roy and co-workers reported that low

molecular weight silicates can be silylated with a mixture of  $(\text{CH}_3)_3\text{SiCl}$ ,  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ , and dimethylformamide.<sup>6</sup>

Shortly after Lentz reported that low molecular weight silicates can be silylated, Kenney and co-workers reported that a polymeric silicate, the sheet silicate chrysotile,  $\text{Mg}_3(\text{OH})_4\text{Si}_2\text{O}_5$ , can be silylated with a mixture of  $(\text{CH}_3)_3\text{SiCl}$ , HCl,  $\text{H}_2\text{O}$ , and 2-propanol.<sup>7</sup> Subsequently, Kenney and other investigators reported additional work on the silylation of chrysotile,<sup>8</sup> apophyllite,<sup>9–12</sup> sepiolite,<sup>13–16</sup> vermiculite,<sup>17</sup> attapulgite,<sup>18,19</sup> halloysite,<sup>20</sup> kenyaite,<sup>21–25</sup> magadiite,<sup>22–26</sup> and imog-

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olite.<sup>27</sup> Additionally, Hefter and Kenney reported that a polymeric silicate of another type, the tube silicate lithidionite,  $\text{NaKCuSi}_4\text{O}_{10}$ , can be silylated with a mixture of  $(\text{CH}_3)_3\text{SiCl}$ ,  $\text{HCl}$ , and dioxane.<sup>28</sup> In later publications, Kenney and others reported further efforts on the silylation of lithidionite and efforts on the silylation of the additional tube silicates  $\text{Na}_2\text{CuSi}_4\text{O}_{10}$  and  $\text{K}_2\text{CuSi}_4\text{O}_{10}$ .<sup>29–33</sup>

The organosilicon sheet and tube polymers obtained by these procedures have unique and potentially valuable property sets. For example, it has been suggested they could be of use as thickening agents in polymeric systems.<sup>29</sup> In addition to silylation of sheet and tube silicates, these polymers can carry functional groups that allow further reactions such as hydrosilylation.<sup>33–41</sup> In this paper, we present studies on silylation of sheet and tube silicates, hydrosilylation of alkenyl sheet and tube polymers, and their characterization.

### Experimental Section

**Materials.** Apophyllite,  $\text{KCa}_4\text{Si}_8\text{O}_{20}(\text{F},\text{OH})\cdot 8\text{H}_2\text{O}$ , was purchased from Ward's Natural Science Establishment, Rochester, NY. Kenyaite ( $\text{Na}_2\text{Si}_{22}\text{O}_{45}\cdot 9\text{H}_2\text{O}$ ) and magadiite ( $\text{Na}_2\text{Si}_{14}\text{O}_{29}\cdot 7\text{H}_2\text{O}$ ) were obtained as gifts from Hoechst, Frankfurt, Germany. Silinaite,  $\text{NaLiSi}_2\text{O}_5\cdot 2\text{H}_2\text{O}$ , was prepared according to a literature procedure.<sup>42</sup>  $\text{K}_2\text{CuSi}_4\text{O}_{10}$  was prepared according to procedures described earlier.<sup>33</sup> All other reagents are commercially available and were used without further purification.

**Characterization.** The infrared spectra were recorded with a Perkin-Elmer model 16 PC Fourier transform infrared spectrometer (Perkin-Elmer, Norwalk, CT). The sample mulls were contained with CsI plates. The spectrometer was calibrated with the  $1602.0\text{-cm}^{-1}$  band of polystyrene. Typical instrument settings used were as follows: spectrometer range  $4000\text{--}400\text{ cm}^{-1}$ , resolution  $4\text{ cm}^{-1}$ , and number of scans 8. The

X-ray powder diffraction patterns were recorded with a Philips APD 3520 diffractometer (Philips Electronic Instruments, Mahwah, NJ) equipped with a Philips XRG 3100 X-ray generator (Cu  $K\alpha$ ) and a Philips graphite monochromator. The instrument was calibrated with the  $3.342\text{-\AA}$  reflection from a  $\text{SiO}_2$  (quartz) plate. Typical instrument settings used were as follows: generator power 40 kV/30 mA, scan mode step scan,  $2\theta$  scan rate  $3^\circ/\text{min}$ ,  $2\theta$  step size  $0.05^\circ$ , and  $2\theta$  range  $3^\circ\text{--}70^\circ$ . The  $^{29}\text{Si}$  NMR spectra were recorded on an MSL-400 Bruker NMR spectrometer (USA Bruker Instruments, Billerica, MA) equipped with a Bruker magic-angle spinning solid probe. TMS was used as a reference. The spectra were deconvoluted with the Bruker LINESIM program. Typical instrument settings used were as follows: spectral frequency 79.494 MHz, field strength 9.4 T, sweep width 23 809 Hz, number of data points 1428, number of scans 600, pulse time  $5\ \mu\text{s}$ , dwell time  $21\ \mu\text{s}$ , delay after pulse  $42\ \mu\text{s}$ , acquisition time 30 ms, delay before following 100 s, line broadening 20 Hz, spin rate 4200 Hz, and decoupler off. The X-ray photoelectron spectra were recorded with a Perkin-Elmer Model 5600 X-ray photoelectron spectrometer equipped with an Al anode X-ray source. Typical instrument settings used were as follows: vacuum  $3 \times 10^{-9}$  Torr, anode potential 15 kV, power 350 W, and number of scans 13. Scanning electron micrographs were taken with a JEOL 35CF scanning electron microscope (JEOL USA, Peabody, MA). C and Au coatings were deposited on the sample in a Bio-Rad E6440 vacuum evaporation chamber (Bio-Rad Corp., Cambridge, MA). Typical instruments settings used were as follows: accelerating voltage 25 kV, probe current  $1 \times 10^{-7}$  A, mode SEI, and magnification  $2000\text{--}20\ 000\times$ .

**Representative Polymer Syntheses.** *Silylated Apophyllite Sheet Polymer*  $[(\text{CH}_3)_3\text{SiO}]_x(\text{HO})_{1-x}\text{SiO}_{1.5}]_n$ ,  $A\text{--}M_3$ . A suspension of apophyllite (120 mesh, 12.4 g, 13.4 mmol), trimethylchlorosilane (70.0 mL, 552 mmol), and dimethylformamide (410 mL, 5.29 mol) was refluxed for 3 h, and the resultant was filtered, washed with acetone (2 times, 100 mL each time), a solution of water and acetone (1:1, 4 times, 200 mL each time), acetone (2 times, 100 mL each time), and vacuum-dried ( $90^\circ\text{C}$ , 3 h) (12.0 g). XRD ( $d(\text{\AA})$  ( $I/I_0$ )): 15.0 (100), 7.7 (6), 4.5 (br, 12). IR (Fluorolube, Nujol mulls,  $\text{cm}^{-1}$ ): 3475 (m br, hydrogen-bonded OH stretch), 2960 (s, CH stretch), 2928 (m, CH stretch), 2856 (w, CH stretch), 1420 (w, CH deformation), 1374 (w, CH deformation), 1254 (m,  $\text{SiCH}_3$  deformation), 1200 (w sh, SiOSi stretch), 1123 (m sh, SiOSi stretch), 1064 (vs br, SiOSi stretch), 842 (s, SiC stretch), 756 (m), 431 (m).  $^{29}\text{Si}$  MAS NMR (400 MHz, TMS as primary reference, 4200 Hz,  $\approx 25^\circ\text{C}$ ):  $\delta$  13.24 (s,  $\text{Si}(\text{CH}_3)_3$ ),  $-99.40$  (s, SiOH),  $-109.8$  (s,  $\text{SiO}_{4/2}$ ). XPS (Si 2p binding energy, deconvoluted spectrum, eV): 103.4 ( $\text{SiO}_{4/2}$ ), 101.5 ( $\text{Si}(\text{CH}_3)_3$ ), 99.80. Level of substitution on the basis of the areas of the SiOH and  $\text{SiO}_{4/2}$   $^{29}\text{Si}$  resonances after they had been deconvoluted (%); found, 59. Level of substitution on the basis of the areas of the  $\text{SiO}_{4/2}$  and  $\text{Si}(\text{CH}_3)_3$  peaks in the deconvoluted XPS spectrum (%); found, 60. Yield of polymer on the basis of a level of substitution of 59% (mmol, %); found, 107, 100. From the XRD spectra, it appears that the polymer contained  $\text{SiO}_2$  as an impurity and thus that the actual yield of it was  $<100\%$ . Bulk density ( $\text{g}/\text{cm}^3$ ): 0.3. The polymer was a white solid. It dispersed but did not dissolve in hexane or toluene. It was very hydrophobic and it did not mix or disperse in  $\text{H}_2\text{O}$ .

*Silylated  $\text{K}_2\text{CuSi}_4\text{O}_{10}$  Tube Polymer*  $[(\text{CH}_3)_3\text{SiO}]_x(\text{HO})_{1-x}\text{SiO}_{1.5}]_n$ ,  $K\text{--}M_3$ . A suspension of  $\text{K}_2\text{CuSi}_4\text{O}_{10}$  (100 mesh; 7.00 g, 16.9 mmol), trimethylchlorosilane (60.0 mL, 473 mmol), and dimethylformamide (280 mL) was refluxed for 4 h, and the resultant was filtered, washed with acetone (2 times, 100 mL each time), a solution of water and acetone (1:2, 2 times, 300 mL each time), and acetone (2 times, 100 mL each time), and air-dried for 10 min (7.10 g). XRD ( $d(\text{\AA})$  ( $I/I_0$ )): 15.9 (100), 9.20 (14), 7.80 (13), 4.4 (br, 19). IR (Fluorolube, Nujol mulls,  $\text{cm}^{-1}$ ): 3480 (m br, hydrogen-bonded OH stretch), 2960 (s, CH stretch), 2917 (s, CH stretch), 2857 (s, CH stretch), 1412 (w, CH deformation), 1372 (w, CH deformation), 1254 (m,  $\text{SiCH}_3$  deformation), 1170 (m sh, SiOSi stretch), 1087 (vs br, SiOSi stretch), 978 (w sh), 855 (m), 845 (s, SiC stretch), 757 (m), 440 (m).  $^{29}\text{Si}$  MAS NMR (400 MHz, TMS as primary reference,

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4100 Hz,  $\approx 25^\circ\text{C}$ ):  $\delta$  12.42 (s,  $\text{Si}(\text{CH}_3)_3$ ),  $-98.66$  (s,  $\text{SiOH}$ ),  $-109.3$  (s,  $\text{SiO}_{4/2}$ ). XPS (Si 2p binding energy, deconvoluted spectrum, eV): 103.4 ( $\text{SiO}_{4/2}$ ), 101.6 ( $\text{Si}(\text{CH}_3)_3$ ), 99.71. Level of substitution on the basis of the areas of the  $\text{SiOH}$  and  $\text{SiO}_{4/2}$   $^{29}\text{Si}$  resonances after they had been deconvoluted (%); found, 61. Level of substitution on the basis of the areas of the  $\text{SiO}_{4/2}$  and  $\text{Si}(\text{CH}_3)_3$  peaks in the deconvoluted XPS spectrum (%); found, 62. Yield of polymer on the basis of a level of substitution of 61% (mmol, %); found, 62.8, 93. The polymer was a light blue solid. Its color was attributed to residual copper(II). It dispersed in but did not dissolve in hexane or toluene. It was very hydrophobic and it did not mix with or disperse in  $\text{H}_2\text{O}$ .

**Hydrosilylated Octenylsiloxo Sheet Polymer**  $[(\text{CH}_3)_3\text{SiO}(\text{CH}_2)_2\text{Si}(\text{CH}_2)_8(\text{CH}_3)_2\text{SiO}]_x(\text{HO})_{1-x}\text{SiO}_{1.5}]_n$  (AO-PM<sub>2</sub>). A suspension of the octenyltrimethylsiloxo sheet polymer (1.00 g, 53% level of substitution, 2.0 mmol), pentamethyldisiloxane (12.2 g, 82.0 mmol), and a solution composed of  $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$  (50 mg) and 2-propanol (1.0 mL) was heated ( $\approx 90^\circ\text{C}$ ) with stirring for 3 h, and the resultant was filtered, washed with 2-propanol (25 mL) and acetone (100 mL), and vacuum-dried ( $90^\circ\text{C}$ , 1 h) (1.25 g). XRD ( $d(\text{\AA})$  ( $I/I_0$ )): 34.7 (100), 17.5 (18), 11.8 (6), 5.2 (br, 7). IR (Fluorolube, Nujol mulls,  $\text{cm}^{-1}$ ): 3485 (m br, hydrogen-bonded OH stretch), 2957 (s, CH stretch), 2922 (vs, CH stretch), 2853 (s, CH stretch), 1470 (w, CH deformation), 1410 (w, CH deformation), 1253 (s,  $\text{SiCH}_3$  deformation), 1203 (m sh, SiOSi stretch), 1118 (m sh, SiOSi stretch), 1060 (vs br, SiOSi stretch), 968 (w), 842 (s, SiC stretch), 808 (m), 748 (w), 433 (m).  $^{29}\text{Si}$  MAS NMR (400 MHz, TMS as primary reference, 4200 Hz,  $\approx 25^\circ\text{C}$ ):  $\delta$  14.44 (s,  $(\text{CH}_2)_8\text{Si}(\text{CH}_3)_2$ ), 7.78, 7.19 (d,  $(\text{CH}_3)_3\text{SiO}(\text{CH}_2)_2\text{Si}$ ),  $-98.98$  (s,  $\text{SiOH}$ ),  $-108.2$  (s,  $\text{SiO}_{4/2}$ ). Level of substitution on the basis of the areas of the  $\text{SiOH}$  and  $\text{SiO}_{4/2}$   $^{29}\text{Si}$  resonances after they had been deconvoluted (%): 51. Yield of polymer on the basis of a level of substitution of 56% (mmol, %); found, 5.07, 80. No C=C-H or C=C bands were observed in the infrared spectrum of this polymer. It was an off-white solid. It dispersed in but did not dissolve in hexane or toluene. The polymer was very hydrophobic and it did not mix with or disperse in  $\text{H}_2\text{O}$ .

## Results and Discussion

**Silicates.** Four sheet silicates and one tube silicate were used in these studies. The sheet silicates used were apophyllite, kenyaite, magadiite, and silinaite. The tube silicate used was  $\text{K}_2\text{CuSi}_4\text{O}_{10}$ . Apophyllite is found in various locations including Rio Grande do Sol, Brazil; Poona, India; and Mont Saint-Hilaire, Canada.<sup>43</sup> No synthesis of it has been reported. The silicate ion in it is a sheet made up of fused 8-membered and 16-membered rings.<sup>44</sup> Pendent oxygen atoms project from both sides of the sheet. Kenyaite is found at Lake Magadi, Kenya.<sup>45</sup> It can be prepared synthetically.<sup>46</sup> It is believed that the silicate ion in it is a complex sheet composed of multiple sheets fused together.<sup>47-49</sup> It is further believed that pendent oxygen atoms project from both sides of the sheet. Magadiite also is found at Lake Magadi, Kenya.<sup>45</sup> It too can be prepared synthetically.<sup>50</sup> It is thought the silicate ion in it is a double sheet similar to that of kenyaite. Silinaite, like apophyllite,

is found in Mont Saint-Hilaire, Canada.<sup>51</sup> It can be synthesized under mild conditions.<sup>42</sup> The silicate ion in it is a sheet composed of fused 12-membered rings.<sup>52</sup> Pendent oxygen atoms project from both sides of the sheet.  $\text{K}_2\text{CuSi}_4\text{O}_{10}$  does not occur naturally. However, it can be synthesized under moderate conditions.<sup>53</sup> Its silicate ion is a tube composed of fused 8-, 12-, and 16-membered rings.<sup>54</sup> Pendent oxygen atoms project outward from the surface of the tube.

**Silicate-Derived Siloxy Sheet and Tube Polymers.** The conditions used to silylate apophyllite are similar to those used earlier to silylate this silicate.<sup>9-12</sup> However, dimethylformamide was used as the reaction solvent rather than an acetone-water solution or an acetone-ether-water solution because it had been shown in work done after the earlier apophyllite work that dimethylformamide is a very good solvent for silylation.<sup>6</sup> Also, an elevated temperature rather than room temperature was used because relatively rapid silylations were desired. The conditions used in the silylation of kenyaite, magadiite, silinaite, and  $\text{K}_2\text{CuSi}_4\text{O}_{10}$  were modeled on those used for apophyllite.

The silicate sheet preservation found in the earlier apophyllite work and the relatively close similarity of the reaction conditions used in this earlier work to those used in the present work suggest that the conditions used in the present work led to sheet preservation. Because the conditions used in the present work were effective with different sheet silicates, it appears that conditions of this type should be generally effective for the silylation of reactive sheet silicates. On the basis of observations made during the synthesis and workup procedures, it appears that the polymers prepared are quite stable. This is to be expected because they are organosiloxanes (which in some cases are functionalized). The syntheses used for the kenyaite-derived and magadiite-derived sheet polymers are simpler than the syntheses used earlier for siloxy sheet polymers derived from these silicates<sup>21-26</sup> because intermediate alkylammonium species are avoided. Because of their simplicity, these new syntheses are superior. A tabulation of symbols and structures of sheet and tube polymer pendent groups studied in this work are given in Table 1.

**X-ray Powder Patterns.** The representative X-ray powder patterns of the siloxy sheet and tube polymers made by silylation are shown in Figures 1-3. The powder patterns of the silicates used as reactants are shown for comparison purposes. A tabulation of the lines in these patterns is given in Table 2. The major low-angle lines in these patterns are assigned to first-order reflections from the polymer sheets. The assignment of the major low-angle line of the apophyllite-derived trimethylsiloxo sheet polymer to a first-order sheet reflection is in agreement with that made earlier for this line.<sup>9-12</sup>

In accordance with the interpretation of the previous X-ray data on the apophyllite-derived trimethylsiloxo

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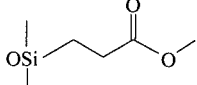
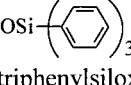
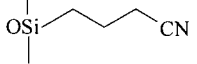
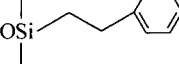

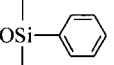
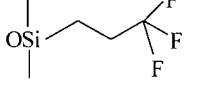
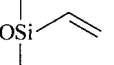
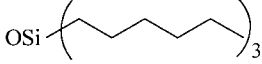
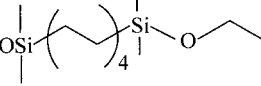
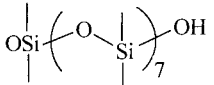
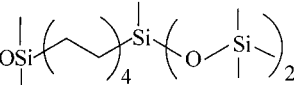
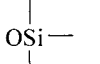
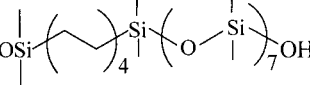
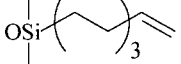
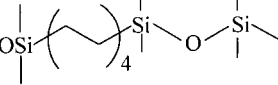

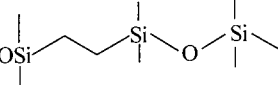
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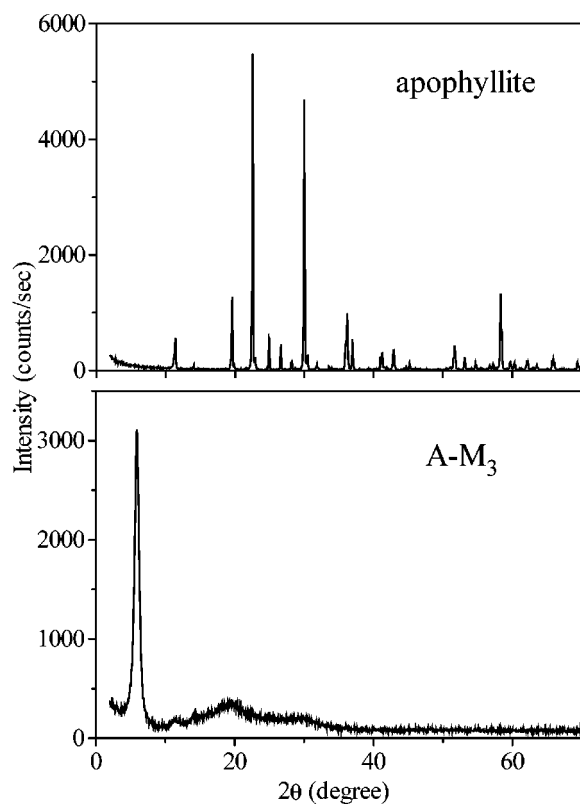
Table 1. Symbols and Structures of Sheet and Tube Polymer Pendent Groups

symbol <sup>a</sup>	structure	symbol	structure
A-AM <sub>2</sub>	 acetoxypropyldimethylsiloxyl	A-P <sub>3</sub>	 triphenylsilyloxy
A-CM <sub>2</sub> K-CM <sub>2</sub>	 cyanopropyldimethylsiloxyl	A-PEM <sub>2</sub>	 phenethylsilyloxy
A-DM <sub>2</sub>	 decyldimethylsiloxyl	A-PM <sub>2</sub>	 phenyldimethylsiloxyl
A-FM <sub>2</sub>	 trifluoropropyldimethylsiloxyl	A-VM <sub>2</sub> K-VM <sub>2</sub>	 vinylsilyloxy
A-H <sub>3</sub>	 trihexylsilyloxy	AO-EM <sub>2</sub>	 (ethoxydimethylsilyloctyl)dimethylsiloxyl
A-HHM <sub>2</sub>	 (hydroxy)(hexadecamethyl)- octasiloxyl	AO-HM <sub>2</sub>	 (heptamethyltrisiloxyoctyl)dimethylsiloxyl
A-M <sub>3</sub> K-M <sub>3</sub> KE-M <sub>3</sub> M-M <sub>3</sub> S-M <sub>3</sub>	 trimethylsilyloxy	AO-HHM <sub>2</sub>	 ((hydroxy)(hexadecamethyl)octasiloxyl)- dimethylsiloxyl
A-OEM <sub>2</sub> K-OEM <sub>2</sub>	 octenyldimethylsiloxyl	AO-PM <sub>2</sub>	 (pentamethyldisiloxyoctyl)dimethylsiloxyl
A-OM <sub>2</sub> M-OM <sub>2</sub> S-OM <sub>2</sub>	 octyldimethylsiloxyl	AV-PM <sub>2</sub> KV-PM <sub>2</sub>	 (pentyamethyldisiloxyethyl)dimethylsiloxyl

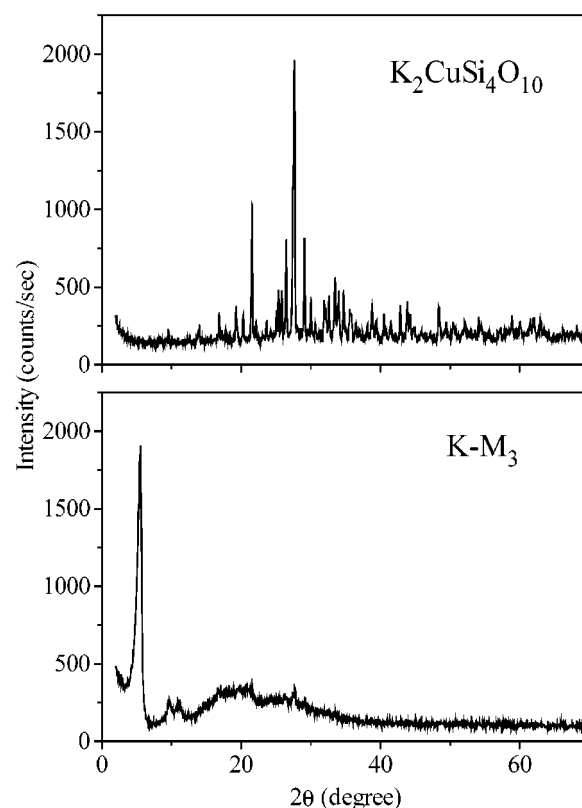
<sup>a</sup> A, apophyllite backbone; K, K<sub>2</sub>CuSi<sub>4</sub>O<sub>10</sub> backbone; KE, kenyaite backbone; M, magadiite backbone; S, silinaite backbone; AO, apophyllite-derived octenyl polymer backbone; AV, apophyllite-derived vinyl polymer backbone; KV, K<sub>2</sub>CuSi<sub>4</sub>O<sub>10</sub>-derived vinyl polymer backbone.

sheet polymer,<sup>9-12</sup> the spacings of these lines yield the interplanar spacings of the sheets. As expected, the magnitudes of these spacings generally correlate with the magnitudes of the lengths of the pendent groups of the polymers. In a number of the patterns, the first-order lines are relatively intense and narrow. This indicates that the sheets in the polymers are quite planar and the spacings between them are quite regular. This in turn indicates that the Si-O frameworks of the parent silicates were carried over into the polymers without major modification. In some of the patterns with intense, narrow first-order lines, low-intensity lines at half the *d* spacing of the first-order lines are present. These low-intensity lines are assigned to second-order reflections from the sheets (Table 2). The existence of

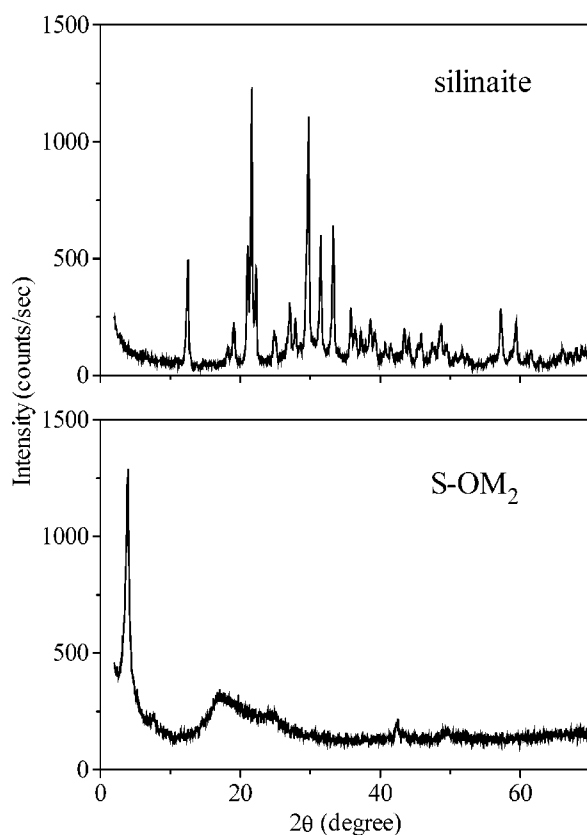
these second-order lines further indicates that the silicon-oxygen frameworks of the parent silicates are carried over into the polymers without major modification. The lack of additional, relatively sharp lines in the patterns of the apophyllite-derived polymers is noteworthy. This shows that while the sheets in these polymers are quite planar and are stacked with regular spacings, they are not in registry with one another. This is not surprising in view of the way in which the polymers are synthesized. It is presumed that the sheets in the other silicate-derived polymers also are not in registry. The assignments of the remaining lines in the patterns of the various polymers are unknown. Probably some of these lines are associated with the sheet backbones.



**Figure 1.** X-ray powder patterns of apophyllite mineral (top) and apophyllite-derived trimethylsiloxo sheet polymer (bottom).



**Figure 3.** X-ray powder patterns of  $K_2CuSi_4O_{10}$  (top) and  $K_2CuSi_4O_{10}$ -derived trimethylsiloxo tube polymer (bottom).



**Figure 2.** X-ray powder patterns of silinaite (top) and silinaite-derived octyldimethylsiloxo sheet polymer (bottom).

*Infrared Spectra.* A tabulation of the major bands in selected sheet and tube polymers and, where possible,

**Table 2.** *d* Spacings of Silicate-Derived Siloxo Sheet and Tube Polymers (Å)

polymer	<i>d</i> spacing								
A-M <sub>3</sub>	15.0 <sup>a</sup>		7.7 <sup>b</sup>	4.5					
A-OM <sub>2</sub>	24.1		12.3	4.7					
A-DM <sub>2</sub>	28.5		14.1	4.8					
A-H <sub>3</sub>	17.8			4.0					
A-PM <sub>2</sub>	17.9			4.6					
A-PEM <sub>2</sub>	20.3		10.2	4.9					
A-P <sub>3</sub>	15.2			3.9					
A-VM <sub>2</sub>	16.1			4.7					
A-OEM <sub>2</sub>	23.6		11.9	5.0					
A-CM <sub>2</sub>	19.6			4.4					
A-FM <sub>2</sub>	21.8			4.5					
A-AM <sub>2</sub>	19.2			4.6					
A-HHM <sub>2</sub>	17.7			4.0					
KE-M <sub>3</sub>	23.6		11.6	7.3	4.6	3.7	3.5	3.4	1.8
M-M <sub>3</sub>	18.8			6.9	4.7		3.6	3.4	1.8
M-OM <sub>2</sub>	24.2	14.3		7.3	4.6		3.5		1.8
S-M <sub>3</sub>	14.6			7.3	4.9				
S-OM <sub>2</sub>	22.4				5.2				
K-M <sub>3</sub>	15.9	9.2		7.8	4.4				
K-VM <sub>2</sub>	16.4	9.3		8.0	4.6				
K-OEM <sub>2</sub>	20.1				4.9				
K-CM <sub>2</sub>	16.1				4.8				
K-CBM <sub>2</sub>	18.4				4.9				

<sup>a</sup> The first-order diffraction. <sup>b</sup> The second-order diffraction.

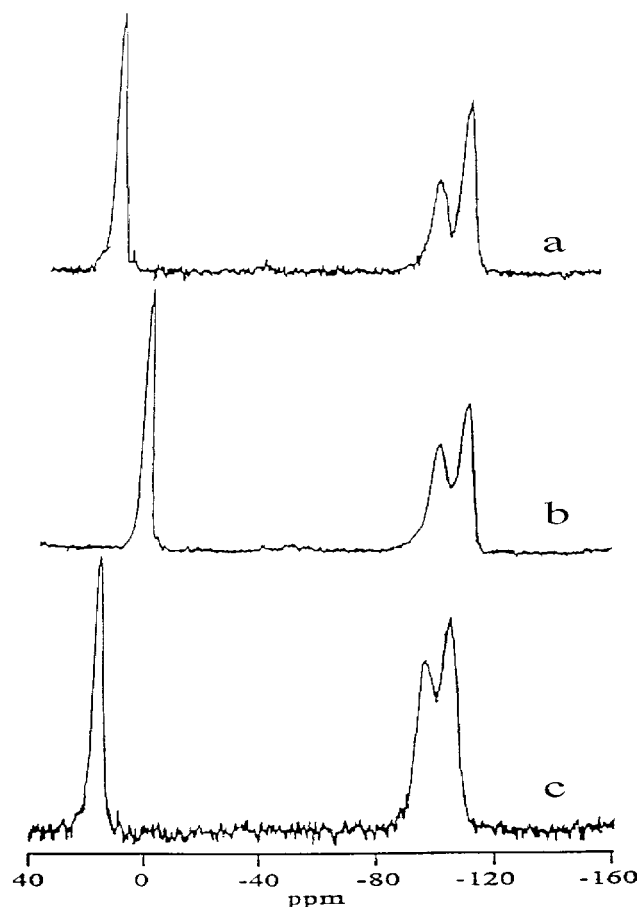
assignments for these bands are given in Table 3. The assignments for the apophyllite-derived trimethylsiloxo sheet polymer are consistent with those made earlier for this polymer.<sup>21–25</sup> Likewise, the assignments for the  $K_2CuSi_4O_{10}$ -derived trimethylsiloxo tube polymer are consistent with those given earlier for this polymer.<sup>31</sup> The spectra show that the pendent groups of the polymers have the structures expected on the basis of the chlorosilanes used even when these chlorosilanes have moderately complex functionalities. The intensities

**Table 3. Infrared Bands (cm<sup>-1</sup>) of Selected Sheet and Tube Polymers**

A-M <sub>3</sub>	A-OEM <sub>2</sub>	A-CM <sub>2</sub>	A-AM <sub>2</sub>	M-M <sub>3</sub>	S-M <sub>3</sub>	K-M <sub>3</sub>	K-OEM <sub>2</sub>	assignment
	3645						3651	free OH stretch
3475	3468	3393	3442	3475	3324	3480	3480	H-bond OH stretch
	3087						3049	C=C-H stretch
2960		2958	2960	2960	2960	2960		CH stretch
2928	2924	2933		2928	2928	2917	2924	CH stretch
2856	2854	2882	2847	2855	2856	2857	2854	CH stretch
		2246						CN stretch
			1740					C=O stretch
	1641						1641	C=C stretch
	1470	1457					1457	CH deformation
1420	1414	1425	1384	1426	1418	1412	1414	CH deformation
1374				1380	1395	1372		CH deformation
1254	1255	1258	1258	1250	1254	1254	1253	SiCH <sub>3</sub> deformation
1200	1207	1173	1183	1202	1168	1170	1163	SiOSi stretch
1123			1123					SiOSi stretch
1064	1062	1065	1062	1073	1073	1087	1079	SiOSi stretch
		963	968	973		978	978	
						855	909	
842	843	839	842	848	846	845	844	SiC stretch
	790	796	794	798			790	
756				757	757	757		
				618				
				574				
431	434	434	436	448	448	440	462	

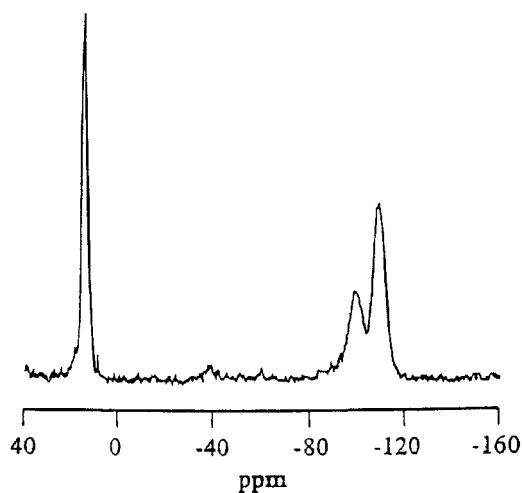
of the characteristic bands in the spectra show that the levels of substitution of the polymers are generally fairly high. As expected, the spectra of polymers with different sheet frameworks but the same pendent groups are very similar (Table 3).

<sup>29</sup>Si MAS NMR Spectra. The <sup>29</sup>Si MAS NMR spectra of the apophyllite-derived trimethylsiloxy, vinyldimethyl-



**Figure 4.** <sup>29</sup>Si MAS-NMR spectra of (a)–(c) apophyllite-derived trimethylsiloxy, vinyldimethylsiloxy, and octenyldimethylsiloxy sheet polymers.

and octenyldimethylsiloxy sheet polymers and K<sub>2</sub>CuSi<sub>4</sub>O<sub>10</sub>-derived trimethylsiloxy tube polymer are shown in Figures 4 and 5, respectively. A listing of the positions of the resonances is given in Table 4. Also given in this table is a listing of the areas of the resonances as determined by direct integration and by integration after spectrum deconvolution. The ca. 10 ppm resonances are assigned to the Si atoms of pendent OSi(CH<sub>3</sub>)<sub>2</sub>R groups, and the ca. -100 ppm resonances are assigned to the Si atoms of sheet SiO<sub>3/2</sub> groups carrying OH groups, that is, to the Si atoms of sheet SiO<sub>3/2</sub>/OH groups. The ca. -109 ppm resonances are assigned to the Si atoms of sheet SiO<sub>3/2</sub> groups carrying pendent OSi(CH<sub>3</sub>)<sub>2</sub>R groups and, to a small extent, to sheet SiO<sub>3/2</sub> groups oxygen-bridged to neighboring sheet SiO<sub>3/2</sub> groups.<sup>55</sup> With the assumption that the SiO<sub>3/2</sub> groups oxygen-bridged to other SiO<sub>3/2</sub> groups are low in abundance and can be neglected, the levels of substitution of the polymers can be determined by dividing the areas of the ca. -109 ppm resonances by the sums of the areas of the ca. -100 ppm and -109 ppm resonances. The values obtained by this procedure



**Figure 5.** <sup>29</sup>Si MAS-NMR spectrum of K<sub>2</sub>CuSi<sub>4</sub>O<sub>10</sub>-derived trimethylsiloxy tube polymer.



**Table 4.**  $^{29}\text{Si}$  MAS NMR Resonances of Apophyllite-Derived and Octenyl Polymer-Derived Siloxy Sheet Polymers and  $\text{K}_2\text{CuSi}_4\text{O}_{10}$ -Derived Trimethylsiloxy Tube Polymer

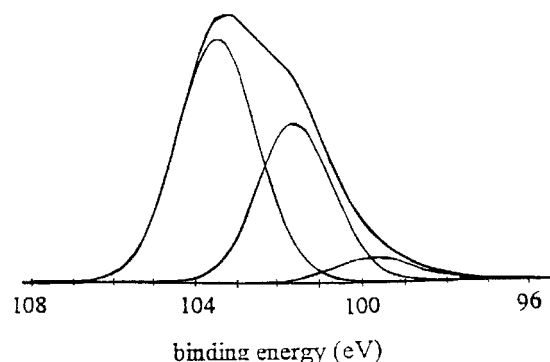
polymer	chemical shift (ppm)	relative area		assignment
		integ	decon	
A-M <sub>3</sub>	13.2	44.0		$\text{O}_3\text{SiO}_3\text{Si}(\text{CH}_3)_3$
	-99.5	25.6	41.2	$\text{O}_3\text{SiOH}$
	-109.8	37.5	58.8	$\text{O}_3\text{SiOSi}(\text{CH}_3)_3$
A-VM <sub>2</sub>	2.0	44.0		$\text{O}_3\text{SiO}_3\text{Si}(\text{CH}_3)_2\text{CH}=\text{CH}_2$
	-100.2	35.1	46.9	$\text{O}_3\text{SiOH}$
	-109.2	40.6	53.1	$\text{O}_3\text{SiOSi}(\text{CH}_3)_2\text{CH}=\text{CH}_2$
A-OEM <sub>2</sub>	14.7	44.0		$\text{O}_3\text{SiO}_3\text{Si}(\text{CH}_3)_2(\text{CH}_2)_6\text{CH}=\text{CH}_2$
	-99.5	47.0	47.1	$\text{O}_3\text{SiOH}$
	-108.0	52.3	52.9	$\text{O}_3\text{SiOSi}(\text{CH}_3)_2(\text{CH}_2)_6\text{CH}=\text{CH}_2$
AO-PM <sub>2</sub>	14.4	5.9		$\text{O}_3\text{SiO}_3\text{Si}(\text{CH}_3)_2(\text{CH}_2)_6\text{CH}=\text{CH}_2$
	7.8, 7.2	9.3		$\text{O}_3\text{SiOSi}(\text{CH}_3)_2(\text{CH}_2)_8\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3$
	-99.0	5.9	49.5	$\text{O}_3\text{SiOH}$
	-108.2	7.5	50.5	$\text{O}_3\text{SiOSi}(\text{CH}_3)_2(\text{CH}_2)_8\text{Si}(\text{CH}_3)_2\text{OSi}(\text{CH}_3)_3$
	12.4	44.9		$\text{O}_3\text{SiO}_3\text{Si}(\text{CH}_3)_3$
K-M <sub>3</sub>	-98.7	26.1	37.7	$\text{O}_3\text{SiOH}$
	-109.3	40.2	62.3	$\text{O}_3\text{SiOSi}(\text{CH}_3)_3$

**Table 5.** Levels of Substitution of Apophyllite-Derived and Octenyl Polymer-Derived Siloxy Sheet Polymers (%)

	A-M <sub>3</sub>	A-VM <sub>2</sub>	A-OEM <sub>2</sub>	AO-PM <sub>2</sub>	K-M <sub>3</sub>
NMR					
without deconvolution	59	54	53	56	61
with deconvolution	59	53	53	51	61
XPS					
with deconvolution	60	57	54		62

using both the direct integration areas and the deconvolution–integration areas are shown in Table 5. These values appear reasonable in light of the infrared data. The positions of the resonances of the  $\text{K}_2\text{CuSi}_4\text{O}_{10}$ -derived trimethylsiloxy tube polymer are similar to those of the apophyllite-derived trimethylsiloxy sheet polymer and the assignments of like resonances are parallel. The assignments of the resonances of the  $\text{K}_2\text{-CuSi}_4\text{O}_{10}$ -derived trimethylsiloxy tube polymer are consistent with those given earlier.<sup>31</sup> Determinations of the level of substitution of the polymer were made by the same types of procedures used with the siloxy sheet polymers. The 61% substitution level appears reasonable in light of the infrared data. The values for the  $\text{K}_2\text{-CuSi}_4\text{O}_{10}$ -derived trimethylsiloxy tube polymer are markedly higher than the value previously reported for it on the basis of  $^{29}\text{Si}$  NMR data.<sup>31</sup> Probably the earlier sample was less highly substituted.

**X-ray Photoelectron Spectra.** The experimental and deconvoluted Si 2p X-ray photoelectron peaks of the  $\text{K}_2\text{-CuSi}_4\text{O}_{10}$ -derived trimethylsiloxy tube polymer are shown in Figure 6. On the basis of the literature data,<sup>56,57</sup> the

**Figure 6.** Experimental and deconvoluted Si 2p X-ray photoelectron peaks of  $\text{K}_2\text{CuSi}_4\text{O}_{10}$ -derived trimethylsiloxy tube polymer.

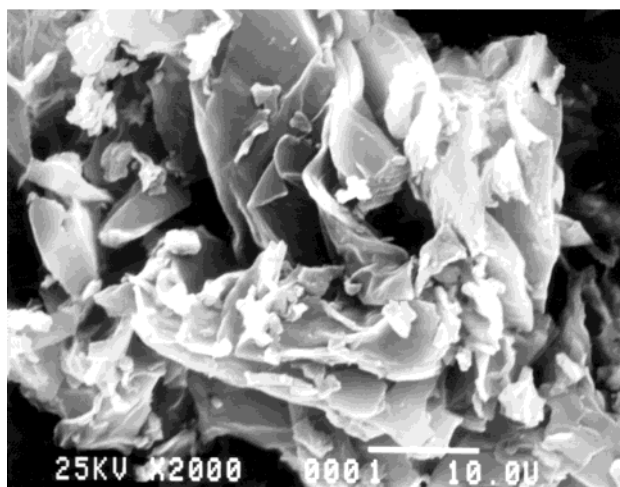
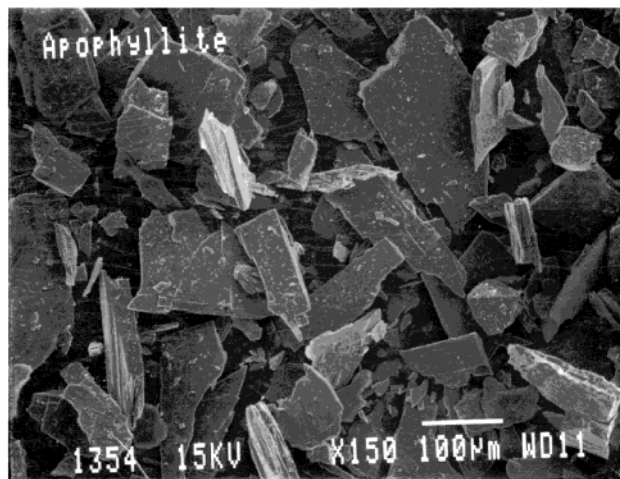
$\sim 101$ -eV peak is assigned to the  $\text{OSiR}_3$  group and the  $\sim 103$ -eV peak is assigned to  $\text{SiO}_{4/2}$ ,  $\text{SiO}_{3/2}(\text{OH})$ , and  $\text{SiO}_{3/2}(\text{OSiR}_3)$  groups. The origin of the  $\sim 100$ -eV peak, if real, is unknown. The levels of substitution of the polymers inferred from the ratios of the areas of the  $\sim 101$ - and  $\sim 103$ -eV peaks are given in Table 5. As inspection shows, these values are in good agreement with those derived from the  $^{29}\text{Si}$  NMR data. The value for the apophyllite-derived trimethylsiloxy polymer is also in good agreement with the value obtained earlier by X-ray photoelectron spectroscopy for this polymer.<sup>10</sup>

**Scanning Electron Micrographs.** Scanning electron micrographs of apophyllite and trimethylsiloxy sheet polymer are shown in Figure 7. Apophyllite powder is composed of irregularly shaped particles ranging from a few micrometers to hundreds of micrometers in size. The particles in apophyllite are more angular and dense than the particles in silylated polymers. As is seen, the trimethylsiloxy sheet polymer is composed of platelike particles of about 5–50  $\mu\text{m}$ . The shapes of these particles provide direct evidence for the sheet structures of the polymers. Although the resolution of the micrographs is not high enough to establish whether the sheets of the polymers are fully delaminated, it is believed that in general they are not. The larger size of the particles of the trimethylsiloxy sheet polymer may be attributable to the smaller size of its siloxy groups and hence the smaller relative movement of the sheets required during the silylation. The appearance of the particles of the apophyllite-derived trimethylsiloxy polymer is generally consistent with that observed earlier for particles of this polymer.<sup>9–12</sup> It is interesting to note that the particles of the dry polymers are crumpled. The forces leading to this are not understood.

**Solubility and Bulk Density Data.** The insolubility of the siloxy sheet and tube polymers in organic solvents is clearly due in part to the sheet and tube structures in them. The low bulk density ( $\sim 0.3$   $\text{g}/\text{cm}^3$ ) of the trimethylsiloxy sheet polymer is ascribed in part to the crumpled nature of the sheets in the dry polymer.

**Alkenylsiloxy Polymer-Derived Siloxy Sheet and Tube Polymers.** The procedure used for the

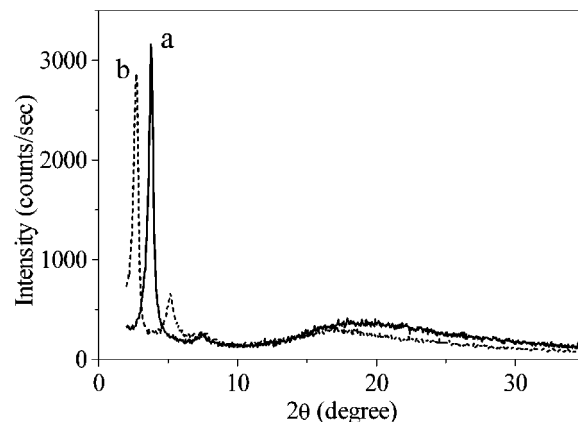
(55) Sindorf, D. W.; Maciel, G. E. *J. Am. Chem. Soc.* **1983**, *105*, 3767.(56) Linton, R. W.; Miller, M. L.; Maciel, G. E.; Hawkins, B. L. *Surf. Interface Anal.* **1985**, *4* (7), 196.(57) Miller, M. L.; Linton, R. W.; Bush, S. G.; Joggenson, L. W. *Anal. Chem.* **1984**, *56*, 2204.



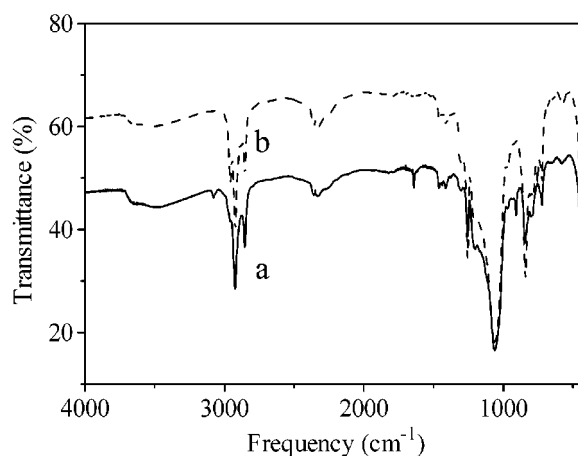
**Figure 7.** Scanning electron micrographs of apophyllite (top) and apophyllite-derived trimethylsiloxy sheet polymer (bottom).

hydrosilylation of the alkenyldimethylsiloxy polymers was modeled on that used commonly for the  $\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$ -catalyzed hydrosilylation of alkenes.<sup>58</sup> However, it differs in that the reaction mixture is not such as to lead to solution of the alkene. Apparently, this is the first instance in which this variation of the procedure has been used successfully for organosilicon polymers (the hydrosilylation of hydrosilane-modified colloidal silica has been reported recently by Brook et al.<sup>59,60</sup>). On the basis of observations made during the synthesis and work-up procedures, the polymers made are stable. As with the silicate-derived sheet polymers, this is not surprising because the polymers are organosiloxanes.

**X-ray Powder Patterns.** The representative X-ray powder pattern of the sheet polymer made by hydrosilylation is shown in Figure 8. For comparison, the powder pattern of the octenyldimethylsiloxy sheet polymer is included. As with the patterns of the silicate-derived siloxy sheet polymers, the major low-angle lines in these patterns are assigned to first-order reflections from the sheets of the polymers. Thus, they yield the interplanar spacings of these sheets. Generally, the



**Figure 8.** X-ray powder patterns of (a) A-OEM<sub>2</sub>, apophyllite-derived octenyldimethylsiloxy sheet polymer, and (b) AO-PM<sub>2</sub>, octenyl polymer-derived (pentamethylsiloxyoctyl)dimethylsiloxy polymer.



**Figure 9.** Infrared spectra (Fluorotube 4000–1320  $\text{cm}^{-1}$ , Nujol 1320–400  $\text{cm}^{-1}$ ) of (a) A-OEM<sub>2</sub>, apophyllite-derived octenyldimethylsiloxy sheet polymer, and (b) AO-PM<sub>2</sub>, octenyl polymer-derived (pentamethylsiloxyoctyl)dimethylsiloxy polymer.

**Table 6.** *d* Spacings of Alkenyl Polymer-Derived Siloxy Sheet Polymers (Å)

polymer	<i>d</i> spacing			polymer	<i>d</i> spacing		
AV-PM <sub>2</sub>	25.6	12.8	8.5	AO-HM <sub>2</sub>	32.7	17.0	11.4
AO-EM <sub>2</sub>	27.2	14.3		AO-HHM <sub>2</sub>	39.3	19.4	12.9
AO-PM <sub>2</sub>	34.7	17.5	11.8		5.2		5.3

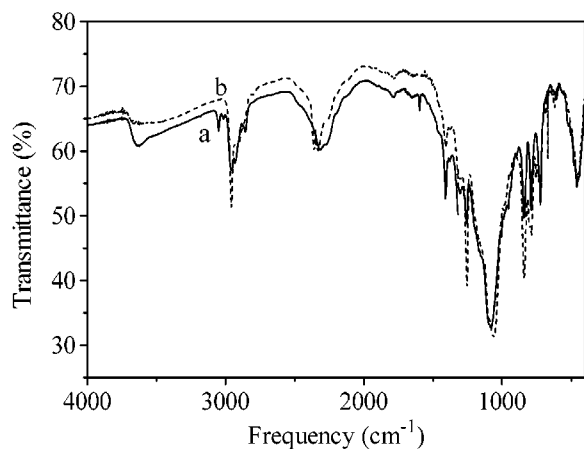
magnitudes of these spacings correlate with the magnitudes of the lengths of the pendent groups of the polymers. In general, the first-order lines in all the patterns are relatively intense and narrow. It is concluded from this that the sheets of the polymers are quite planar and the spacings between them are quite regular. In addition, it is concluded that the sheet frameworks of the parent silicates are carried over into the polymers without major alteration. As shown in Table 6, moderate- to low-intensity lines at half the *d* spacing of the first-order lines are present. These lines are assigned to second-order reflections from the sheets. In addition, low-intensity lines at a third of the *d* spacing of the first-order lines are present in all but one of the patterns. These lines are assigned to third-order reflections from the sheets. The existence of these higher order lines provides additional evidence for concluding that the sheet frameworks of the parent silicates are carried over into the polymers without major alteration.

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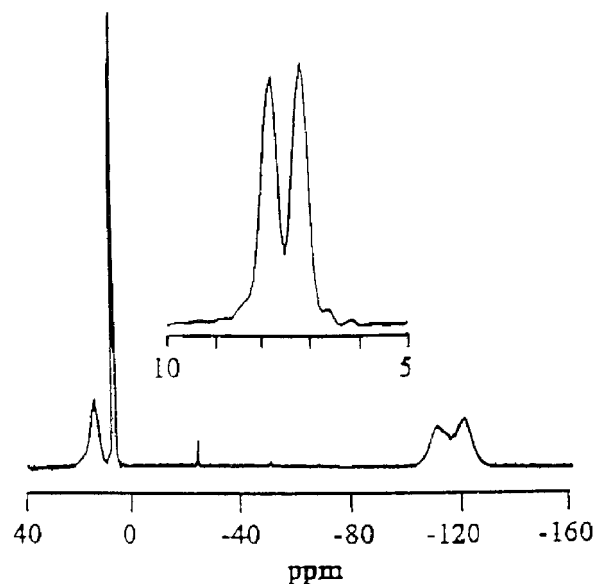


**Figure 10.** Infrared spectra (Fluorotube 4000–1320  $\text{cm}^{-1}$ , Nujol 1320–400  $\text{cm}^{-1}$ ) of (a) K-VM<sub>2</sub>, K<sub>2</sub>CuSi<sub>4</sub>O<sub>10</sub>-derived vinyl dimethylsiloxo tube polymer, and (b) KV-PM<sub>2</sub>, vinyl polymer-derived (pentamethyl disiloxoethyl) dimethylsiloxo polymer.

Just as in the case of the patterns of the apophyllite-derived siloxo sheet polymers, the lack of additional sharp or relatively sharp lines in these patterns is of interest. Again, it is concluded that while the sheets are quite planar and stacked with regular spacings, they are not in registry with one another.

**Infrared Spectra.** The representative infrared spectra of sheet and tube polymers made by hydrosilylation are shown in Figures 9 and 10, respectively. For comparison, IR spectra of octenyldimethylsiloxo sheet polymer and vinyl dimethyl tube polymer are included. The spectra show that the pendent groups of the polymers have the structures expected on the basis of the hydrosilanes used. It should be noted that the C=C band disappears and the intensity of the SiCH<sub>3</sub> band increases after the hydrosilylation reaction. The relative intensities of characteristic bands in the spectra show that the level of substitution of the polymers is generally fairly high.

**<sup>29</sup>Si MAS NMR Spectra.** The <sup>29</sup>Si MAS NMR spectrum of the (pentamethyl disiloxoethyl)-dimethylsiloxo sheet polymer is shown in Figure 11. The positions of the resonances of this polymer and the areas of these resonances as determined by direct integration and by integration after deconvolution are listed in Table 4. Also listed in this table are assignments for these resonances. As with the apophyllite-derived sheet polymers, it is believed that while the ca. -108 ppm resonance is attributable to both the Si atoms of sheet SiO<sub>3/2</sub> groups carrying OSi(CH<sub>3</sub>)<sub>2</sub>R' groups and to the Si atoms of SiO<sub>3/2</sub> groups oxygen-bridged to neighboring SiO<sub>3/2</sub> groups, it is mostly attributable to the former. Of particular interest in this spectrum is the presence of the pair of resonances (7.8 and 7.2 ppm) assignable to the Si atoms of the pentamethyl disiloxo groups. The existence of these resonances provides unambiguous support for the structure assumed for the pendent



**Figure 11.** <sup>29</sup>Si solid-state MAS-NMR spectrum of AO-PM<sub>2</sub>, octenyl polymer-derived (pentamethyl disiloxoethyl) dimethylsiloxo sheet polymer.

groups of this polymer. Levels of substitution of the polymer determined on the same basis as that used with the apophyllite-derived polymers are given in Table 5. The similarity of these values to those for the apophyllite-derived octenyldimethylsiloxo polymer indicates that a significant loss of pendent siloxo groups did not occur during hydrosilylation.

## Conclusions

It is concluded on the basis of the present work that a wide variety of stable and potentially useful organosilicon sheet and tube polymers can be prepared by the silylation of sheet and tube silicates or by the hydrosilylation of alkenylsiloxo sheet and tube polymers in the presence of a platinum catalyst. On the basis of the characterization data accumulated on the polymers, it is concluded that their backbones are like those of the parent silicates except for the presence of some additional intrasheet cross-links. It is further concluded that the patterns of attachment of the pendent groups on their frameworks generally follow the patterns of attachment of the oxygen atoms on the frameworks of the parent silicates. The procedure for preparing organosilicon sheet and tube polymers is of particular interest because it leaves the sheet and tube frameworks of the reactant polymers essentially unchanged and at the same time allows the properties of the product polymers to be tailored so as to permit the attainment of unique, very specific, potentially useful property sets.

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