Polysiloxanes Derived from Chrysotile Asbestos via Acid–Leaching and Silylation Processes

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ABSTRACT: Chrysotile asbestos was transformed into polysiloxanes through processes involving selective acid leaching and the reaction with various silylation reagents. The silylation with trialkoxy(vinyl)silanes followed by adding chlorotrialkylsilane effectively proceeded to afford a polymer with a low-silanol residue. The obtained polymers were radically crosslinked producing a polymer with a good thermal stability. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 2891–2897, 2008

Key words: chrysotile asbestos; polysiloxanes; silicas; silylation

INTRODUCTION

Recently, we reported the transformation of chrysotile asbestos into a silicone polymer through several steps including acid leaching and silylation.[1] That is, during the process, the selective leach of the brucite layer of magnesium hydroxide from chrysotile [$Mg_3Si_2O_5(OH)_4$] by an acid affording a silica[2–4] and treatment of a tetrahydrofuran (THF) solution of the silica with a silylation reagent,[5–8] such as chlorodimethylvinylsilane (VDMSCl) (Scheme 1), were successfully combined and performed to give a silicone polymer. The obtained polymers were totally soluble in various organic solvents.[1] This should be a potential method for the disposal and utilization of hazardous chrysotile asbestos wastes as a nontoxic and valuable material.

Chrysotile fibrils possess a tubular and cylindrical structure that comprised a tetrahedral sheet of silicate and a magnesium hydroxide brucite layer.[9] The silica obtained by the acid leaching of the brucite layer has a fibrous morphology originating from the chrysotile. In addition, the resulting polymer from the silylation reaction has an MQ-type silicone polymer structure and may mainly consist of a ladder-like main chain, again probably affected by the original silicate sheet structure in the starting chrysotile or the leached silica.[1] Therefore, the polymer produced in this process should be characteristic and may have some novel functions.

In this study, further investigations on the conversion process from the chrysotile asbestos to the silicone polymer were carried out. Two types of chrysotile asbestos, such as serpentine slag[1] and Class 4 chrysotile as the starting material and various reagents, as shown in Scheme 2, for the silylation step were used. The structure and thermal property of the obtained polymers were examined.

EXPERIMENTAL

Measurements

The powder X-ray diffraction (XRD) patterns were obtained using monochromated CuKα radiation with a Rigaku RINT-2100ultima diffractometer. The chemical compositions were determined by X-ray fluorescence using a Shimadzu EDX-800 spectrometer. The specific surface area was measured by the BET method. The scanning electron micrographs (SEM) were taken by a Hitachi High-Technologies FE-SEM S4700 apparatus. The ^{1}H NMR spectra were measured in chloroform-*d* using a Varian Unity-Inova spectrometer (500 MHz for ^{1}H). The infrared (IR) spectra were recorded using a Horiba FT-720 spectrometer. The size exclusion chromatographic (SEC) analyses were performed using a JASCO PU-2080 Plus equipped with a JASCO RI-2031 Plus detector and Shodex KF-806L and KF-803L columns
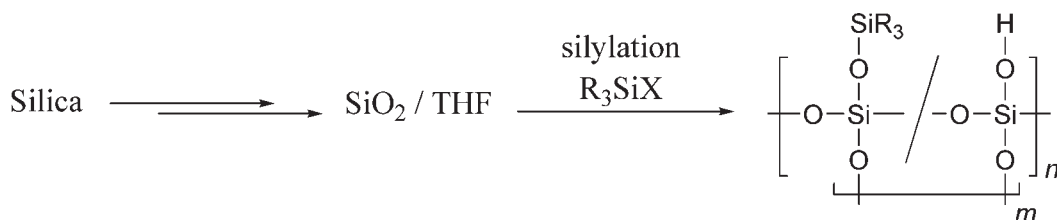
Scheme 1   Silicone polymer synthesis from silica derived from chrysotile asbestos.

connected in series [eluent: THF, flow rate = 1.0 mL/min, calibration: polystyrene standard]. The thermogravimetric (TG) analyses were recorded using a Rigaku Thermoplus TG8120 apparatus (heating rate: $10°C$/min, under N_2). The viscosity was measured using an SV-10 vibro-viscometer (A and D Instruments) in hexane at $20°C$.

Materials

Serpentine slag containing chrysotile asbestos mined in Furano, Hokkaido, Japan (Nozawa Co.) and Class 4 chrysotile mined in Canada (Cassir Mining Co.) was used as the starting materials, and the Silicas **1**[1] and **2** were prepared by the acid leaching of these materials, respectively, according to a previously reported procedure (caution!: the asbestos must be treated carefully, because the fibrils cause serious health hazards, such as asbestosis and carcinogenesis of respiratory systems.). The chemical composition (%, fluorescent X-ray) of silicas was SiO_2, 96.6; Al_2O_3, 2.4; Fe_2O_3, 0.2 for **1** and SiO_2, 97.1; Al_2O_3, 2.5; Fe_2O_3, 0.2 for **2**. The surface area was 178 and 122 m^2/g, respectively.

The silica gel **3** [Kanto, Tokyo, Japan; silica gel 60 N, spherical (particle size, 63–210 μm); neutral; chemical composition, SiO_2 >99%; surface area, 650 m^2/g] and silylation reagents, such as chlorotrimethylsilane (TMSCl), triethoxyphenylsilane (PhTEOS) (Across), triethoxyvinylsilane (VTEOS) (Aldrich, Tokyo, Japan), VDMSCl, and trimethoxyvinylsilane (VTMOS) (TCI) (Scheme 2), were used as received.

Procedure for silylation with trialkoxy(alkyl)silane and TMSCL

A mixture of the silica (10 g) and aqueous NaOH (0.4 M, 200 mL) was stirred at room temperature for 3 h. After filtration of the slurry to remove any insoluble residue, the solution was added to HCl (2.76 M, 200 mL) with stirring at room temperature, followed by the addition of THF (400 mL) and NaCl (120 g). The organic layer was separated and dried over $MgSO_4$, and then, the THF solution was concentrated by evaporation to the total volume of 100 mL.

Trialkoxy(alkyl)silane was added to the prepared THF solution of silica at room temperature. After

stirring for 2 h, TMSCl was added, and the stirring was further continued for 4 h. The reaction mixture was extracted with chloroform and water. After evaporation of the solvents, the products were isolated as the methanol–water [1/1 (v/v)]-insoluble fraction by centrifugation followed by drying under reduced pressure at $60°C$ for 12 h.
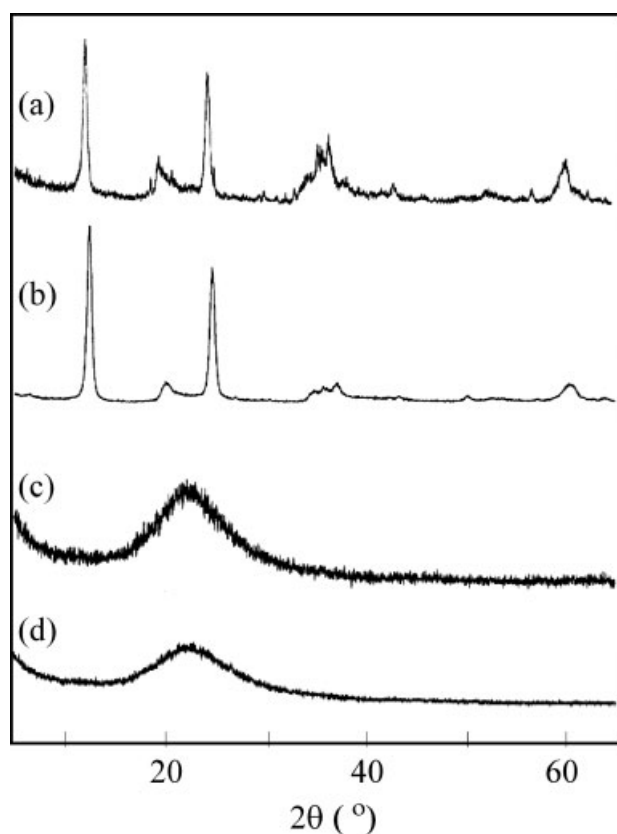
RESULTS AND DISCUSSION

The XRD patterns of the starting and the resulting materials, **1** and **2**, by leaching with sulfuric acid are shown in Figure 1. The peaks at 12.1, 24.2, and $60.2°$, based on the chrysotile, disappeared and a broad peak due to amorphous silica was observed for the leached materials. These results supported the fact that the magnesium hydroxide layer was effectively removed during the process. The SiO_2 contents of **1** and **2** were found to be 96.6%[1] and 97.1%, respectively, by the fluorescent X-ray analysis. Figure 2 shows the SEM images of the obtained silica materials, which have a fibrous morphology. The silica **2** derived from the Class 4 chrysotile is composed of much longer fibrils than found in **1**.

The silylation reaction was carried out using a THF solution prepared from the obtained silica by adding TMSCl (0.6 equiv.) at room temperature (Scheme 1). The results are shown in Table I, together with that of the reaction using the commercially available silica gel **3** as the starting material. During the preparation of the THF solution of the silica, **1** and **2**, a large amount of the aqueous sodium hydroxide (0.4 M)-insoluble part remained, whereas the silica gel **3** almost completely dissolved. The silica **2** contains a higher amount of insoluble residue than **1**, and the insoluble fraction of **1** decreased when a higher concentration or greater
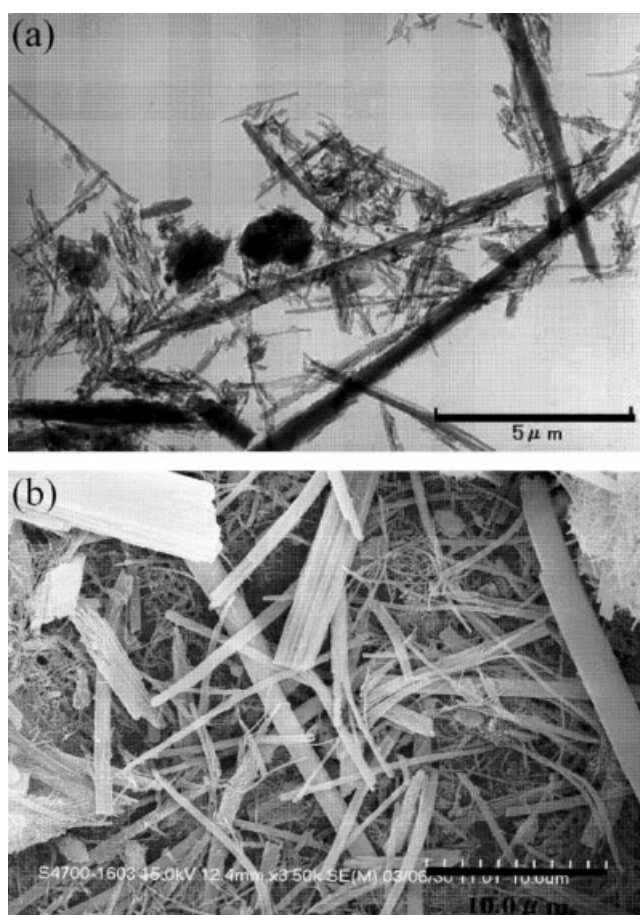

R = vinyl; R' = Me: VTMOS   R" = Me: TMSCl
R = vinyl; R' = Et: VTEOS   R" = vinyl: VDMSCl
R = Ph; R' = Et: PhTEOS
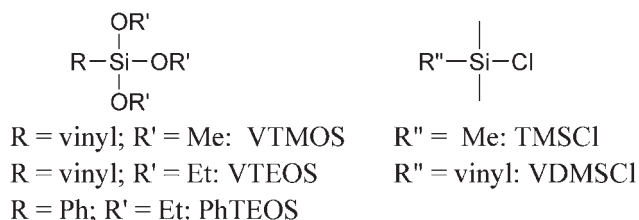
Scheme 2   Silylation reagents.

Figure 1 X-ray powder diffraction patterns of (a) serpentine slag, (b) Class 4 chrisotile, (c) **1**, and (d) **2**.

Figure 2 SEM images of (a) **1** and (b) **2** [bars indicate (a) 5 μm and (b) 10 μm].

amount of aqueous NaOH was used. Therefore, the fibrous structure of the silica that originated from chrysotile should significantly affect its solubility in an aqueous alkaline solution.

During every silylation reaction with TMSCl, the polymer was obtained in a moderate yield, which was a white solid and totally soluble in CHCl₃ and THF. However, the results for the reactions of **1** and **2** (Table I, Entries 1–4) were clearly different from that of the silylation of **3** (Table I, Entry 5). For example, the ratio of the silanol residue (HOSi-) of

the polymers obtained from silica, **1** and **2**, was determined to be around 12% based on a ^{1}H NMR analysis, the value of which is higher than that for the polymer prepared from **3** (5%).

The TG analysis of the polymers obtained from **1** and **3** (Table I, Entries 1 and 5) was conducted, and the value for the weight-loss percentage at 1000°C was determined to be 37 and 45%, respectively.

TABLE I
Silylation of Various Silicas with TMSCl

| Entry	NaOH-soluble part		Silylation			
	Silica	(%)	Yield (%)[a]	Me₃Si : HOSi[b]	M_w ($\times 10^3$)[c]	M_n ($\times 10^3$)[c]
1[d]	**1**	67	55	88 : 12	3.1	2.2
2[e]	**1**	67	53	87 : 13	3.5	2.7
3[d]	**2**	53	52	89 : 11	3.3	2.5
4[e]	**2**	53	51	89 : 11	3.1	2.4
5[d]	**3**	99	59	95 : 5	4.4	3.1

[a] MeOH–water (1/1 v/v)-insoluble part.
[b] Determined by ^{1}H NMR analysis.
[c] Determined by SEC in THF (polystyrene standard).
[d] TMSCl (0.6 equiv.) was used for silylation reaction (reaction time: 4 h, room temperature).
[e] TMSCl was added in two portions (0.3 equiv. × 2).

SiMe$_3$
|
O
|
—O—Si—
|
O
|
—O—Si—
|
O
|]$_n$
SiMe$_3$

SiMe$_3$
|
O
|
—O—Si—
|
O
|]$_n$
SiMe$_3$

m = 1   *m* = 2
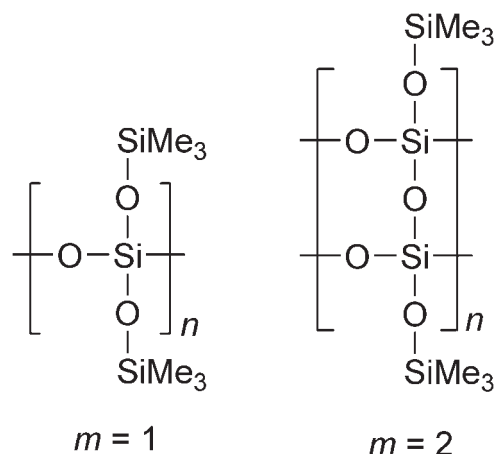
Scheme 3 Single chain (*m* = 1) and ladder polymers (*m* = 2).

Supposing that the methyl groups of the polymer side chain thermally decompose during the TG analysis, the ideal weight-loss value at 1000°C was calculated to be 41% for the single-chain polymer (*m* = 1) and 32% for the ladder polymer (*m* = 2) (Scheme 3). These results suggest that the main-chain structure should be different between the polymers obtained from **1** and **3**, and the former polymer may have a ladder-type main-chain structure, which is derived from the original chrysotile structure.[1]

The intrinsic viscosity [η] of the polymers obtained from **1** and **3** with TMSCl (0.8 equiv.) (the former polymer: Table III, Entry 1; the latter: Me$_3$Si : HOSi = 93 : 7, M_w = 6.0 × 10^3, M_n = 4.0 × 10^3) was estimated to be ∼6.0 and 3.8 mL/g, respectively, (in hexane at 20°C). The shape factor (α) is defined by the equation, [η] = KM_w^α, where K is a constant for a particular pair of the polymer and solvent at a particular temperature. Accordingly, the α value of the former polymer is higher than that of the latter, judging from the [η] and M_w values, that is, the polymer obtained from **1** is more rigid than that prepared from **3**.[10] This result again supports the fact that the former polymer may possess a main chain with a ladder-like structure.

As previously reported, the silylation reaction of the silanol residue with VDMSCl did not quite proceed, even if an excess amount of reagent was used.[1] The silylation of **1** with TMSCl (0.8 equiv.) also afforded a white solid polymer with a degree of silylation value of 86% (Table III, Entry 1). These are mainly due to the bulkiness of the silylation reagent. The silylation of **1** with trialkoxy(alkyl)silane [RSi(OR′)$_3$, 0.6 equiv.], in which each alkoxy group (R′O) can react with a silanol, followed by the addition of chlorotrialkylsilane [R″$_3$SiCl, 0.8 equiv.], was then examined (Scheme 4). The results are summarized in Table II.

The polymers were obtained as a clear and viscous liquid. A significant increase in the silylation degree was observed, whereas the unreacted alkoxy group of the trialkoxy(alkyl)silane remained on the polymer. For instance, the reaction with VTEOS and TMSCl gave a polymer with a silylation degree (vinyl-Si + trimethyl-Si) of 97% and a ratio of the vinyl group to the unreacted ethoxy group (vinyl-Si : EtO-Si) of 1 : 1.3 (Table II, Entry 1). Figure 3(a,b) shows the IR spectra of **1** and the obtained polymer. A small absorption for the residual silanol group appeared around 3400 cm^{-1} and typical peaks for the vinyl group, as shown in the figure, were observed for the latter. The ^{1}H NMR spectrum of the same polymer is depicted in Fig. 4, and each peak was assigned as shown in the figure. These results indicated that the silylation reaction with VTEOS followed by capping of the silanol residue by the trimethylsilyl group effectively occurred.

The silylation reagent, VTMOS, was more reactive than VTEOS to give a polymer with a ratio of the vinyl group to the unreacted methoxy group of 1 : 0.50 (Table II, Entry 2). The silylation of the silica gel **3** with VTMOS and TMSCl also afforded a polymer as a clear and viscous liquid. The percentage of the residual silanol was again lower than those observed for the polymers obtained from **1**, and the degree of silylation reached 99% (Table II, Entry 5). These results should support the ladder-type structure of the polymer derived from **1**, probably because the rigid ladder-like main chain prevents the silylation

SiO$_2$ / THF $\xrightarrow[\text{r.t., 2 h}]{\text{RSi(OR')}_3}$ $\xrightarrow[\text{r.t., 4 h}]{\text{R''}_3\text{SiCl}}$
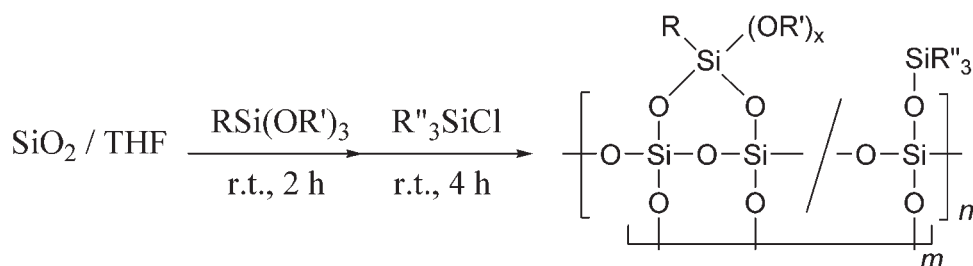
Scheme 4 Silylation reaction with trialkoxy(alkyl)silane and chlorotrialkylsilane.

TABLE II
Silyation of 1 with Various Silylation Reagents[a]

Entry	RSi(OR')$_3$	R''$_3$SiCl	Yield (g)[b]	RSi : R''$_3$Si : HOSi[c]	R : R'O[c]	M_w ($\times 10^3$)[d]	M_n ($\times 10^3$)[d]
1	VTEOS	TMSCl	1.10	42 : 55 : 3	1 : 1.3	4.3	3.6
2	VTMOS	TMSCl	1.16	49 : 47 : 4	1 : 0.50	3.8	3.2
3	PhTEOS	TMSCl	1.55	55 : 37 : 8	1 : 1.7	4.2	3.2
4	PhTEOS	VDMSCl	2.07	48 : 48 : 4	1 : 1.0	5.5	2.2
5[e]	VTMOS	TMSCl	1.77	51 : 48 : 1	1 : 1.0	4.6	3.8

[a] 1: 12 mmol; RSi(OR')$_3$: 0.6 equiv.; R''$_3$SiCl: 0.8 equiv.
[b] MeOH–water (1/1 v/v)-insoluble part.
[c] Determined by ^{1}H NMR analysis.
[d] Determined by SEC (polystyrene standards).
[e] Silica 3 (18 mmol) was used.

of the side-chain silanol group by bulky silylation reagents. On the other hand, the 100 MHz ^{29}Si NMR spectrum of the polymer obtained from 1 (Table II, Entry 2) showed broad peaks based on the Q^4 (-114 ppm), T^3 (-77 ppm), and M units (5 ppm).[11] Therefore, the regularity of the ladder structure should be low.

The silylations with VTMOS and TMSCl under various conditions were further investigated (Table III). By increasing the amount of VTMOS, both ratios of the vinyl group introduced into the polymer and the unreacted methoxy group increased, whereas the percentage of the residual silanol hardly changed. Although the temperature significantly affected the reaction of VTMOS, the unprotected silanol still remained (Table III, Entry 4).

The silylation with trialkoxy(alkyl)silane and chlorotrialkylsilane allows the introduction of various functional groups to the polymer. Here, as the vinyl group has a polymerizable functionality and the obtained polymer is a viscous liquid, the radical crosslinking reaction with benzoyl peroxide (BPO) in bulk [conditions, BPO = 3 wt %, 60°C, 48 h] was

carried out. The crosslinking effectively proceeded to give a transparent polymer gel. Figure 3(c) shows the IR spectrum of the product after the radical reaction of the polymer prepared with VTMOS and TMSCl (Table II, Entry 2). The absorptions based on the vinyl group almost disappeared, indicating that the crosslinking of the vinyl group took place during the radical reaction.

The TG traces of the crosslinked and the original polymers (Table II, Entry 2) are shown in Figure 5. The thermal stability of the crosslinked polymer significantly increased in comparison with that of the original one. The observed 5% weight-loss temperature was 447°C for the former and 272°C for the latter. The 5 and 10% weight-loss temperatures for the various crosslinked and original polymers are listed in Table IV. Every crosslinked polymer showed a much higher thermal stability than that of the original one. Interestingly, although the polymer prepared from the silica gel 3 with VTMOS and TMSCl (Table II, Entry 5) showed a rather higher 5% weight-loss temperature (291°C) than that of the polymer of 1 (272°C) (Table II, Entry 2), the

TABLE III
Silylation of 1 with VTMOS and TMSCl[a]

Entry	VTMOS (equiv.)	Yield (g)[b]	Vinyl : Me$_3$Si : HOSi[c]	Vinyl : MeO[c]	M_w ($\times 10^3$)[d]	M_w/M_n[d]
1	0	0.66	– : 86 : 14	–	3.8	2.9
2	0.2	0.89	30 : 66 : 4	1 : 0.08	3.6	3.3
3	0.4[e]	0.77	45 : 50 : 5	1 : 0.50	3.5	2.9
4[f]	0.4	0.91	41 : 55 : 4	1 : 0.09	3.1	2.6
5[g]	0.4	0.92	46 : 49 : 5	1 : 1.0[h]	6.0	5.0

[a] 1: 12 mmol; TMSCl: 0.8 equiv.
[b] MeOH–water (1/1 v/v)-insoluble part.
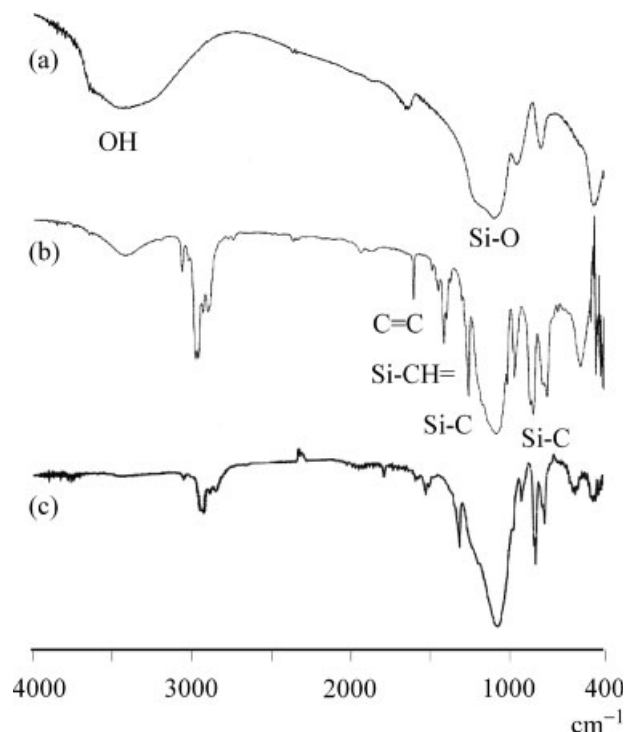[c] Determined by ^{1}H NMR analysis.
[d] Determined by SEC (polystyrene standards).
[e] Reaction time, 4 h.
[f] Temp., 50°C.
[g] VTEOS was used.
[h] Ratio of vinyl : EtO.

Figure 3 IR spectra of (a) **1**, (b) the polymer obtained with VTEOS (Table II, Entry 1), and (c) the crosslinked polymer (the original polymer: Table II, Entry 2) (KBr).
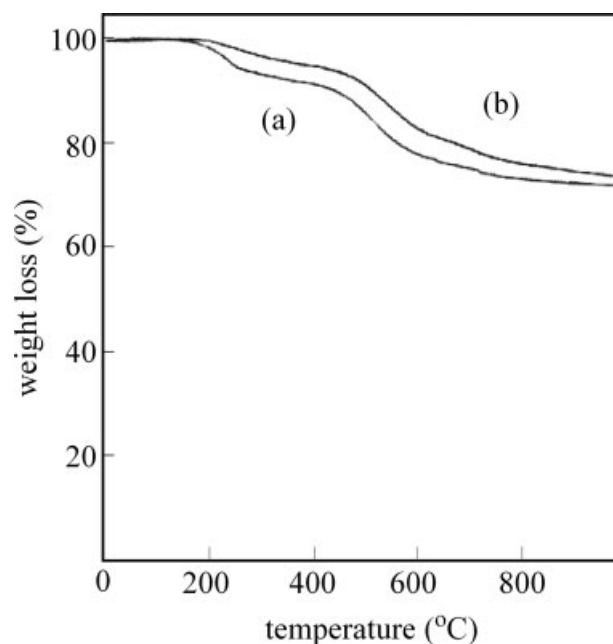
temperature for its crosslinked polymer, 408°C, was much lower than that of the polymer of **1** with cross-linking (447°C). The main chain, such as the single-chain-like and ladder-like structure, may influence the thermal property.[12–14]

CONCLUSIONS

Chrysotile asbestos was transformed into polysiloxanes through the processes involving the selective acid leaching and reaction with various silylation reagents. It was suggested that the obtained poly-
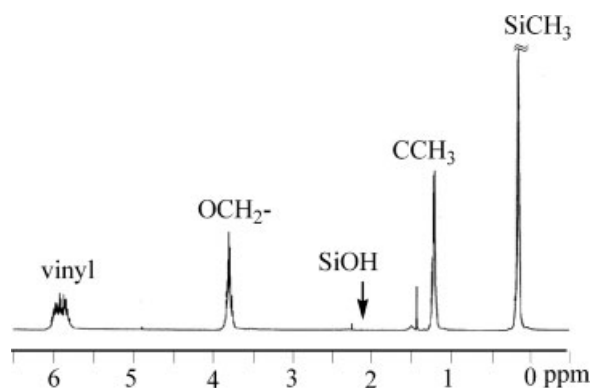
Figure 4 500 MHz ^{1}H NMR spectrum of the polymer obtained with VTEOS (Table II, Entry 1) (CDCl$_3$, 60°C).

Figure 5 TG traces of (a) the original polymer (Table II, Entry 2) and (b) the crosslinked polymer.

TABLE IV
The 5 and 10% Weight-Loss Temperatures of the Obtained Polymers

Original polymer in Table II	Crosslinking[a]	T_5[b] (°C)	T_{10}[c] (°C)
Entry 1	∼	235	271
Entry 1	+	370	458
Entry 2	∼	272	465
Entry 2	+	447	536
Entry 3	∼	247	280
Entry 5	∼	291	417
Entry 5	+	408	526

[a] "+": crosslinked; "∼"original polymer.
[b] Five percent weight-loss temperature.
[c] Ten percent weight-loss temperature.

mers may have a ladder-type main chain derived from the chtysotile structure. The silylation with tri-alkoxy(alkyl)silanes easily occurred to give a polymer with a very low silanol content. The polymers bearing the vinyl group were radically crosslinked to effectively produce a polymer gel, which showed a good thermal resistance property.

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