Curing System Involving SiH-Containing Organic Oligomers

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SYNOPSIS

We describe here the preparation and properties of a novel curing system, which has been derived from an SiH-containing organic oligomer 1 and an allyloxy end-blocked organic oligomer 2. The composition of these oligomers could be crosslinked via a platinum-catalyzed hydrosilylation reaction, that is, the addition reaction of the SiH bonds of 1 to the allyl functionality of 2, above 100°C, yields a rubbery material in a short period of time. The compatibility of the SiH-containing oligomer 1 with the allyloxy end-blocked oligomer 2 was governed by the oligomer main chain employed. Hence the SiH-containing oligomer 1 was completely miscible with 2, having the same main chain and, thus, the system yielded a homogeneously cured material. The poly(propylene oxide) curing system 1a/2a was systematically investigated in detail to manifest its curing behavior and crosslink structure. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Various types of curing reactions involving urethane linkage,[1] epoxy functionality,[2] disulfide linkage,[3] siloxane linkage,[4] and acrylic ester functionality, under catalysis or by UV/EB irradiation,[5] have been developed for reactive liquid organic oligomers. Each of the curing systems is widely employed for various industrial applications by using their properties associated with their curing process and crosslinked structures.

On the other hand, the hydrosilylation reaction has been employed only for the curing of well-known, addition-type polysiloxanes. This type of polysiloxane has several excellent properties associated with the hydrosilylation reaction:

- Good dimensional stability is achieved because there are no volatile components during the curing process.
- The curing rate is greatly dependent on the temperature; the rate is large at high temperatures in particular.
- The crosslinking is performed through the formation of stable SiC bonds.
- Good sealing properties are obtained because of little shrinking during curing.
- Cured samples with large thicknesses can be prepared, as long as the platinum catalyst is well dispersed in the curing system.
- The curing reaction is not hindered by the presence of oxygen, unlike radical-type curing.

Therefore, the incorporation of the hydrosilylation curing reaction into organic oligomers seemed worth developing to present a totally new curing system.

In this article, we describe the basic properties of the new curing system (Scheme 1), composed of an SiH-containing oligomer 1 and an allyloxy end-blocked oligomer 2.
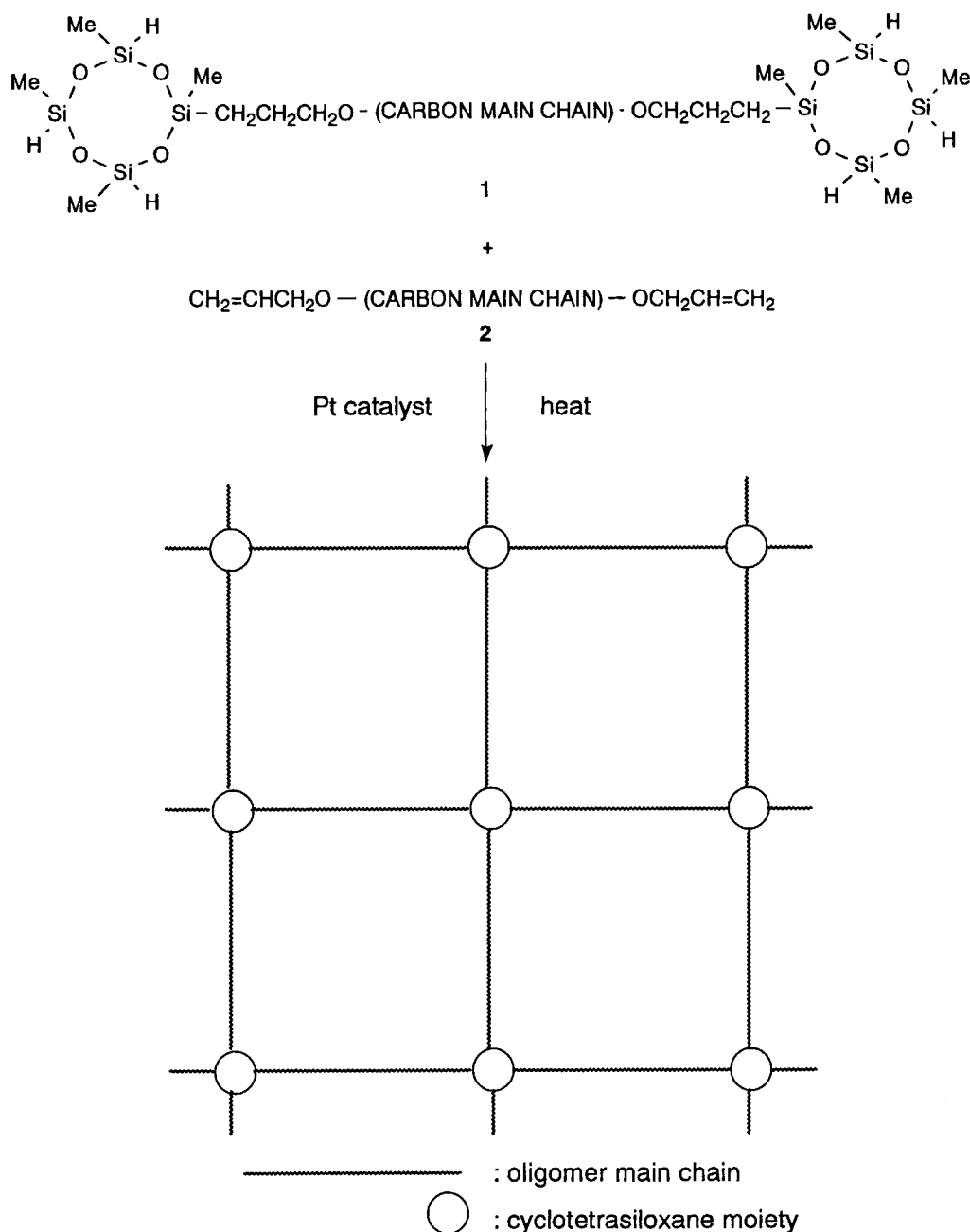
The SiH-containing oligomer 1 and the allyloxy end-blocked oligomer 2, the syntheses of which were reported elsewhere,[6] were employed for evaluation. They are listed in Table I.

EXPERIMENTAL

Measurement of Gel Time

The measurement of gel time was carried out according to the Japanese Industrial Standard (JIS)

Scheme 1   Schematic crosslinking via the *Pt*-catalyzed hydrosilylation reaction.

C-2104 for testing methods of oil-soluble 100% phenolic resins for electrical insulating varnishes [corresponding to the American Society for Testing and Materials (ASTM) D 2471]. A GT-D-type apparatus for gel time measurement, purchased from Nisshin Kagaku, was used.

Certain amounts of an SiH-containing oligomer **1**, an allyloxy end-blocked oligomer **2**, and a chloroplatinic acid catalyst solution were well mixed at room temperature. (The chloroplatinic acid catalyst

solution was prepared by dissolving 1.0 g of H_2PtCl_6 × 6 H_2O in 1 mL of EtOH and 9 mL of 1,2-dimethoxyethane, and then by diluting it 10-fold with the same solvent mixture. The solution was prepared more than one month before use.) About 0.1 g of the mixture was then put in a 20 mm-diameter hollow area on the hot plate of the apparatus, whose temperature was already controlled at a certain value. The sample was quickly spread and mixed at the rate of 60 ± 5 rpm with a toothpick with approxi-

Table I   SiH- and Allyl-Containing Oligomers 1 and 2, Employed for Evaluation

Compound	Carbon Main Chain in 1 and 2	Molecular Weight[a]	
		M_n	M_w
1a	CH_3 $\qquad\qquad$ CH_3	16,800	47,000
2a	$-(CHCH_2O)_n-CH_2-(OCH_2CH)_n-$	9900	26,600
1b		—	—
	$-(CH_2CH_2CH_2CH_2O)_{n-1}CH_2CH_2CH_2CH_2-$[b]	3500	8100
2b			
1c	O $\qquad\qquad\qquad$ O	5800	24,000
2c	$-CO(CH_2CH_2CH_2CH_2)_nOC-$	2500	7900
1d	CH_3	—	—
2d	$-(CH_2CHCH_2CH_2)_n-$[c]	2500	7800
1e	O $\quad$ CH_3 $\quad$ O	6400	16,000
2e	$-CO(CH_2CHCH_2CH_2)_nOC-$[c]	3800	8500
1f, 1f′	a Copolymer Composed of O $\quad$ CH_3 $\quad$ O $\quad$ O[c]	8750	17,800[d]
2f, 2f′	$[O(CH_2)_5C]_l$ $[OCH_2CCH_2O]_m$ $[C(CH_2)_4)C]_n$ $\qquad\qquad\qquad CH_3$	4400	9000[e]

f: $l = 10$–12, $m = 4$–5, $n = 3$–4; f′: $l = 18$, $m = 5$, $n = 4$

[a] By GPC. Upper values for 1 and lower ones for 2.
[b] For 1b, a cyclopentasiloxane $[CH_3(H)SiO]_5$ was used instead of $[CH_3(H)SiO]_4$ for the synthesis.
[c] An assumed structure, based on ^1H-NMR.
[d] For 1f.
[e] For 2f.

mately a 30 degree angle dihedral to the plate. The time when the sample turned to an elastomer was determined as an endpoint. The interval between the time when a sample was put on the plate and the endpoint was defined as the gel time. At the endpoint measurement, the sample was carefully treated, so as not to be lifted from the plate.

Evaluation of Compatibility of Oligomers' Composition and Its Cured Materials

Compatibility was evaluated, both before and after curing, for a composition consisting of an SiH-containing oligomer 1 and an allyl-containing one 2, with differing main chains.

To 1.0 g of an allyloxy end-blocked oligomer 2 was added a certain amount of an SiH-containing oligomer 1, so that the molar ratio of SiH/allyl was unity. The composition was well mixed, was centrifuged to remove bubbles, and was left at 80°C for 1

h. After the sample was cooled down to room temperature, the compatibility was evaluated qualitatively by eye. To the composition was added the 1 wt % chloroplatinic acid solution (1×10^{-4} equivalent relative to allyl), and the reaction system was well mixed, was debubbled, and was cured at 100°C for 1 h. Homogeneity and cloudiness of curing of the cured materials were qualitatively evaluated.

Preparation of Cured Sheet and Its Tensile Test

The poly(propylene oxide) curing system provides an example. A composition, consisting of 62.7 g of the allyloxy end-blocked poly(propylene oxide) 2a (allyl content = 13.7 mmol), 28.0 g of the SiH-containing poly(propylene oxide) 1a (SiH content = 13.7 mmol), 0.91 g of 2,2′-methylenebis 4-methyl-6-tert-butylphenol (2.67 mmol) (Nocrac NS-6, from Ohuchi Shinkou Kagaku, was used as a hindered phenol antioxidant for poly(propylene oxide) to

prevent oxidative pyrolysis.), and 72 μL of 1 wt % chloroplatinic acid catalyst solution (1.4 $\times$ 10^{-3} mmol, 1 $\times$ 10^{-4} mol, relative to 1 mol of allyl groups), was well mixed. The composition was poured in an Al mold (70 $\times$ 60 $\times$ 5 mm), with bottom and sides covered with a Teflon sheet, attached with double-sided adhesive tape (13 g $\times$ 5 pieces). After bubbles were removed at room temperature under vacuum, the composition was cured at 100°C (A circulation type oven HPS-212 from Tabai was used). Thus, a rubber-like, homogeneously cured sample, with a thickness of 2.5–3.0 mm, was obtained. From this sheet, several pieces of dumbbell were sampled, according to JIS K7113. They were then submitted to tensile test at a rate of 200 mm/min (n = 3).

Gel Content of the Cured Poly(propylene Oxide)

About 0.1 g of the cured, sheet-like sample was wrapped in a sheet of stainless net. The sample weights, both before and after acetone extraction (48 h at room temperature and drying at 80°C for 2 h), yielded the gel content.

Viscoelasticity of the Cured Poly(propylene Oxide)

A sample, with 10-mm diameter and $ca.$ 3-mm thickness, was taken from a cured sheet. It was submitted to dynamic mechanical analysis by means of a Rheometrics Solid analyzer, RSA 2, from Rheometrics Inc. The conditions were, frequency 62.7998 rad/s, strain 0.1% compression, time/measurement 1.0 (min), rate 2.0 (°C/min), and temperature -100 $\sim$ +100°C.

Solid State ^{29}Si NMR Spectra of the Cured Poly(propylene Oxide)

About 0.3 g of a 2.5 mm-thick sheet-like poly(propylene oxide) sample, cured under a certain condition, was taken and cut into pieces, which were then powdered at -196°C. The sticky powders were placed in a 10-mm NMR tube for measurement under the following conditions: Varian XL-300, frequency 59.591 MHz, spectral width 22675.7 Hz, acquisition time 79.0 msec, relaxation delay 20.0 sec, pulse width 84 degrees, ambient temperature, number of repetitions 2800, gated decoupling, spin rate 4000 Hz, and double precision acquisition.

RESULTS AND DISCUSSION

Curing Rate

The curing rate of the system was evaluated by the gel time. This method has been widely used for qualitative evaluation of curing rate of thermosetting resins, due to its simplicity and convenience.[2] Because most of the cured samples were rubber-like materials in our systems, we regarded the gel point as the time when the tested sample turned to rubber-like elastomer from the liquid state. The evaluating test, even if qualitative, revealed that the curing systems have the attributes listed below, which are associated with hydrosilylation reaction.

General Tendency

Independent of the main chain of the oligomers employed, features of the curing process are the same as those of the well-known, addition-type silicone;

Table II   Gel Time of Several Compositions of 1 and 2

No.	Type of Oligomers[a]	Pt Cat. (equiv.)	Gel Time 80°C	100°C	120°C
1	Poly(propylene oxide) **1a/2a**	1 $\times$ 10^{-3}	0'57"	0'19"	0'11"
2	Poly(propylene oxide) **1a/2a**	1 $\times$ 10^{-4}	2'30"	0'50"	0'28"
3	Poly(propylene oxide) **1a/2a**	2 $\times$ 10^{-5}	7'30"	2'10"	1'00"
4	Poly(tetramethylene oxide) **1b/2b**	1 $\times$ 10^{-3}	1'11"	0'26"	0'10"
5	Poly(tetramethylene oxide) **1b/2b**	1 $\times$ 10^{-4}	3'05"	0'56"	0'21"
6	Hydrogenated Poly(isoperene) **1d/2d**	1 $\times$ 10^{-4}	3'45"	0'53"	0'23"
7	Noncrystalline Poly(caprolactone) **1f'/2f'**	1 $\times$ 10^{-3}	0'53"	0'18"	0'14"
8	Noncrystalline Poly(caprolactone) **1f'/2f'**	1 $\times$ 10^{-4}	1'24"	0'29"	0'18"

[a] SiH/allyl = 1 (1.31 for Nos. 4 and 5).

the curing rate of the system was dependent on both temperature and the amount of Pt catalyst (Table II). In particular, a fast curing rate, corresponding to a 10-sec to 2-min gel time, was observed at 100°C or above. The observation of the dependence on the Pt catalyst concentration over $10^{-3} \sim 10^{-4}$ equivalent does not seem surprising, although the hydrosilylation in liquid phase proceeds well in the presence of the $10^{-5} \sim 10^{-7}$ equivalent Pt level[7]; the functional groups at the oligomer main chain must react under the environment of high viscosity and low concentration at the last stage of the curing. In addition, the contact of the functionalities on the Pt catalyst becomes disadvantageous as the reaction proceeds from the liquid phase to the solid phase.

Molar Ratio of SiH/Allyl

Regardless of the main chain of the oligomers, the fastest curing rate has been observed when the ratio of SiH/allyl is between 1 and 2 (Fig. 1). Beyond the hydrosilylation reaction, the SiH bond seems to have been consumed by the interaction with moisture under the measurement conditions.[8] The gel time became extremely long, or curing did not occur when one component of the two was in large excess over the other, especially in the case of a large excess of the allyl component.

Molecular Weight

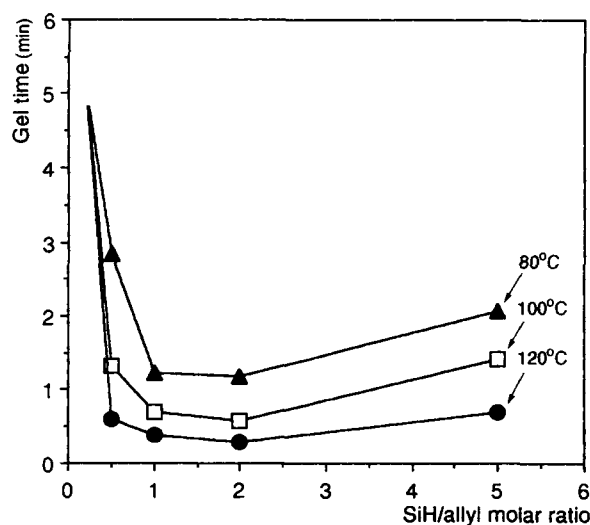Dependence of the molecular weight of the oligomer on the gel time was not observed among the

Figure 1   Gel time of the poly(propylene oxide) system (1a/2a) and the effects of SiH/allyl molar ratio. Pt: 1 × 10^{-4} mol, relative to 1 mol of allyl. Curing did not occur within 30 min at any temperature when the SiH/allyl molar ratio was 0.25.

Table III   Effects of Benzothiazole (BZ) on Gel Time of Poly(propylene oxide) Composition 1a/2a[a]

No.	BZ Added (equiv.)[b]	Gel Time		
		80°C	100°C	120°C
1	0	0'57"	0'25"	0'13"
2	10	1'05"	0'30"	0'16"
3	20	1'15"	0'33"	0'18"
4	10[c]	2'05"	0'48"	0'23"
5	20[c]	2'50"	1'02"	0'27"

[a] SiH/allyl = 1, Pt cat. = 1 × 10^{-4} equiv.
[b] Relative to the amount of the Pt cat. for synthesis.
[c] After 50°C, storage of 1a containing BZ for 27 days.

oligomers examined. Dependence of the type of the oligomer main chain of the gel time was also not observed.

Addition of Benzothiazole

We have examined the effects of various kinds of coordinating compounds to improve the storage stabilities of SiH-containing oligomers 1.[6,9] We have studied the influence of the addition of benzothiazole, which works as one of the best storage-improving reagents, on the curing ability of the present curing system (Table III).

It has been revealed that the gel time of the system with benzothiazole was almost the same as that of the system without it at 120°C, although the gel time tends to be longer at 80°C. From this observation, benzothiazole seemed reversibly to coordinate to Pt and to dissociate at higher temperature, so that the hydrosilylation curing reaction could not be deterred.

The curing ability deteriorated,·to some extent, after the storage, although the curing rate was still fast at higher temperature.

Compatibility

The compatibility of an SiH-containing oligomer 1 with an allyl-containing oligomer 2, whose main chain was the same as that of the former oligomer, was excellent and the composition was homogeneously clear, both before and after curing (Table IV). This was probably because the oligomers' compatibility was mainly governed, not by the hydrocyclotetrasiloxane moiety, but by the main chain, whose molecular weight is much higher than that of the hydrocyclotetrasiloxane moiety ($M_w = 240$).

A combination of poly(propylene oxide) and poly(tetramethylene oxide) (either 1a/2b or 1b/

Table IV   Compatibility of Compositions and Their Corresponding Cured Substances' Various Oligomer Combinations

		SiH-Containing Oligomers			
		1a	**1c**	**1e**	**1f**
Allyloxy End-Blocked	**2a**	O	O	O	△
Oligomers	**2a**	O	O	×	△
	2c	O	O	×	△
	2c	O	O	×	△
	2e	△	△	O	×
	2e	△	×	O	△
	2f	×	×	×	O
	2f	△	△	×	O

(Upper row) before curing: (O) clear, (△) cloudy, (×) separated. (Lower row) after curing: (O) clearly cured, (△) cured with cloudiness, (×) separated and partially cured or poorly cured.

2a), with both **1** and **2** of the polyether type, yielded a homogeneously cured sample with good compatibility, although keeping the composition without the *Pt* catalyst sometimes led to the precipitation of the crystalline oligomer **2**.

A system, composed of oligomers whose main chains differed from each other, did not produce good compatibility and led to cloudiness or phase separation. It was sometimes observed that compatibility improved more after curing than before, which was probably because block-type polymers were formed from the both oligomers at the vicinity of their interface in the course of curing and these polymers seemed to improve the compatibility.

Properties of the Cured Materials

Mechanical Properties and Gel Content

Mechanical properties varied extensively, depending on both crosslinking density and oligomer backbone. As the crosslinking density decreased, that is, the molecular weight increased, the modulus became lower and the elongation larger (Table V).

Within the same oligomer, poly(propylene oxide) system **1a/2a**, the mechanical properties have changed dramatically, depending on cure time, temperature, and amount of the *Pt* catalyst (Tables V and VI). If the curing reaction proceeded ideally, the crosslink structure would be as shown in Scheme 1. During the curing process, however, the structure should have some defects in it and should contain the uncrosslinked free oligomer fraction.

The modulus still increased, even after the gel content reached a constant value, because the hydrosilylation reaction of the unreacted oligomer ends (SiH and allyl) slowly proceeded, even in the solid state, and the network structure seemed to become more ordered.

The fact that the gel content did not reach 100%, that is, there were some fractions that were not involved in the crosslink structure, may indicate that side reactions, such as isomerization and reduction, which accompany hydrosilylation, took place.

Dynamic Viscoelasticity

Dynamic viscoelasticity spectra were taken for the crosslinked samples, whose curing time was both 13 and 240 min (samples from Table VI), by giving a periodic 0.1% compression stress. The results are in Figures 2 and 3, which reveal the following points:

Table V   Tensile Test of the Cured Oligomer Composition[a]

No.	Type of Oligomer	Cure Time (min)	*Pt* Cat. (equiv.)	Modulus kg/cm^2[b]				TB[c] kg/cm^2	EB[d] (%)
				M 10	M 30	M 50	M 100		
1	Poly(propylene oxide) **1a/2a**	10	1×10^{-4}			2.0	3.1	6.4	310
2	Poly(propylene oxide) **1a/2a**	60	1×10^{-4}			2.4	3.8	7.4	270
3	Poly(tetramethylene oxide) **1b/2b**	60	1.3×10^{-4}	1.7	4.4			4.5	30
4	Hydrogenated poly(isoprene) **1d/2d**	10	1.6×10^{-4}	0.8	1.7	2.6		3.4	80
5	Hydrogenated poly(isoprene) **1d/2d**	60	1.6×10^{-4}	1.2	2.9	4.3		6.7	80

[a] Curing conditions: 100°C, SiH/allyl = 1 (1.3 for No. 2).
[b] M 10 means the tensile modulus at 10% elongation. The others are similar.
[c] Tensile strength at break.
[d] Elongation at break.

Table VI   Properties of Poly(propylene oxide) Cured Material 1a/2a[a]

Cure Time (min)	Modulus (kg/cm²)			TB kg/cm²	EB (%)	Gel Content (%)	M_c^b from M 100
	M 50	M 100	M 150				
13	0.5	0.8	1.1	9.6	920	71	7530
16	1.0	1.6	2.0	9.3	740	83	4060
18	1.4	2.1	2.7	11.9	680	88	3820
20	2.1	3.1	4.0	9.1	420	89	3440
30	2.3	3.5	4.5	8.5	350	94	3310
240	2.5	3.9	5.1	8.1	290	94	3170

[a] Curing conditions: 80°C, Pt cat.; 5×10^{-5} mol relative to 1 mol of allyl, SiH/allyl = 1.
[b] Molecular weight between crosslink points, according to the literature.[10]

- Both the dynamic mechanical tests showed the T_g (glass transition temperature) of the two cured poly(propylene oxide) systems as a peak top of tan delta diagram, around −50°C, to each of the crosslinked samples. The value of the T_g is higher than that of polydimethyl siloxane (−127°C),[11] which indicates that poly(propylene oxide) cured materials are not as elastic as the polydimethyl siloxane.
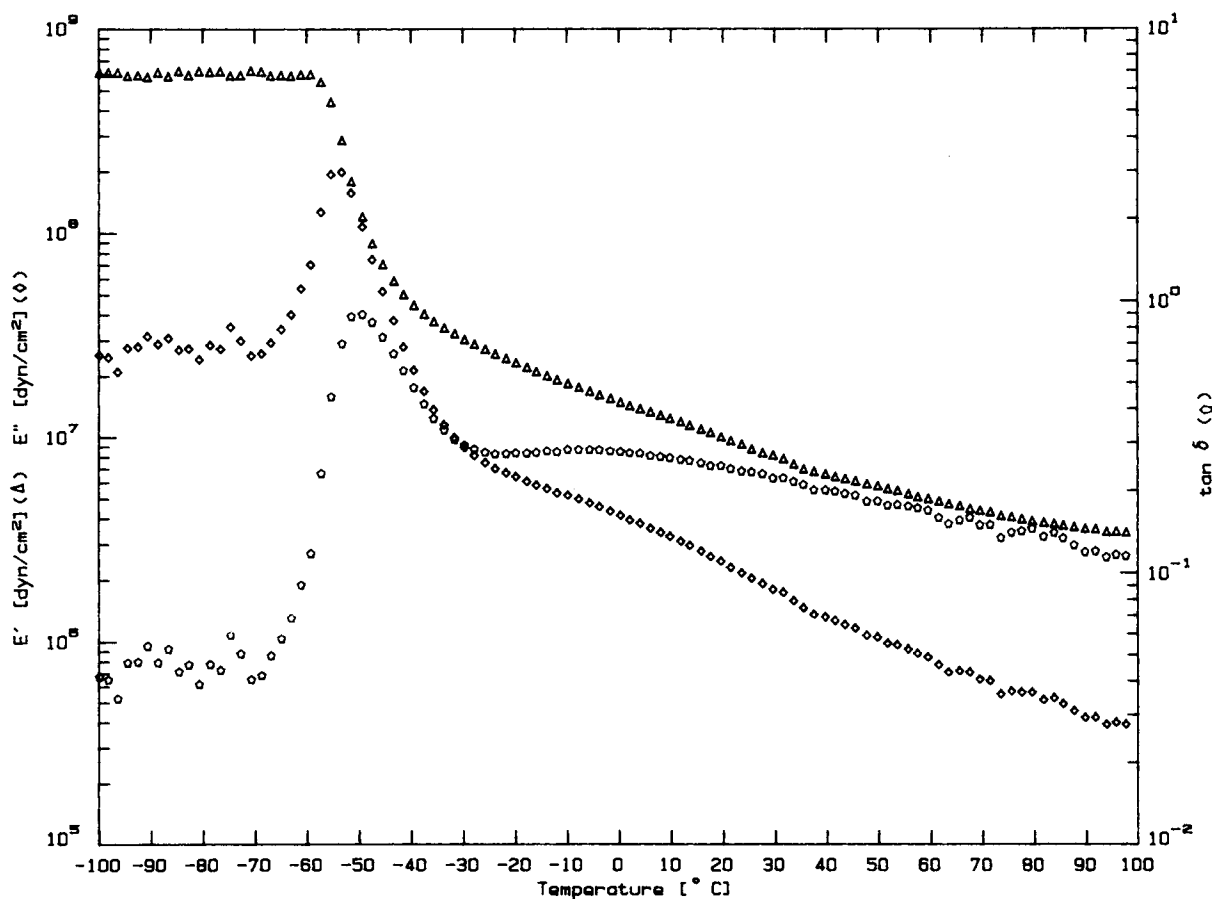
- At higher temperature than T_g, the tan delta

Figure 2   Dynamic mechanical spectra of poly(propylene oxide), cured for 13 min, from Table VI.
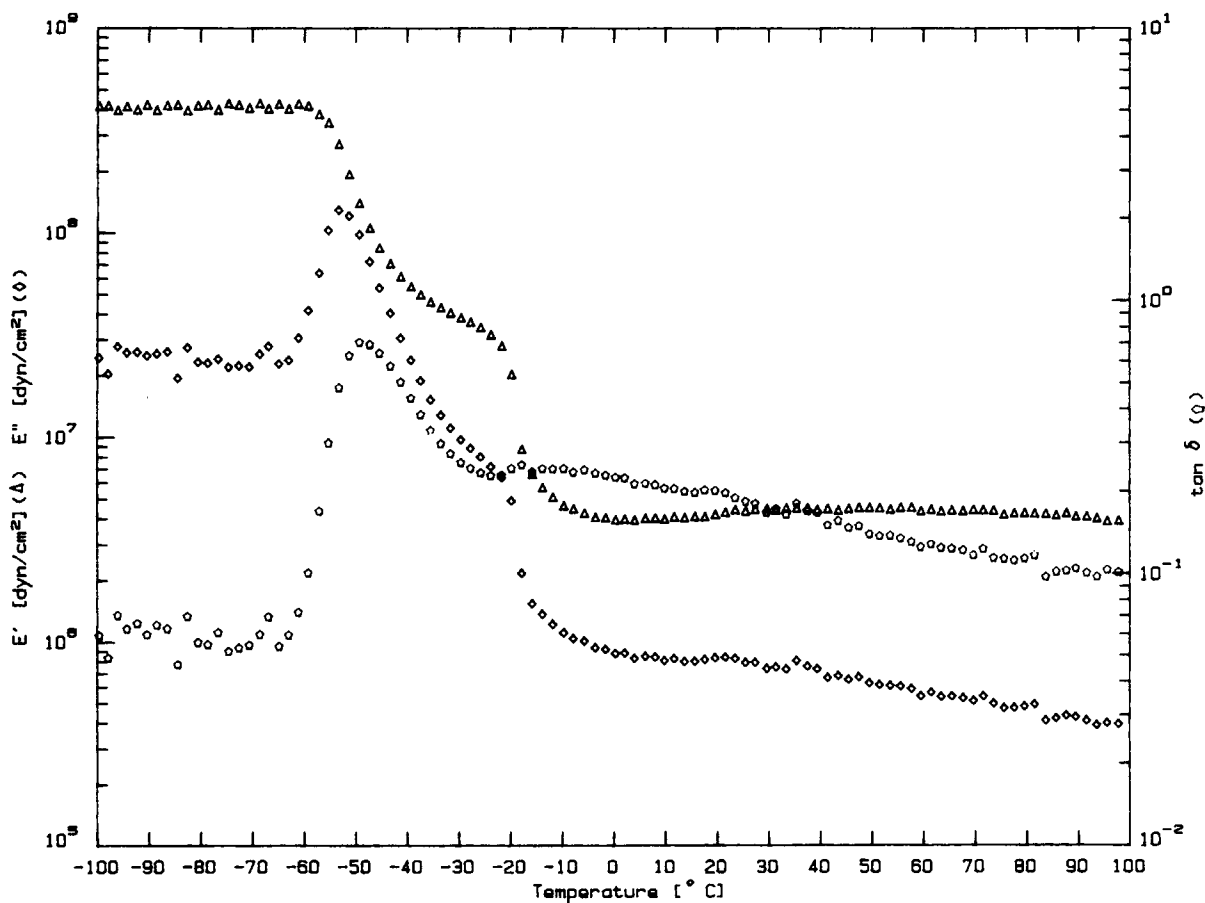
Figure 3 Dynamic mechanical spectra of poly (propylene oxide), cured for 240 min, from Table VI.

of Figure 2 is larger than that of Figure 3. This indicates that the former has a larger contribution of viscosity. In other words, a sample of Figure 3 has larger elasticity with more developed crosslinking.

- Both the storage modulus E' and loss modulus E'' of Figure 2 decreased as the measurement temperature increased. A viscosity decrease in the uncrosslinked components probably caused the decrease of the modulus as a whole.
- On the other hand, E' of Figure 3 is almost constant above 0°C, probably because of the presence of a small amount of uncrosslinked oligomers. No explanation is available for the sudden modulus decrease around −20°C.

Solid State ²⁹Si NMR

Solid state ²⁹Si NMR spectra were taken for the same samples as were taken for the dynamic vis-

coelasticity measurement, whose cure time was 13 and 240 min (Fig. 4). Although a signal around delta −35 ppm, due to SiH, was clearly observed in the lower spectrum of Figure 4, it almost disappeared in the upper one and only a signal around −20 ppm, due to SiC bonds, was observed; this fact probably indicates that the hydrosilylation reaction has almost been completed even in the solid state.

CONCLUSION

The hydrosilylation reaction, which has been limited to polysiloxanes, was successfully developed for several carbon-based oligomers. Features during the curing process of the oligomer compositions originated from the hydrosilylation; faster cure occurred at higher temperature, for instance. Properties of the cured materials were dependent on the crosslink
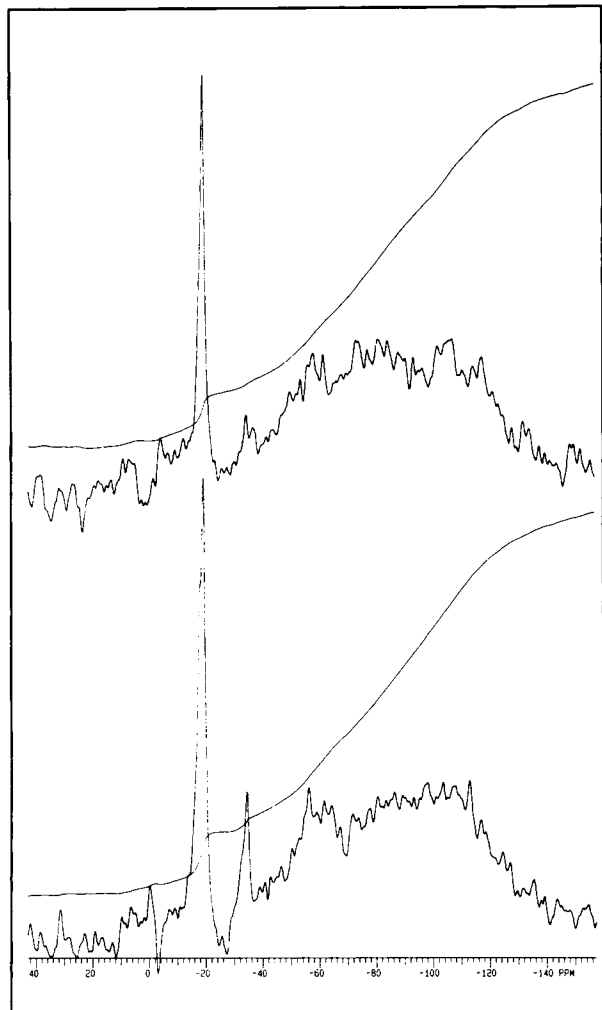
Figure 4 (lower) Solid state ²⁹Si NMR of poly(propylene oxide), cured for 13 min, from Table VI; (upper) Solid state ²⁹Si NMR of poly(propylene oxide), cured for 240 min, from Table VI.

density, as well as nature of the oligomer backbone. The practical application of this novel carbon-based oligomer curing system is now under investigation.

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