

Synthesis, Thermal and Mechanical Properties of Poly(methylphenylsilmethylene)s

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The synthesis, thermal and mechanical properties of poly(methylphenylsilylmethylene)s (PMPSMs) were investigated focusing on the effect of polymer microstructure on these properties. Stereoisomers of 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane were used as monomers to provide a series of PMPSMs having different molecular weights and tacticities. The monomers easily underwent bulk polymerization without catalyst as well as catalytic polymerization in the presence of Pt or Rh compounds to give high molecular weight PMPSMs. It is suggested by the ¹³C NMR analysis that the stereochemical configuration of the starting material may be retained during polymerization. ¹³C NMR spectrometry was also utilized to calculate the meso dyad content (X_m) which is regarded as a measure of the polymer tacticity. According to the relationship between X_m and the glass transition temperatures (T_g s) of PMPSMs, T_g s tend to decrease with increasing X_m s. PMPSM showed the excellent thermostability represented in terms of the 5% weight loss temperature as high as 460 °C in the TG-DTA analysis. Pyrolysis of PMPSM both in air and in nitrogen gave a network material with Si–H functionality which can be a precursor for Si–H functional ceramics. Dynamic and static mechanical properties of PMPSMs were also discussed.

Introduction

Silicon-containing polymers have been attracting much interest because of their unique thermal, mechanical, and optoelectrical properties as well as the pyrolytic behavior, and various kinds of silicon-based polymers have been widely studied for about 30 years.^{1,2} Poly(silmethylene)s in which the backbone is composed of Si–C repeating units are one of the most well-examined polymers among the poly(carbosilane) family, and a number of research activities, almost all of which were focused on the polymerization methods, have been found in the literature.^{3–17} The largest interest in the study

of poly(silmethylene)s seems to be the pyrolytic profiles of these polymers to SiC ceramics.¹⁸ Despite of the above situation, few reports have been published dealing with the material properties, such as thermal or mechanical properties rather than pyrolytic properties, of poly(silmethylene)s.

From the stereochemical point of view, it is quite interesting that polymers with different tacticities exhibit appreciable changes in the physical properties. The most visible and important property includes the glass transition temperature (T_g) of polymers. Effects of tacticities and/or molecular weights of polymers on the T_g s have been investigated for poly(methyl methacrylate),¹⁹ poly(vinyl chloride),²⁰ poly(α -methylstyrene) (PMST)^{21–23} in which methyl and phenyl substituents are on C atoms instead of on Si atoms in the case of poly(methylphenylsilmethylene) (PMPSM), poly(dimethylsiloxane),²⁴ and poly(methylphenylsiloxane)^{25,26} in which Si atoms are linked to oxygen atoms, not to methylene groups. Properties other than T_g are also of

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interest to interpret the relationship between the nature of polymers and their structural variation. Several reports have been published with regard to the β -transition,²³ flex-energy,²⁷ and damping factor²⁸ of PMST.

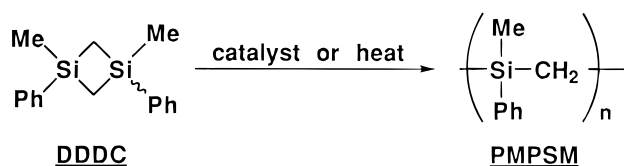
We have already reported the stereochemical course of hydrosilylation to the Si–C bond of 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutanes and the ring-opening polymerization of these compounds in the presence of platinum catalyst.²⁹ It was also found by the ¹³C NMR analysis that PMPSMs obtained by the Rh-catalyzed polymerization have tacticities slightly different from that of PMPSM prepared by Pt-catalyzed method.³⁰ In this article, synthesis of PMPSMs by catalytic and noncatalytic ring-opening polymerization methods in addition to the thermal properties of PMPSMs are discussed focusing on the tacticity of the polymers. We also report the dynamic and static mechanical properties of various PMPSM samples.

Experimental Section

Materials. All liquid solvents are reagent grade and distilled under nitrogen from appropriate drying agents prior to use. A monomer for the present study, which is 1,3-dimethyl-1,3-diphenyl-1,3-disilacyclobutane (DDDC), was prepared according to the literature.³¹ A pure trans isomer of DDDC was isolated from a mixture of cis/trans isomers by recrystallization.

Characterization. Analytical gas chromatography (GC) was performed using a Shimadzu GC-14A gas chromatograph equipped with a DB-5 capillary column (J & W Scientific). Infrared (IR) spectra were obtained with a Jasco FT/IR-5300 spectrophotometer. ¹H, ¹³C, and ²⁹Si NMR spectra were recorded with a Bruker ACP300 spectrometer using tetramethylsilane or 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt as an internal or external standard, respectively. Gas chromatograph–mass spectrometry (GC-MS) was carried out with a Shimadzu GCMS-QP1000EX system in an EI mode. Gel permeation chromatography (GPC) was performed using chloroform as the eluent with a Tosoh HLC-8020 gel permeation chromatograph equipped with two TSKgel GMHHR-H columns and a refractometer. Average molecular weights and the polydispersities were calculated by use of polystyrene standards, and the absolute molecular weights were determined by low-angle laser light scattering (LALLS) method using a Tosoh HLC-8020 equipped with a Tosoh LS-8000 laser light detector. Chloroform was used as an eluent. Differential scanning calorimetry (DSC) was performed using a Perkin-Elmer DSC 7/1022 system under a nitrogen atmosphere. Glass transition temperatures (T_g s) of PMPSMs were recorded as follows. Each sample was heated at a rate of 10 °C/min to 60 °C and was kept at that temperature for 1 min. The sample was put into liquid nitrogen afterward (quenching) and was finally heated at a rate of 20 °C/min. Thermogravimetry–differential thermal analysis (TG-DTA) was performed using a Rigaku TG8101D at a heating rate of 10 °C/min in air or in nitrogen. Approximately 5 or 8 mg of sample was used in each measurement. Thermogravimetry–mass spectrometry (TG-MS) was carried out by a thermal analytical system in which Rigaku TG8101D and Shimadzu QP1000EX were combined. Dynamic mechanical properties were examined using a Rheometrics RDA II dynamic analyzer in a torsion mode. Each specimen (10 × 30 × 1 mm) was prepared by compression

Scheme 1. Synthesis of PMPSMs



molding at 70 °C. The tensile properties were studied with an Instron 4301 universal testing machine at 25 °C. Film specimens with an average thickness of 250–350 μ m were also prepared by compression molding at 70 °C.

Polymer Synthesis. *Ring-Opening Polymerization of DDDC with a Platinum Catalyst.* Dimethylphenylsilane (6 mg; 0.04 mmol) and bis(triphenylphosphine)platinum(II) dichloride (2.5 mg) were dissolved in 3 mL of THF and the homogeneous solution was kept at the reflux temperature of THF. To the solution was added the trans isomer of DDDC (2.0 g; 7.4 mmol) in THF (7 mL), and the resulting mixture was kept at 80 °C (bath temperature) for 24 h. After cooling, the reaction product was diluted with chloroform to give a 50 mL solution. This polymer solution was poured into ca. 3000 mL of methanol to form a polymeric material. Filtration followed by vacuum drying at 70 °C gave a colorless solid (1.53 g; yield 77%). ¹H NMR (C_6D_6 , ppm) δ 0.0–0.1 (multi), and 7.1–7.4 (br, multi). ¹³C NMR (C_6D_6 , ppm): δ –0.24, 0.05, 6.0, 6.2, 6.4, 127.8, 128.8, 134.0, 141.4. ²⁹Si NMR (C_6D_6 , ppm) δ = –4.8. Molecular weight (M_w by LALLS) 80 900.

Ring-Opening Polymerization of DDDC with a Rhodium Catalyst. A trans isomer of DDDC (2.0 g; 7.4 mmol) and bis(1,5-cyclooctadiene)dirhodium(I) dichloride (1.1 mg; 0.002 mmol) were dissolved in 9 mL of toluene and heated at 45 °C for 45 h. To the reaction mixture was added 25 mL of chloroform to dilute the solution. This polymer solution was poured into ca. 2000 mL of methanol to form a polymeric material. Filtration followed by vacuum drying at 70 °C gave a pale yellow solid (1.38 g; yield 69%). ¹H NMR (C_6D_6 , ppm): δ 0.0–0.1 (multi), 7.1–7.4 (br, multi). ¹³C NMR (C_6D_6 , ppm) δ –0.24, 0.05, 6.0, 6.2, 6.4, 127.8, 128.8, 134.1, 141.4. ²⁹Si NMR (C_6D_6 , ppm) δ –4.9. Molecular weight (M_w by LALLS) 341 000.

Ring-Opening Polymerization of DDDC without Catalyst. A trans isomer of DDDC (2.0 g, 7.4 mmol) was heated at 170 °C for 2 h. After cooling the product was dissolved in 160 mL of chloroform and poured into 2000 mL of methanol to form a polymeric material. Filtration followed by vacuum drying at 70 °C gave a colorless solid (1.76 g, yield 88%). ¹H NMR (C_6D_6 , ppm) δ 0.0–0.1 (multi), 7.1–7.4 (br, multi). ¹³C NMR (C_6D_6 , ppm) δ –0.25, 0.04, 6.0, 6.2, 6.4, 127.8, 128.8, 134.0, 141.4. ²⁹Si NMR (C_6D_6 , ppm) δ –4.9. Molecular weight (M_w by LALLS) 2 348 000.

Results and Discussion

Synthesis of PMPSMs. PMPSMs were synthesized by ring-opening polymerization of DDDC as shown in Scheme 1.

It has already been reported by Kriner that a mixture of stereoisomers of DDDC easily underwent catalytic polymerization in the presence of $PtCl_6^{2-}$, $PtCl_2$, $IrCl_6^{2-}$, $RuCl_6^{2-}$, $AuCl_4^-$, $PdCl_2$, or RuI_3 species to form PMPSMs.⁴ In the present study three synthetic methods, which involve Rh-catalyzed polymerization, Pt-catalyzed polymerization, and bulk polymerization without catalyst, were employed. Two stereoisomers of DDDC, which are called cis and trans isomers in this article based on the configuration of two phenyl groups on Si atoms of DDDC, were formed by the reported synthetic method³¹ and could be separated by preparative GC as was demonstrated.²⁹ Either cis or trans isomer of DDDC or a mixture of cis/trans isomers of DDDC was used as the starting material to afford PMPSMs with a wide variety of tacticities. The Pt-

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Table 1. Molecular Weights, Tacticities, and T_g s of PMPSMs

polymer	[trans]/[cis] ^a	method ^b	M_w (LLS) ^c	M_w/M_n ^d	tacticity ^e	T_g (K) ^f
1	74/26	A	1.19×10^5	2.07	37/49/14	294
2	100/0	A	1.75×10^5	3.10	0/51/49	297
3	100/0	A	3.41×10^5	2.67	0/52/48	297
4	0/100	A	1.35×10^5	1.86	51/49/0	294
5	100/0	B	8.09×10^4	1.67	0/50/50	299
6	100/0	B	1.35×10^4	1.88	0/50/50	296
7	54/46	C	2.22×10^5	2.35	28/49/23	295
8	83/17	C	3.81×10^5	2.95	41/49/10	294
9	100/0	C	2.35×10^6	2.34	0/52/48	300

^a [cis-DDDC]/[trans-DDDC] molar ratio. ^b Preparative method; A, Rh-catalyzed polymerization; B, Pt-catalyzed polymerization; C, bulk polymerization. ^c Determined by GPC with a laser light scattering detector. ^d Measured by GPC. ^e Represented as the [isotactic triad]/[heterotactic triad]/[syndiotactic triad] molar ratio calculated from the ¹³C NMR analysis. ^f Determined by DSC at a heating rate of 20 °C/min.

catalyzed polymerization in the present study was performed using a Pt(PPh₃)₂Cl₂/Me₂HSiPh system as was briefly shown in our recent report.²⁹ The polymerization proceeds by hydrosilylation mechanism and the molecular weight of the resulting polymer is almost controllable by altering the monomer/Me₂HSiPh molar ratio. Polymers were obtained in a moderate yield of 70–80% by this method. It was also found that this monomer can be polymerized by use of a rhodium complex as the catalyst. The molecular weight of the polymer can be altered to some extent by changing the monomer/catalyst molar ratio but not be adjustable with high accuracy. The microstructure (tacticity) of the polymers prepared by this method was slightly different from that obtained by the Pt-aided method. The polymer yields were also moderate (60–70%). Furthermore, we demonstrated bulk polymerization of this monomer at elevated temperature. The molecular weights of the resulting PMPSMs were not controllable at all. PMPSM with the highest molecular weight in the present study was synthesized by this method when a pure trans isomer was used as a monomer. Although which mechanism, such as radical or ionic, is correct for the bulk polymerization of DDDC has not been clarified, this polymerization route is noteworthy because 1,1,3,3-tetramethyldisilacyclobutane does not undergo bulk polymerization. The molecular weights, tacticities, and glass transition temperatures of PMPSMs are summarized in Table 1.

Characterization of PMPSMs by NMR Spectrometry. We have already clarified that the stereochemical configuration within DDDC is retained during the Pt-catalyzed hydrosilylation and no racemization takes place about the Si atom.²⁹ Polymerization using the same catalytic system was of interest for examination by NMR spectrometry. NMR spectrometry is well-known to be a useful method to elucidate the polymer microstructure.³² For this polymer system, the differences in tacticities of the series of PMPSMs were clearly observed by measuring ¹³C NMR spectra. The region of methyl and methylene carbons of ¹³C NMR spectra for three PMPSMs synthesized by the Pt-catalyzed method are illustrated in Figure 1. The bottom spec-

trum of this figure is for PMPSM derived from a mixed monomer (cis/trans = 50/50). Three sharp resonances assigned to methyl carbons by an experiment without ¹H decoupling were found at around –0.24, 0.05, and 0.35 ppm. It is very reasonable to assume that these resonances are caused by three triad sequences, which are denoted as *mm*, *mr*, and *rr*. These resonances should exhibit the relative intensity ratio of 1 (*mm*):2 (*mr*):1 (*rr*) according to theoretical calculation if no stereochemical induction is observed in the course of polymerization. The actual intensity ratio of a set of resonances is close to the above value, and the central resonance is undoubtedly derived from the carbons with *mr* configuration. In other words, this resonance is assignable to the central carbons of the heterotactic triad sequence. According to the top and the middle spectra of this figure, which are for PMPSMs derived from cis-DDDC and trans-DDDC, respectively, only two resonances at 0.05 and 0.35 ppm were detected for the former while a different set of resonances at –0.24 and 0.05 ppm were found for the latter. Taking into account the mechanistic similarity of the polymerization reaction to hydrosilylation, this suggests that a stereospecificity of the addition toward the Si–C σ -bond was induced for conversion of DDDC to PMPSM, which implies that the stereochemical configuration of DDDC may be retained during polymerization. Two possible triad sequences for PMPSMs derived from cis-DDDC are *mm* and *mr* and those for PMPSMs derived from trans-DDDC are *mr* and *rr*. Hence, the resonances at –0.24 and 0.35 ppm can be assigned to the central carbons of the syndiotactic triad sequence and the isotactic triad sequence, respectively. All resonances assignable to methyl carbons in these spectra split into 2–5 resonances, probably owing to the presence of pentad sequences having different chemical shifts.

The resonances caused by methylene carbons can also be used to estimate the polymer microstructure. They should split theoretically into two due to two dyad sequences, each of which might split into three by three tetrad sequences. A set of resonances at around 6 ppm in each spectrum split into about three, but interpretation of these phenomena is difficult because of overlapping of several resonances resulting in three major resonances. ¹H and ²⁹Si NMR spectrometries are also possible tools for this purpose. However, they were not suitable to distinguish polymers with different microstructures for this polymer system. Stereoisomerism of poly(methylphenylsiloxane)s synthesized by ring-opening polymerization of 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane has been analyzed by means of ¹H NMR, and three resonances assignable to triad sequences were found in the spectra.³³

It is also found that polymerization of DDDC using a rhodium compound proceeds in a stereospecific manner as was observed for Pt-aided polymerization. Although the polymerization mechanism may be different from the Pt-aided one, the methyl carbon region of ¹³C NMR spectrum of PMPSM derived from a trans isomer of DDDC comprises only two sets of resonances as that for PMPSM by the Pt-catalyzed method did. This suggests that the Rh-catalyzed polymerization proceeds with retaining stereochemical configuration of DDDC.

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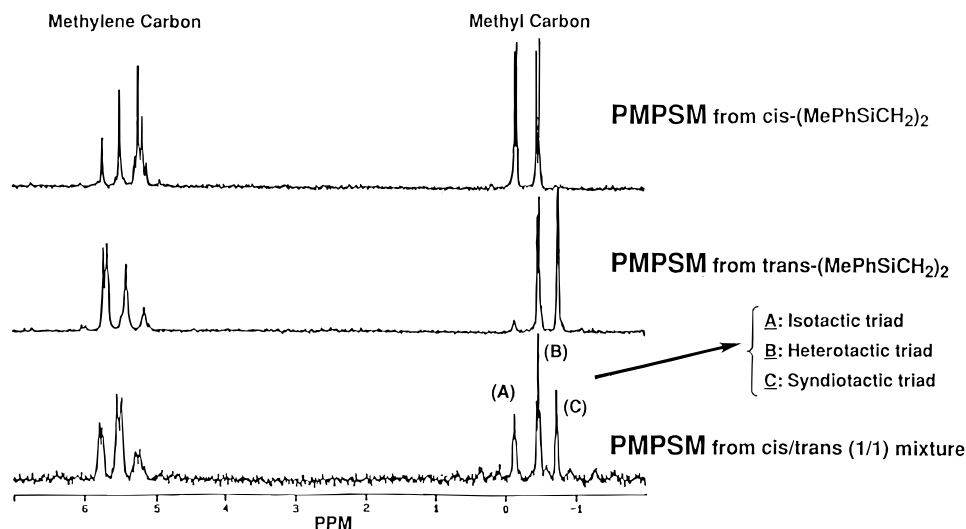


Figure 1. ^{13}C NMR spectra (methylene and methyl carbons region) of PMPMSs derived from various DDDC stereoisomers.

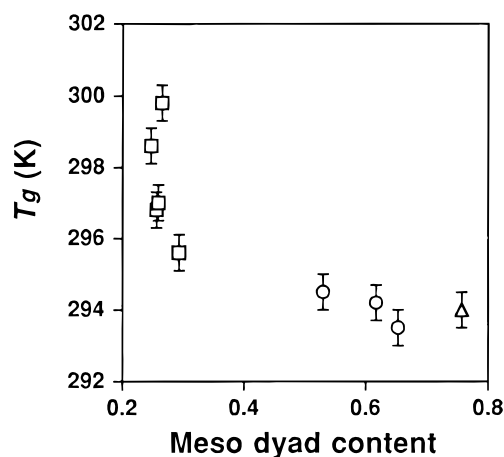


Figure 2. Glass transition temperatures as a function of meso dyad contents of PMPMSs: square, polymers from a pure trans isomer; circle, polymers derived from a mixture of cis/trans isomers; triangle, a polymer from a pure cis isomer.

Furthermore, the ^{13}C NMR analysis revealed that a bulk polymerized PMPSM showed a behavior in stereochemistry similar to that observed for the catalytic methods. No mechanistic study has been tried, but it is quite interesting that bulk polymerization takes place stereospecifically.

Glass Transition Temperatures (T_g s) of PMPMSs.

T_g s of a series of PMPMSs having different molecular weights and tacticities were measured by DSC. The results are listed in Table 1. No transition except for the T_g was observed for all samples. The meso dyad content X_m derived from the following eq 1 was used as a measure of the polymer tacticity.

$$X_m = (\text{fraction of isotactic triad}) + 0.5 \times (\text{fraction of heterotactic triad}) \quad (1)$$

Polymers derived from a trans isomer of DDDC showed relatively small X_m because polymerization proceeds with retaining configuration of the monomer units as described above. The T_g s as a function of the X_m s are illustrated in Figure 2 in which square, circle, and triangle data points represent data of polymers derived from a pure trans isomer, a mixture of cis/trans isomers, and a pure cis isomer of DDDC, respectively. It is evident that polymers having relatively large X_m

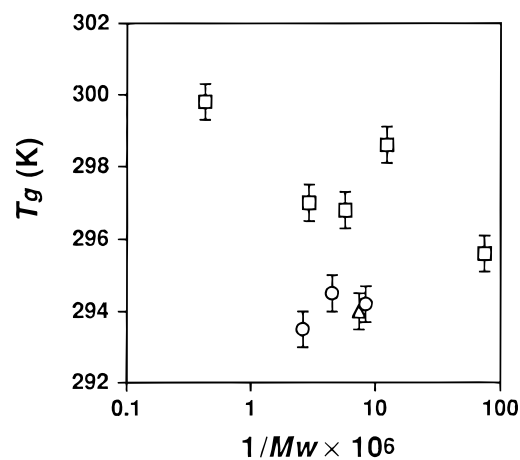


Figure 3. Glass transition temperatures as a function of molecular weights of PMPMSs.

tend to exhibit lower T_g s than those with small X_m . These results may suggest that PMPMSs with low X_m have a high content of polymer species with small free volume. The relationship between the two parameters of X_m and T_g has been reported by Momper and co-workers using poly(methylphenylsiloxane)s with various tacticities, a result similar to that of the present study was conducted.²⁵

The relationship between the molecular weights (M_w s) and the T_g s (Fox-Flory relation) of PMPMSs are summarized in Figure 3. The symbols for data points used in this figure were identical with those in Figure 2. The data points seem to be scattered at two areas in the figure in which data points for polymers derived from a mixture of cis/trans isomers are found in the lower area. In the upper area, T_g s decrease with decreasing molecular weights of PMPMSs. It is well-known that T_g s of polymers increase up to the cut point at which it remains essentially constant as the molecular weights increase,^{22,24-26} and the critical value of the molecular weights is usually located between 10^4 and 10^5 . A more detailed study by Turner regarding the M_w - T_g relationship revealed that a plot of T_g versus reciprocal M_w gave two lines which intersect at a specific molecular weight, M_g , and an increased elevation of T_g at molecular weights greater than M_g is attributed to a high concentration of polymer entanglements.³⁴ An

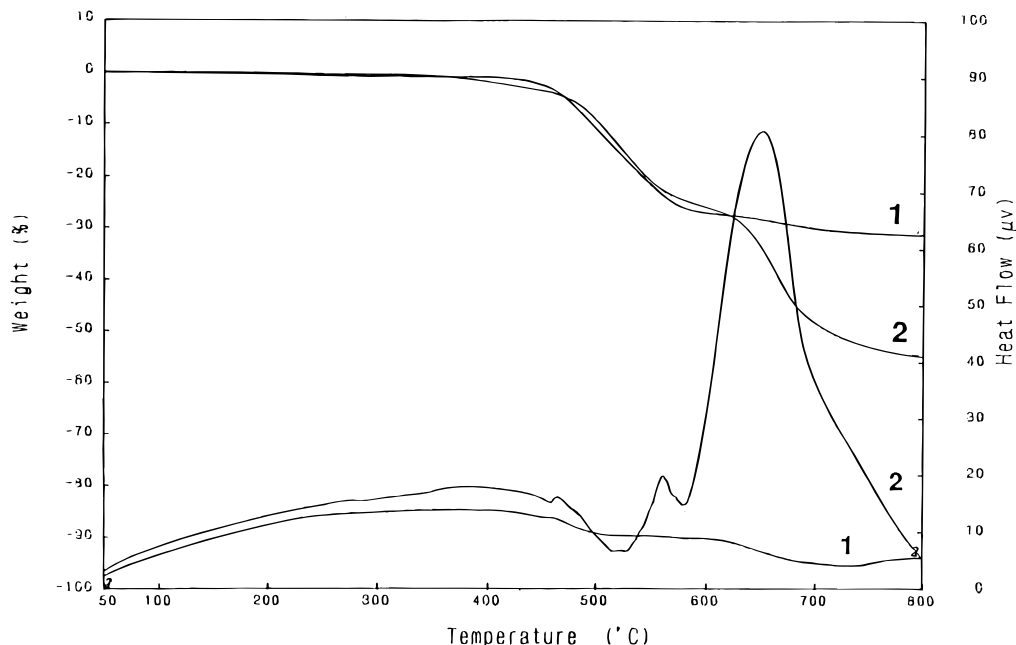


Figure 4. TG-DTA traces of polymer-9 in a nitrogen atmosphere (curve 1) and in air (curve 2) at a heating rate of 10 °C/min.

Table 2. Thermal Properties of PMPSMs

polymer	in N ₂		in air	
	<i>T</i> _{d5} (°C) ^a	<i>W</i> ₈₀₀ (%) ^b	<i>T</i> _{d5} (°C) ^a	<i>W</i> ₈₀₀ (%) ^b
3	506	69	467	41
7	462	68	456	37
8	467	68	467	41
9	472	69	472	45

^a 5% weight loss temperature. ^b Weight percentage of the residue after heating to 800 °C.

increasing *T*_g was observed in the present study even at molecular weights higher than 10⁶.

It can be concluded that *T*_gs of PMPSMs depend on both the tacticities and the molecular weights. Polymers with low meso dyad contents exhibit higher *T*_gs than those with high meso dyad contents, but molecular weight may be a predominant factor by which *T*_gs of PMPSMs are affected when the meso dyad contents of the polymers are close each other.

Thermogravimetric Analysis of PMPSMs. The thermostability of PMPSMs was investigated by the weight loss behavior in the TG-DTA analysis. The TG-DTA traces for polymer-9 in air and in nitrogen are shown in Figure 4. This polymer remained almost unchanged in weight up to about 400 °C, and thermal decomposition resulting in weight loss until around 600 °C was found afterward under nitrogen. On the other hand, it exhibited a two-step weight loss in the temperature range between ca. 400 °C and ca. 700 °C in an air atmosphere. The first decomposition step of the latter process is elimination of the methyl and phenyl groups, which will be discussed in the next section, while the subsequent weight loss is due to oxidative decomposition that is evident from a large exothermic peak in the DTA trace. The thermal parameters obtained by the analysis along with the molecular weights of PMPSMs are listed in Table 2. PMPSMs have very good thermostability according to the 5% weight loss temperature (*T*_{d5}) measurements in a ni-

trogen atmosphere, and these values are comparable to those of crystalline poly(diphenylsilmethylene).³⁵ Polymer-3 obtained by Rh-catalyzed polymerization showed remarkably high *T*_{d5}. The residual catalyst may be responsible for this improved thermostability.³⁶

*W*₈₀₀ in Table 2 denotes a weight percentage of the material obtained after heating a polymer sample to 800 °C. The values obtained in air were much smaller than those in N₂ and are in fair agreement with the calculated amounts of weight loss (44%) based on an assumption that silicon-based polymers are converted into silica upon heating in air. It is noteworthy that PMPSMs in the present study gave solid materials in an appreciable yield after pyrolysis up to 800 °C in both atmospheric conditions. In other words they presumably do not decompose by backbiting. Polysiloxanes such as poly(dimethylsiloxane) and poly(methylphenylsiloxane) lose their weights through a backbiting process resulting in a *W*₈₀₀ of almost zero. The weight loss behavior of PMPSMs also contrasted with that of poly(dimethylsilylmethylene) which showed a very low (almost zero) value of *W*₈₀₀ in N₂ due to backbiting, and oxidative decomposition in air to form a silica-like material.³⁷

Analysis of Volatile Pyrolyzed Products of PMPSM. Thermogravimetry-mass spectrometry (TG-MS) was applied to identify volatile compounds formed during pyrolysis of PMPSM. Polymer-8 was heated in a helium atmosphere up to 800 °C at a heating rate of 10 °C/min. One broad peak was recorded in the total ion chromatogram. The major product formed upon pyrolysis of PMPSM was benzene, but several minor compounds were identified according to the detailed analysis. They included toluene, xylene, and biphenyl. Because of the following two reasons, these minor compounds are likely to be formed by several types of

(35) Ogawa, T.; Murakami, M. *J. Polym. Sci., Part B: Polym. Phys.*, in press.

(36) The role of transition-metal compounds including Cs, Ir, Mo, Rh, and Pt compounds in combustion inhibition has been described in a patent. Williams, T. *U.S. patent 4701488*, Union Carbide Corp., 1987.

(37) Levin, G.; Carmichael, J. B. *J. Polym. Sci., Part A-1* **1968**, *6*, 1.

reactions of aryl fragments liberated by dearylation of PMPSMs which presumably took place prior to backbone cleavage reactions.

(a) The retention times of those minor compounds were longer than that of the major component.

(b) No Si-containing compounds were detected in any measurement.

While no mechanistic study was conducted in this work, formation of biphenyl is evidence for the radical cleavage of the Si-aryl bonds of PMPSMs. A study by Telegina et al. revealed that the predominant pyrolysis process for linear and cyclic oligomethylphenylsiloxanes (tetra- or pentasiloxanes) was elimination of benzene, and cyclic siloxanes containing *o*-phenylene group were formed as reaction products.^{38,39} Methane and ethylene were the most prominent evolved gases according to the report regarding TG-MS analysis of cross-linked siloxanes containing CH₂CH₂ units.⁴⁰

A heating experiment in a sealed tube was carried out for quantitative analysis of liberated compounds upon pyrolysis of PMPSM. Polymer-8 was heated in a glass tube under reduced pressure for 5 h at around 540 °C, which is close to the temperature at which the first stage of complete weight loss in the TG analysis. Since it was quite difficult to remove air completely from the reaction vessel containing a rubber-like substrate, a small quantity of air would remain even after this degas process. The ether-soluble components of the pyrolyzed product were analyzed by GC. Identification of each peak in the GC trace was performed by referring to the retention times of authentic compounds and to the GC-MS data. The major liberated product was benzene, and its quantity corresponds to ca. 9.5 wt % of the initial weight of this sample. Toluene was also detected in the amount of ca. 0.5 wt % in addition to trace amounts of several compounds such as biphenyl and methyl-substituted biphenyl.

Spectroscopic Analysis of Pyrolyzed Products of PMPSMs. The pyrolysis products of PMPSM were analyzed by IR. The IR spectra of the samples, which are brown solids obtained by heating to 540 °C both in air and in nitrogen using a TG-DTA apparatus, are shown in Figure 5. It is noticeable that each of them exhibited a distinct peak at around 2115 cm⁻¹, probably assignable to Si-H functionality.⁴¹ Peak patterns in the wavenumber range between 1000–1200 cm⁻¹ are different to some extent presumably because of the presence of Si-O-Si linkages formed upon pyrolysis for the sample treated in air. In addition, the intensity of the Si-H peak for the sample obtained in N₂ was larger than that of the sample obtained in air. According to these IR results, each pyrolyzed product must be a branched or cross-linked material consisting of Si-H, Si-C, C-H, aryl and Si-O-Si (only for the pyrolyzed sample in air) groups. The formation of a ring structure along the chain is also possible. In the case of poly-(diphenylsilylmethylene), the similar peak pattern due to Si-H functionality was observed when the sample

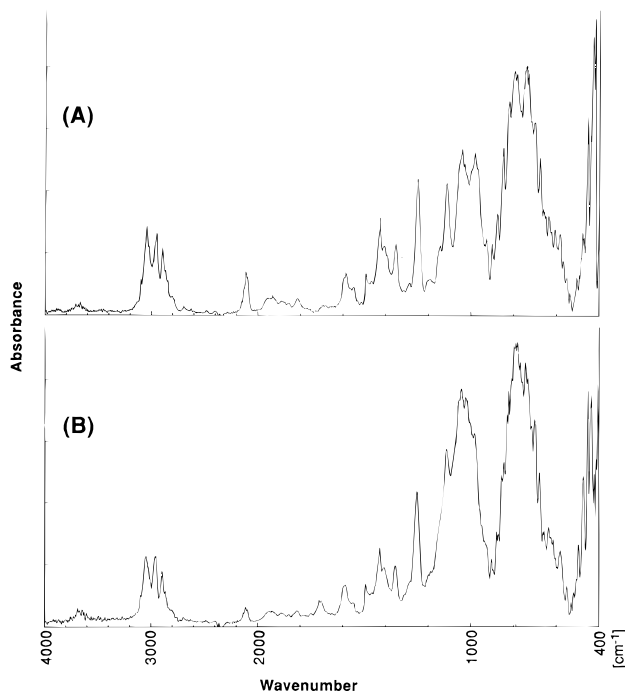


Figure 5. IR spectra of pyrolyzed products of PMPSM obtained by heating to 540 °C at a rate of 10 °C/min in N₂ (A) and in air (B).

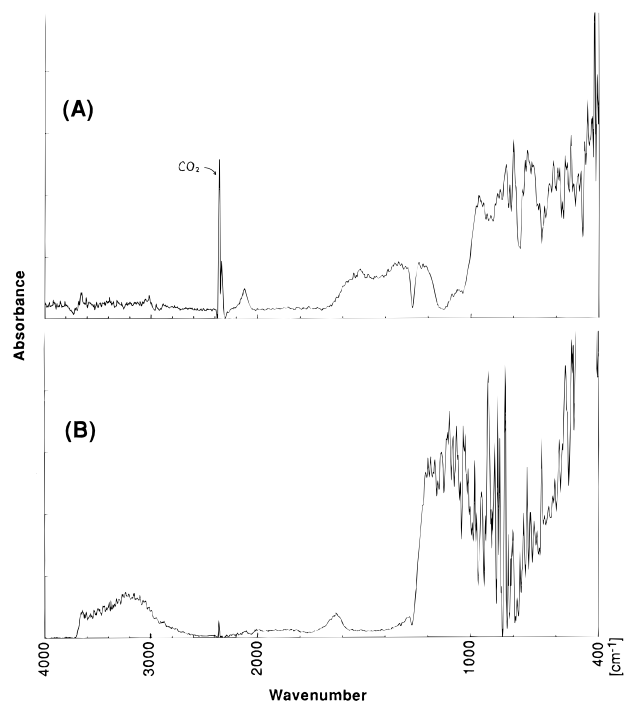


Figure 6. IR spectra of pyrolyzed products of PMPSM obtained by heating to 800 °C at a rate of 10 °C/min in N₂ (A) and in air (B).

was pyrolyzed only in an inert atmosphere.³⁵ The presence of Si-H groups was also observed for a pyrolyzed product of PMPSM obtained by heating to 800 °C under N₂ as was shown in Figure 6A. No sign of aryl or alkylene groups was found for this black material. Hence, this may be a mixture of amorphous carbon and an Si-H functional Si-C network material. The formation of Si-H groups has not been mechanistically clarified yet, but hydrogen abstraction by Si[•] radical formed via homolysis of Si-Ph linkage is a possible explanation. On the other hand, a peak assignable to

(38) Telegina, N. P.; Bochkarev, V. N.; Palamarchuk, N. A.; Lozovskaya, V. S.; Agapova, T. A.; Kondratova, N. A.; Polivanov, A. N. *Zh. Obshch. Khim.* **1974**, *44*, 2695; *J. General Chem.* **1974**, 2649.

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(40) Michalczyk, M. J.; Farneth, W. E.; Vega, A. J. *Chem. Mater.* **1993**, *5*, 1687.

(41) Lipp, E. D.; Smith, A. L. *The Analytical Chemistry of Silicones*; Smith, A. L., Ed.; John Wiley & Sons: New York, 1991; Chapter 11.

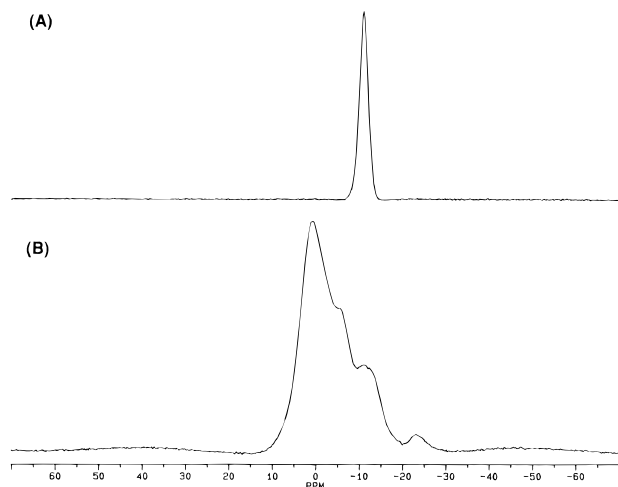


Figure 7. ^{29}Si CP/MAS NMR spectra of PMPSM before (A) and after (B) pyrolysis in a sealed tube at 540 °C.

Si–H functionality was not detected in the IR spectrum of Figure 6B when a PMPSM sample was heated to 800 °C in air. The product may be a silica-like material containing small amount of impurities formed via insufficient conversion of the substrate into silica, which is responsible for several sharp peaks in the IR spectrum. Absence of the Si–H groups in the final material can easily be explained by oxidation of Si–H to Si–OH groups followed by condensation to provide Si–O–Si bonds.

A pyrolyzed PMPSM obtained by heating at 540 °C in a sealed tube was analyzed by means of solid-state NMR. ^{29}Si CP/MAS NMR spectra before and after pyrolysis are shown in Figure 7. The pyrolyzed sample displayed a very broad resonance centered at 1.0 ppm with shoulders at around -5.5 and -10 ppm in addition to a small resonance centered at -23 ppm, whereas the spectrum of the polymer before pyrolysis comprises one sharp peak centered at -10 ppm. The shoulder at -10 ppm suggests remaining MePhSiC_2 units in the pyrolyzed product. It is obvious that there are at least two types of Si-containing structural units in the pyrolyzed product, possible components of which are CPhSiC_2 , CMeSiC_2 , CPhHSiC , CMeHSiC , and C_2SiC_2 . The largest resonance at around 1 ppm is assignable to Si atoms surrounded by four carbon atoms, and it is likely that H-attached silicon atoms caused the resonance at around -5.5 ppm. Several kinds of siloxy units can also be considered because the pyrolysis was conducted with a small amount of air in a sealed tube, but the content of these species does not seem very high according to Figure 7.

Dynamic Mechanical Properties of PMPSMs.

Dynamic mechanical properties of PMPSM are also informative to understand the low-temperature behavior of this polymer and to differentiate the polymers with various tacticities. Each PMPSM obtained by different synthetic conditions was molded into a rectangular specimen, and the dynamic moduli as a function of temperature were studied first to gather information concerning the transition temperatures. Dynamic mechanical spectra of polymer-9 are illustrated in Figure 8. An ambiguous peak at around -120 °C in addition to a clear peak caused by the glass transition at around 20 °C was observed in the loss modulus profile for each sample. No visible drop of the storage modulus

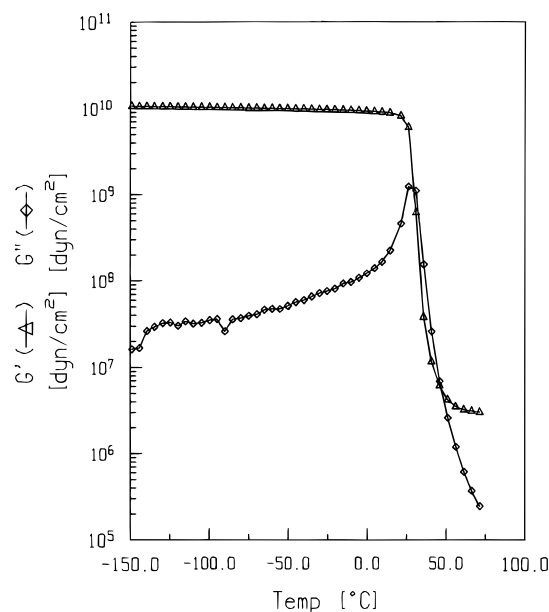


Figure 8. Temperature dependence of storage modulus G' and loss modulus G'' of polymer-9 at a constant frequency of 6.28 rad/s and a constant strain of 1%.

Table 3. Tensile Properties of PMPSMs

polymer	tensile stress (MPa)	elongation (%)	Young's modulus (MPa)
1	5	750	200
3	6	500	300
7	4	850	100
8	6	500	200
9	16	200	850

was found at the former temperature range. Several kinds of amorphous polymers show a γ transition at around 150 K as well as β transition sometimes being a shoulder on the low temperature side of the T_g . The β transition is suggested to be related to the amount of free volumes, whereas the height of the γ transition seems to follow the reciprocal of the molecular weight of the polymer.⁴² Although it is not clear that the ambiguous loss peak observed in the present study should be denoted as β or γ transition, rotation, or other mode of motions by phenyl groups seems to be possible explanation for this transition.

Static Mechanical Properties of PMPSMs. The tensile properties of PMPSMs were investigated. A cross-head speed of 50 mm/min was employed for the test, and the tensile properties of several samples are summarized in Table 3. All samples showed great elongation at break (ϵ_b) higher than 200%. Polymer-9 showed high tensile stress (σ_y) as well as Young's modulus (G) compared with other four samples presumably because of its slightly higher T_g than the temperature at which the test was performed. The higher T_g also causes the relatively low ϵ_b of this sample. This sample is comparable to several types of organic rubber materials such as chloroprene rubber and butyl rubber in the tensile properties. One can find the effect of molecular weight on the properties by comparison among polymer-1, polymer-3, and polymer-8. These two samples showed a similarity in polymer tacticity in terms of meso dyad content, but sample 1 exhibited greater ϵ_b than polymer-8 due to its lower molecular

weight. In fact polymer-3 and polymer-8 showed comparable performances although the tacticities of samples are different each other to some extent. If one compare polymer-7 and polymer-3, there is an appreciable difference in the values of ϵ_b and G . These two samples showed a relatively large difference in the tacticities although the difference in the molecular weights was not very significant. Hence, the lower G in addition to the higher ϵ_b may be led by the relatively high meso dyad content. It is well-known that elastomeric materials alter the tensile profiles when any crystalline phases are present.⁴³ No sign of crystallinity was found for polymers in the present study, but a slightly altered polymer tacticity might change the cohesive interaction between molecules being responsible for the tensile properties.

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These tensile properties of PMPSMs are not very remarkable for elastomeric materials, but they were achieved without cross-linking. We cannot obtain such moldable materials with fair tensile properties and good thermostability by taking any linear siloxane homopolymers.

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