New Highly Heat-Resistant Polymers Containing Silicon: Poly(silyleneethynylenephenyleneethynylene)s

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ABSTRACT: Six kinds of poly(silyleneethynylenephenyleneethynylene)s [−Si(R)H−C≡C−C_6H_4−C≡C−], wherein the phenylene group was the meta-, para- or ortho-form and R represents a phenyl, methyl, or hydrogen atom, were prepared, and the properties of the resulting polymers were investigated. The polymers, especially poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] (R = Ph), which were thermosetting, soluble in solvent, fusible, and moldable, showed high heat-resistant and burning-resistant properties. A cross-linking reaction mechanism concerning the Si−H and C≡C bonds was proposed, and the correlation between the molecular structures and the thermal properties was discussed. Fiber-reinforced polymers prepared using glass, carbon, or SiC fibers showed sufficient mechanical strength even at 400 °C under air. A black, hard, and glassy material (C−SiC) was obtained when poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] was heated above 1000 °C under argon.

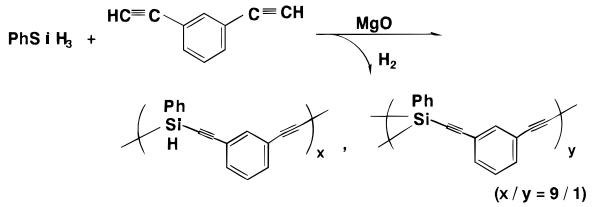
Introduction

Metals such as iron (specific gravity 8) and titanium (specific gravity 4.3) are highly heat-resistant and tough but heavy. Aluminum (specific gravity 2.7) is light but not very heat-resistant (ca. 300 °C). Ceramics such as SiC, Si_3N_4, and silica glass (SiO_2) are lighter (specific gravities 2−3) than metals and highly heat-resistant, but are not tough and not moldable. Many engineering plastics have been synthesized which are light (specific gravities 1−1.5), moldable, and have good mechanical properties. Polyimide (Vespel, DuPont) has the highest heat resisitance of all plastics with a heat destortion temperature of 360 °C. Several polymers such as polybenzyimidazole, polybenzothiazole, and polybenzooxazole, which have a higher heat resistance than the polyimide, have been developed, but they are not moldable and are flammable.

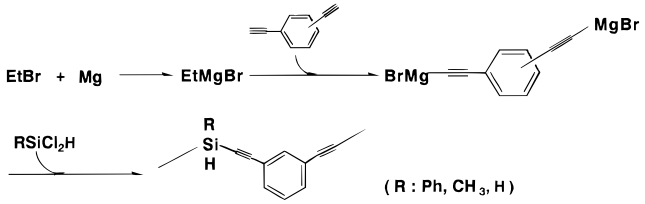
The purpose of the study is to synthesize new materials which are light, highly heat-resistant, nonflammable, and moldable. We thought that an organic polymer which was able to be cross-linked like metals or ceramics would provide such a material. Chemical bonds of Si−H, Si−Cl, Si−OR, and Si−Si are reactive; especially the Si−H bond also reacts with many chemical bonds such as C=C, C≡C, C=O, OH, NH, and C≡N. The Si atom forms thermally stable inorganic compounds such as SiC or SiO_2. Therefore, we postulated that a silicon-containing organic polymer is favorable for making such a material by the cross-linking reaction. On the basis of the above concept, we designed and prepared several polymers which contained a Si−H bond and another functional group in a molecule.

Recently, we found that poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] [−Si(Ph)H−C≡C−C_6H_4−C≡C−] (abbreviated MSP), which is prepared by the dehydrogenative coupling polymerization reaction between phenylsilane and *m*-diethynylbenzene in the presence of magnesium oxide, has an extremely high thermal stability, which we have briefly previously reported.[1] In this paper we show the details of the preparation and the properties of some poly(silylene-ethynylenephenyleneethynylene)s which have both an Si−H bond and C≡C bond like MSP and refer to the correlation between the structures and the properties of the polymers.

Scheme 1



Scheme 2



In recent years many studies of silicon-containing polymers composed of [−SiR_2−C≡C−] (R = alkyl or phenyl) units have been reported because of their potential applications in areas such as ceramic precursors and conducting materials.[2−8] There are a few reported cases in the literature of a polymer containing the Si−H bond (R = H) in a molecule. Only poly[(phenylsilylene)ethynylene-1,3- phenyleneethynylene] [−Si(Ph)H−C≡C−C_6H_4−C≡C−],[1,2] poly[(phenylsilylene)-diethynylene] [−Si(Ph)H−C≡C−C≡C−],[3] and poly[(methylsilylene)ethynylene] [−Si(CH_3)H−C≡C−][4] have been prepared, but there was almost no information about the properties of the polymers, except for our short report.[1]

Experimental Section

The silicon-containing polymers were prepared by two methods, which are the dehyrogenative polymerization reaction using magnesium oxide as a catalyst (Scheme 1 and the condensation reactions using organic magnesium reagents (Scheme 2).

Preparation of MSP. MSP was prepared according to the same method previously reported by us,[1] except for the reaction

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scale. (The scale was about 2000 times larger than in our previous report.)

Phenylsilane, *m*-diethynylbenzene (DEB), and toluene were distilled and dried over 3A molecular sieves prior to use. A magnesium oxide catalyst (specific surface area was 340 m^2/g) was obtained by calcining magnesium hydroxide in vacuo at 400 °C for 7 h.

To a 150 L volume reaction vessel of stainless steel were added 10.14 kg of magnesium oxide, 4.02 kg (37.1 mmol) of phenylsilane, 4.51 kg (35.8 mmol) of *m*-diethynylbenzene, and 70 L of toluene as a solvent. These reactants were then allowed to react, in a nitrogen atmosphere, at 28 °C for 3 h, at 40 °C for 1 h, at 50 °C for 1 h, at 60 °C for 1 h, and then at 80 °C for 2 h (8 h total). After completion of the reaction, the reaction solution was filtered through a polyester filter to separate and remove the magnesium oxide present. The resulting filtrate was distilled under reduced pressure to remove some of the toluene, and about 16 kg of the condensed polymer solution (concentration of the polymer was ca. 34 wt. %) was dispersed in 206 L of *n*-heptane to cause precipitation. The resulting precipitates were filtered off and dried at 55 °C for 24 h to give 3.28 kg (MSP yield, 40%). The filtrate of *n*-heptane and toluene was distilled at 55 °C for 17 h using an evaporator to give 2.31 kg of a viscous oily product (28% yield).

Preparation of Poly(phenylsilyleneethynylene-1,3-phenyleneethynylene) (≡ Polymer a). An organic magnesium reagent was prepared as follows. Flaky magnesium metal (1.22 g, 50.1 mmol) was introduced into a 300 mL four-necked flask and the atmosphere in the flask was replaced with dry nitrogen gas. THF (20 mL), which had been dried over lithium aluminum hydride and then subjected to simple distillation, was introduced into the flask, a small piece of iodine was added, and the mixture was stirred to activate the magnesium. To the activated magnesium was added dropwise a solution of 4.93 g (45.2 mmol) of ethyl bromide in THF (20 mL) at room temperature over about 20 min, and the mixture was reacted while being refluxed with heating over 2 h to produce ethylmagnesium bromide. To the reaction system was added a solution of 2.71 g (21.5 mmol) of *m*-diethynylbenzene in THF (30 mL) dropwise at room temperature over 20 min with stirring, and the reaction was continued for an additional 1 h while being refluxed with heating to produce the intended organic magnesium reagent (21.5 mmol).

A polymer was then prepared in the following manner. The reaction was performed subsequent to the foregoing preparation of the organic magnesium reagent. A solution of 3.81 g (21.5 mmol) of dichlorophenylsilane in THF (20 mL) was dropwise added to the flask containing the organic magnesium reagent at room temperature over a period of 20 min with stirring. White precipitates of the organic magnesium reagent immediately disappeared before the completion of the dropwise addition, and the solution became almost clear. The reaction system was further reacted for 1 h while being refluxed with heating. The reaction system was then post-treated. More specifically, 2.17 g (20.0 mmol) of trimethylsilyl chloride (Me_3SiCl) was added to the reaction solution. Another 500 mL flask was filled with 300 mL of a 0.5 N aqueous solution of hydrochloric acid and ice-cooled. A dropping funnel was fitted to the 500 mL flask, the reaction solution in the 300 mL flask was transferred to the dropping funnel and the hydrochloric acid aqueous solution was gently stirred while the reaction solution was slowly added dropwise through the dropping funnel (over 30 min). Benzene (50 mL) was then added to the reaction solution and the resulting oil phase was separated using a separatory funnel and dried by adding sodium sulfate and allowed to stand overnight. The solution was filtered through a glass filter to remove the dehydrating agent. The solvent was distilled off from the solution using an evaporator to give a viscous oily crude product. The crude prouct was dissolved in 40 mL of THF and dispersed in methanol to cause precipitation. The resulting precipitates were filtered off and dried to give 3.71 g (75% yield) of the intend polymer.

Preparations of Poly(phenylsilyleneethynylene-1,4-phenyleneethynylene) (≡ Polymer b) and Poly(phenylsilyleneethynylene-1,2-phenyleneethynylene) (≡ Polymer c). The same procedures used for polymer **a** were repeated, except that *p*-diethynylbenzene and *o*-diethynylbenzene were substituted for *m*-diethynylbenzene used for polymer **a** to give polymer **b** (78% yield) and polymer **c** (41% yield), respectively.

Preparation of Poly(methylsilyleneethynylene-1,3-phenyleneethynylene) (≡ Polymer d) and Poly(silyleneethynylene-1,3-phenyleneethynylene) (≡ Polymer e). The same procedures used for polymer **a** were repeated, except that about 20 mmol of dichloromethylsilane and dichlorosilane were substituted for dichlorophenylsilane used for polymer **a** to give polymer **d** (64% yield) and polymer **e** (34% yield), respectively.

All of the polymers were pale yellow solids. Their infrared (IR), ^1H NMR, ^{13}C NMR, and ^{29}Si NMR spectra were employed to determine the structures of the polymers. Molecular weights were obtained by gel permeation chromatography (GPC) with retention times calibrated against polystylene samples. Thermogravimetric analysis (TGA), differential thermal analysis (DTA), and differential scanning calorimetry (DSC) measurements under argon and air were used to study the thermal properties of the polymers.

Results

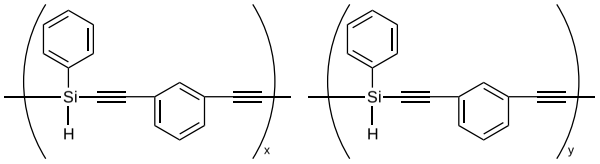
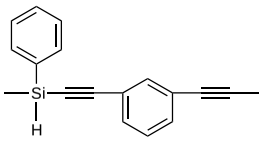
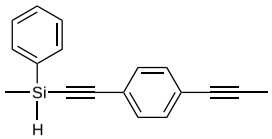
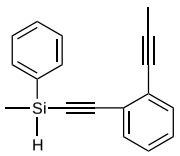
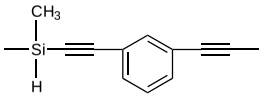
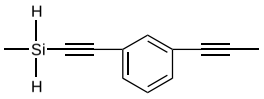
Molecular weights, IR and NMR spectral data, and some thermal properties of the poly(silyleneethynylenephenyleneethynylene)s are shown in Table 1.

MSP. In the ^{29}Si NMR spectrum of MSP, the signal assigned to the tertiary silicon ((CDCl$_3$/TMS) δ −69.3 ppm (Ph)Si═) was observed in addition to the secondary silicon (−63.5 ppm (Ph)SiH−),[1] which indicates that the main structure of MSP is poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] [−Si(Ph)H−C≡C−C_6H_4−C≡C−], with some branches also existing. The ratio of branched silicon was constant at ca. 10% for all reaction conditions. The end structure of the polymer was −Si(Ph)H_2 or −C≡CH; the ratio of −Si(Ph)H_2 to −C≡CH was nearly 1.

The polymer which had a molecular weight (M_w) above 2000 was a pale yellow and amorphous solid, and that with a M_w under 2000 was a viscous yellow liquid. The GPC curve of MSP is shown in Figure 1. The solid polymer was highly soluble in benzene, toluene, THF, and NMP. The glass transition temperature (T_g, determined by the DSC) of the polymer (M_w = 5000−6000) was about 50 °C. The polymer was fusible and moldable, and it was possible to melt-spin the polymer at 100−150 °C. The polymer gradually changed to black and cured above 200 °C. (The curing temperature was ca. 150−210 °C. The melt viscoelasticity and complex elastic modulus of MSP measured using a dynamic mechanical spectrometer (Rheometrix Inc. RDS-II) are shown in Figure 2).

From the TGA−DTA curves of MSP, which were previously reported by us, there was very little weight loss during thermal cracking under argon. The T_{d_5} (temperature of 5% weight loss) was 860 °C and the residue at 1000 °C was 94%. These values are much higher than those of the polyimide (Kapton, DuPont; T_{d_5} was 586 °C and the residue at 1000 °C was 55%). The dynamic modulus measured using a DMS (Seiko Instruments Inc.) under air is shown in Figure 3. The storage bending modulus of MSP cured at above 300 °C decreased within 20% even at 500 °C. These facts indicate that MSP has a high thermal stability and is heat resistant. An exothermic peak at 210 °C was observed in the DTA curve which would be caused by a cross-linking reaction (curing reaction), as will be mentioned in the following discussion.

Table 1. Spectral Data and Thermal Properties of Poly(silyleneethynylenephenyleneethynylene)s

polymer structure	molecular weight M_w, M_n [M_w/M_n]	spectral data				thermal properties[a]			
		IR (neat) cm^{-1}	^{1}H-NMR ($CDCl_3$/TMS)	^{13}C-NMR ($CDCl_3$/TMS)	^{29}Si-NMR ($CDCl_3$/TMS)	T_g (°C)	T_{d_5} (°C) in argon	residue (%) at 1000 °C in argon	T_{d_5} (°C) in air
MSP 	4700 2300 [2.0]	ν(Si−H, C≡C) 2159 δ(Si−H) 800	δ 3.07 (s, C≡CH) 4.71 (s, (Ph) SiH_2) 5.11 (s, (Ph)SiH) 7.3−7.9 (m, PhH)	δ 78.2, 82.4 (C≡CH) 86.6 (C≡C−C_6H_4−) 107.2 (C≡C−C_6H_4−) 123−136 (Ph)	δ −59.7 ((Ph)SiH_2) −63.5 ((Ph)SiH) −69.3 ((Ph)Si≡)	48	860	94	567
polymer **a** 	7900 3900 [2.0]	ν(Si−H, C≡C) 2158 δ(Si−H) 812	δ 5.11 (s, (Ph)SiH) 7.3−7.9 (m, PhH)	δ 86.6 (C≡C−C_6H_4−) 107.2 (C≡C−C_6H_4−) 123−136 (Ph)	δ −63.5 ((Ph)SiH)	85	894	94	573
polymer **b** 	26000 5400 [4.8]	ν(Si−H, C≡C) 2163 δ(Si−H) 822	δ 5.12 (s, (Ph)SiH) 7.5−7.8 (m, PhH)	δ 88.0 (C≡C−C_6H_4−) 107.7 (C≡C−C_6H_4−) 123−135 (Ph)	δ −63.5 ((Ph)SiH)	ND[b]	577	92 (at 650 °C)	476
polymer **c** 	3200 1700 [1.9]	ν(Si−H, C≡C) 2170 δ(Si−H) 820	δ 5.15 (s, (Ph)SiH) 7.2−7.8 (m, PhH)	δ 90.4 (C≡C−C_6H_4−) 106.3 (C≡C−C_6H_4−) 125−135 (Ph)	δ −62.9 ((Ph)SiH)	71	561	88	567
polymer **d** 	15700 7800 [2.0]	ν(Si−H, C≡C) 2159 δ(Si−H) 839	δ 0.53 (d, CH_3) 4.6 (q, SiH) 7.3−7.7 (m, PhH)	δ −2.7 (CH_3) 88.1 (C≡C−C_6H_4−) 105.9 (C≡C−C_6H_4−) 123−136 (Ph)	δ −60.6 ((CH_3)SiH)	72	850	94	546
polymer **e** 	9800 3100 [3.2]	ν(Si−H, C≡C) 2160 δ(Si−H) 850	δ 4.6 (s, SiH_2) 7.3−7.7 (m, PhH) 123−136 (Ph)	δ 83.8 (C≡C−C_6H_4−) 107.0 (C≡C−C_6H_4−)	δ −83.9 (SiH_2)	72	>1000	97	572

[a] All polymers were yellow powders and soluble in solvents, and they were fusible, except for polymer **b**. [b] A peak assigned to T_g was not detected.

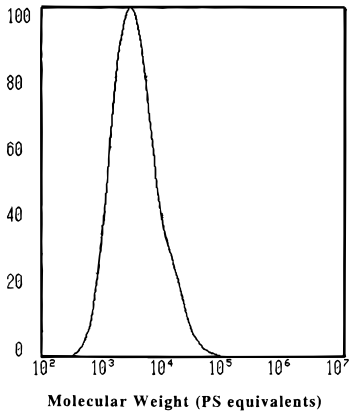


Figure 1. GPC curve of MSP.

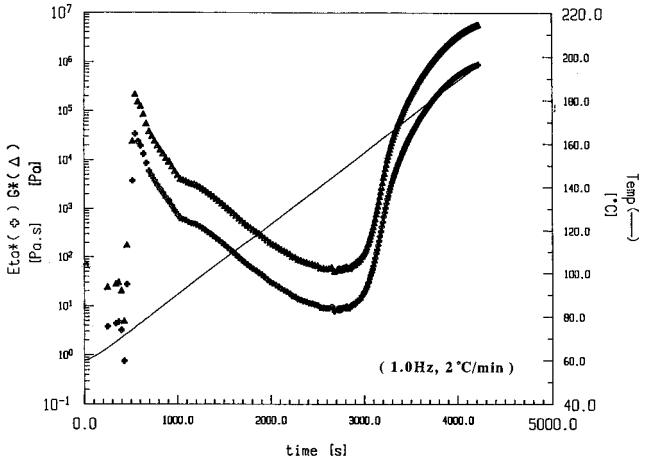


Figure 2. The melt viscoelasticity (Eta*) and complex elastic modulus (G^*) of MSP.

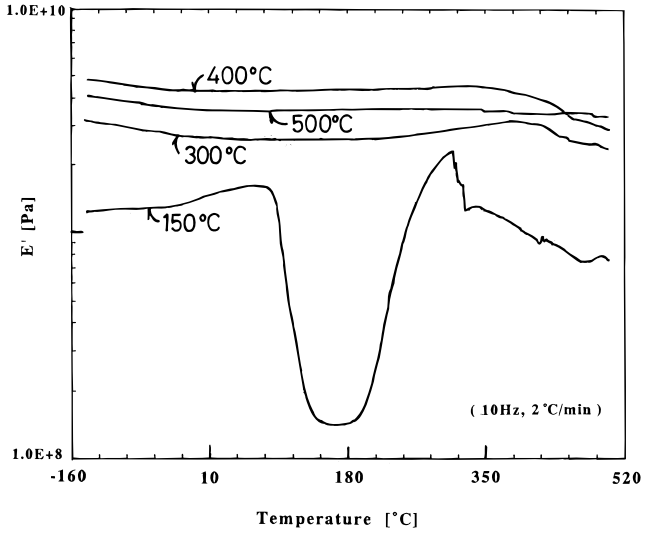


Figure 3. The dynamic modulus of MSP.

The T_{d_5} (567 °C) of MSP under air was nearly equal to that of the polyimide, and the limiting oxygen indices (LOI, minimum oxygen concentration for the polymer to continue combustion) of MSP cured at 400 and 500 °C were 40−42, and 54, respectively (LOI of the polyimide is 53). MSP is quite noncombustible in air. In the fire from a gas burner, the molded MSP test piece turned red but did not burn and had no smoke. When the flame was removed, the test piece recovered its original black surface.

The change in densities are shown in Figure 4. The

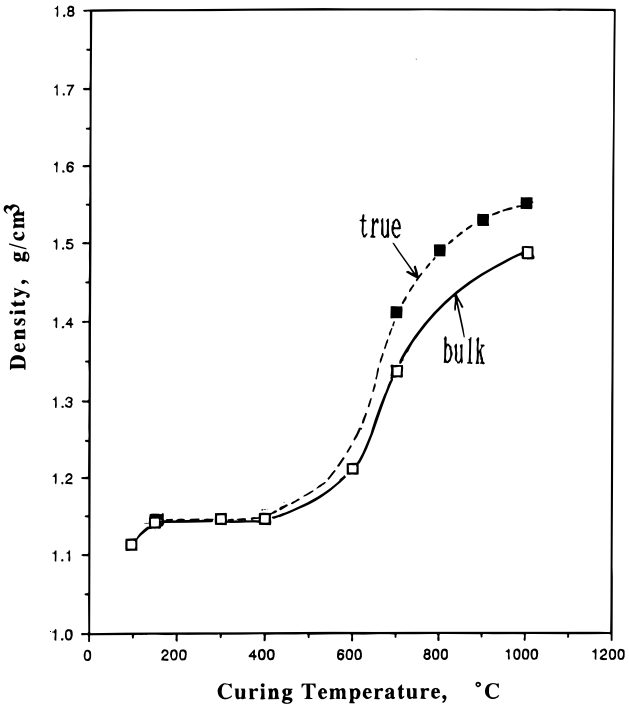


Figure 4. The density change of MSP.

Table 2. Properties of MSP[a]

T_{d_5}	860 °C (in argon)	567 °C (in air)
oxygene index	40−42 (a)	46 (b)
water absorbability (a)	1.0%	
flexural modulus (a)	5.5 GPa	
bending strencth (a)	10 MPa	
coefficient of linear thermal expansion (a)	2.0×10^{-5}/°C	
volume specific resistance (a)	3×10^{16} cm	
specific dielectric constant (a)	3.77	
dielectric dissipation factor (a)	0.002	

[a] Samples were heated at 400 °C for 2 h (a) under argon or (b) under air.

value was 1.14 and constant in the range of 150−500 °C. No change in size of the molded test piece was observed at this temperature. The thermal, combustible, dynamic, and electric properties are summarized in Table 2. The solid MSP was a hard and fragile insulator.

MSP has an extremely high ceramics yield (94%), as shown above. The specific gravity gradually increased at above 500 °C and the value at 1000 °C was about 1.5, which is nearly equal to that of glassy carbon prepared from an organic compound such as phenol resin. The specific gravity, specific surface area, pore volume, and average pore size of MSP heated at 2000 °C were 0.3 m^2/g, 2×10^{-3} mL/g, and 25 nm, respectively. The materials obtained by heating MSP at 1000 or 2000 °C under argon are glassy and hard. A block of MSP pretreated at 400 °C contracted by ca. 10% in every dimension when heated at 1000 and 2000 °C. X-ray diffraction patterns and Raman spectra of the materials heated at 800 °C, 1000 °C and 2000 °C are shown in Figures 5 and 6, respectively. The material was composed of carbon and silicon carbide (SiC 17−18%), and a strong absorption band at 1360 cm^{-1}, which is assigned to the noncrystal part of graphite, was observed other than that at 1580 cm^{-1}, assigned to the crystal graphite.

The structures of MSP cured at several temperatures under argon were studied in order to elucidate the

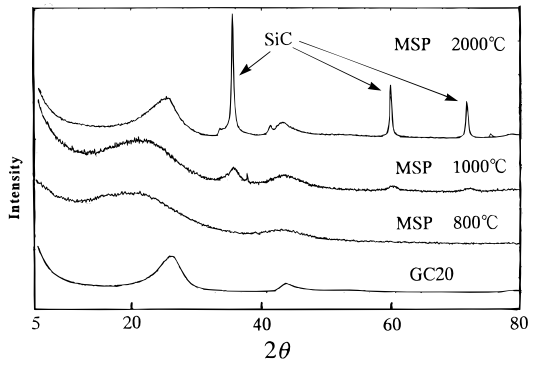


Figure 5. X-ray diffraction patterns of the materials obtained by heating MSP at high temperature. [GC20: Glassy carbon of Tokai Carbon Co., Ltd.]

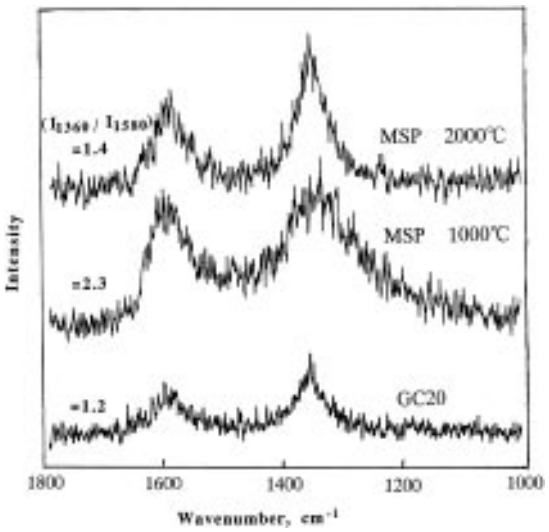


Figure 6. Raman spectra of the materials obtained by heating MSP at high temperature.

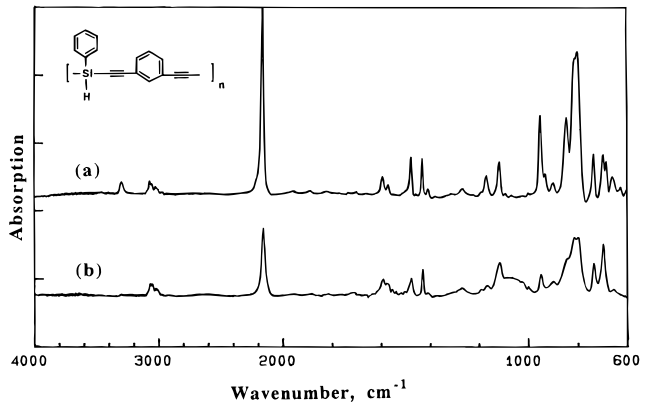


Figure 7. IR spectra of MSP. (a) [−Si(Ph)H−C≡C−C_6H_4−C≡C−], (b) [−Si(Ph)D−C≡C−C_6H_4−C≡C−]

generation mechanism of the thermal stability. IR spectra and the changes in the IR absorption bands characteristic of some chemical bonds are shown in Figures 7 and 8, respectively. In this study, we used the polymer [−Si(Ph)D−C≡C−C_6H_4−C≡C−] which was synthesized from phenylsilane ($PhSiD_3$) and 1,3-diethynylbenzene, because the two IR absorption bands characteristic of the Si−H and C≡C bonds are at the same position (2160 cm^{-1}). The ^{29}Si- and ^{13}C-NMR spectra are shown in Figures 9 and 10, respectively. All bands in the IR spectrum and all signals in the NMR spectra gradually decreased with the pretreatment temperature.

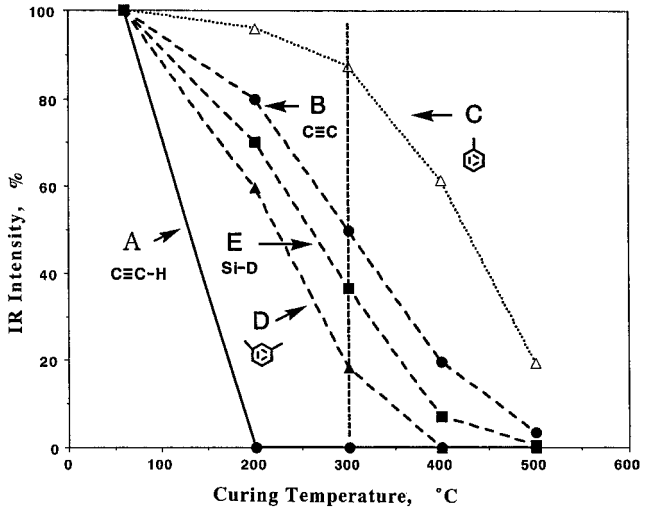


Figure 8. The changes in the IR adsorption bands characteristic of some chemical bonds of MSP [−Si(Ph)D−C≡C−C_6H_4−C≡C−].

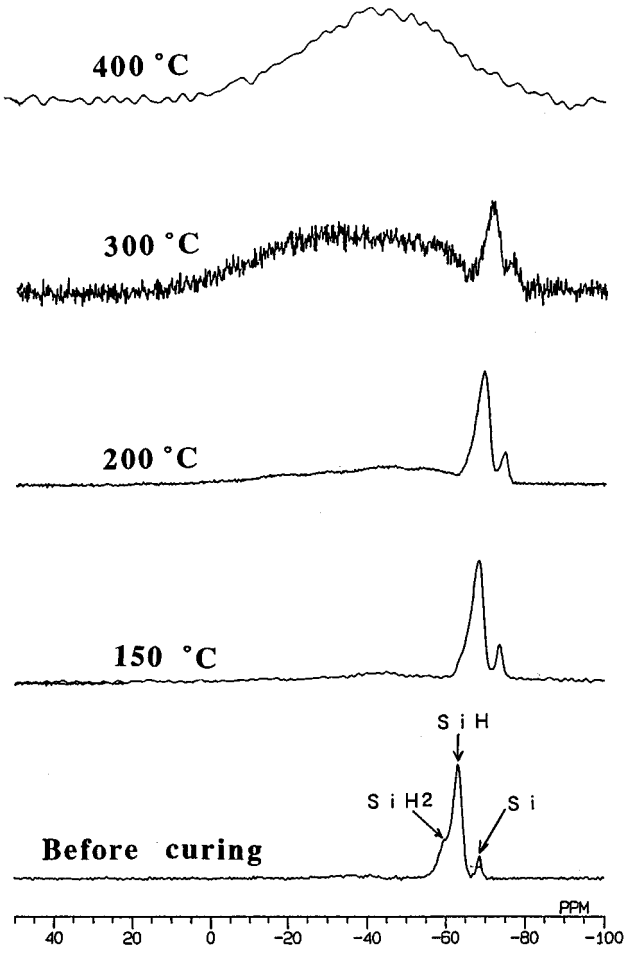


Figure 9. ^{29}Si-NMR spectrum of MSP cured at various temperatures.

Other Poly(silyleneethynylenephenyleneethynylene)s (≡Polymers a−e). The spectral data and some characteristics of the three structural isomers (polymers **a**−**c**) of the polymer [−Si(Ph)H−C≡C−C_6H_4−C≡C−] and two polymers which have methyl group [−Si(CH_3)H−C≡C−C_6H_4−C≡C−] (polymer **d**) or a hydrogen atom [−SiH_2−C≡C−C_6H_4−C≡C−] (polymer **e**) instead of the phenyl group of polymer **a**, which were prepared using organic magnesium reagents, are shown in Table 1. The molecular structure of polymer **a** is

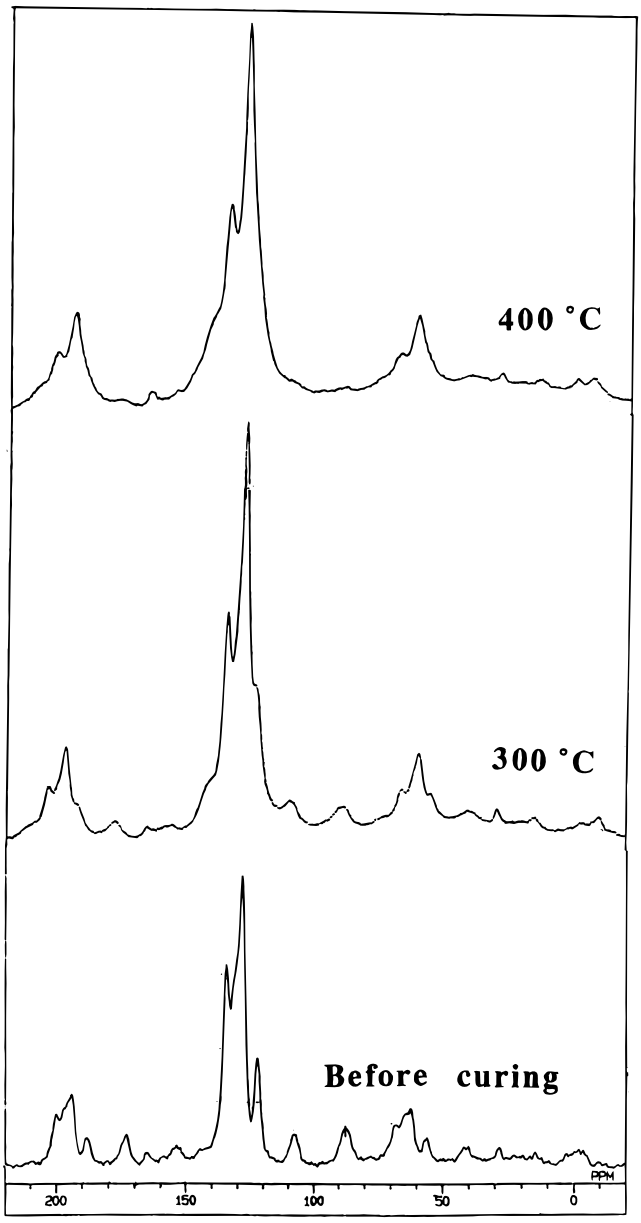


Figure 10. ^{13}C-NMR spectrum of MSP cured at various temperatures.

slightly different from MSP. Polymer **a** had no branches, had a high molecular weight, and the end structure of the polymer was $-Si(CH_3)_3$, which was formed by treatment with trimethylchlorosilane after the polymerization reaction.

The thermal properties of the polymers were studied by TGA−DSC (see Table 1 and Figure 11). Polymer **a** (meta-isomer as MSP) was as stable as MSP, but the other two isomers (polymers **b** and **c**) were less stable than MSP. The para-isomer (polymer **b**) was as amorphous as MSP, but not moldable. Polymer **d** was as stable as MSP. Polymer **e** was more stable than MSP.

Discussion

In general, transition metal complexes have effectively been used as catalysts for many reactions concerning organometallic compounds. But such homogeneous catalysts are expensive and difficult to separate from the reaction system. In the dehydrogenative coupling polymerization reaction using a magnesium oxide catalyst, the catalyst can be easily separated by

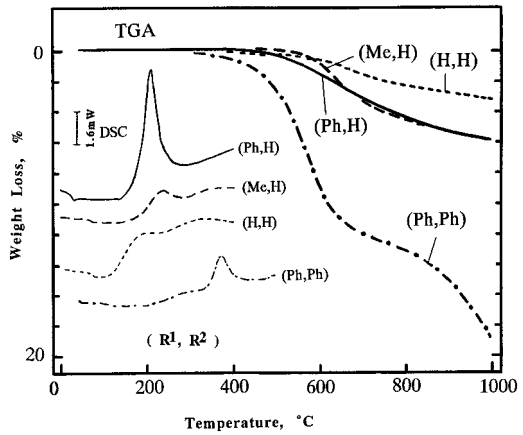


Figure 11. TGA−DSC traces of poly(silileneethynylene-phenyleneethynylene)s $[-SiR^1R^2-C\equiv C-C_6H_4-C\equiv C-]$.

filtration after the reaction. Only less than 10 ppm of the magnesium oxide was found in MSP. A very pure and stable polymer can be obtained and there is no problem in keeping the polymer under air for long periods.

The T_{d_5}s (860 °C) of MSP and polymer **a** are much higher than that of the polyimide (Kapton, DuPont), which indicates the high thermal stability of the polymers. On the other hand, the T_{d_5} under air is equal to that of the polyimide. A further increase in thermal stability under air could be developed by some modifications of the polymers. As there was almost no difference in the TGA−DTA curves between MSP prepared by the dehydrogenative polymerization reaction and polymer **a** prepared by using the organic magnesium oxide catalyst, the cross-linking reactions and the thermal stabilities are not affected by the chain branching and the end structures of the polymers.

As shown in our previous report,[1] the T_{d_5} of poly[(phenylsilylene) ethynylene-1,3-phenyleneethynylene] $[-Si(Ph)H-C\equiv C-C_6H_4-C\equiv C-]$ (MSP and polymer **a**) under argon is much higher than those of poly[(diphenylsilylene)ethynylene-1,3-phenyleneethynylene] $[-Si(Ph)_2-C\equiv C-C_6H_4-C\equiv C-]$ (T_{d_5} 547 °C), which has no Si−H bond, and poly(methylsilylene-1,4-phenylene) $[-Si(CH_3)H-C_6H_4-]$ (T_{d_5} 320 °C)[9] and poly(silylene-1,3-phenylene) $[-SiH_2-C_6H_4-]$ (T_{d_5} 355 °C),[10] which have no C≡C bond. The polymer $[-Si(Ph)H-C\equiv C-C_6H_4-C\equiv C-]$ had an exothermic peak at 210 °C in the DTA curve. The infrared absorption bands characteristic of the Si−H and C≡C bonds of MSP were reduced to half the initial absorption band when the polymer was treated at 240 °C for 2 h, as shown in Figure 8. These facts suggest that an addition cross-linking reaction involving the Si−H and C≡C bonds might have occurred to form a highly thermally stable structure, especially at about 210 °C. The infrared adsorption bands characteristic of a C=C bond and C−C bond, which would be formed by additional cross-linking reactions between the Si−H and C≡C bonds, were not observed, but some new signals assigned to a C=C bond (about 140 ppm) were observed in the ^{13}C-NMR spectra. The cured structure would be formed by the hydrosilylation reaction between the Si−H bond and the C≡C bond, as shown in the Scheme 3.

All peaks of the infrared and ^{29}Si- and ^{13}C-NMR spectra decreased with the curing temperature and disappeared in the range of 500−600 °C. When MSP was cured at above 500 °C under argon, small amounts of hydrogen and benzene were generated by the thermal

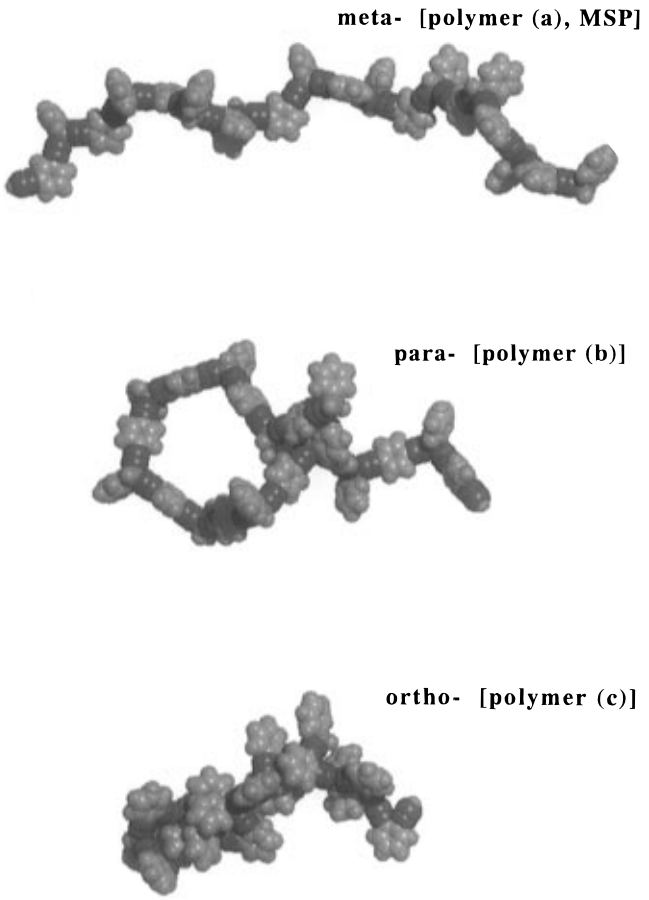
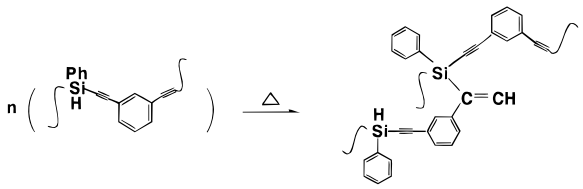


Figure 12. Polymer conformation of three isomers of poly-[(phenylsilylene)ethynylenephenyleneethynylene]s.

Scheme 3



decomposition. This suggests that the chemical bonds of MSP would be rearranged and MSP would gradually change to an inorganic compound (C−SiC) above 500 °C. These changes in spectra correspond with that of the densities shown in Figure 4. Further study will be needed to clarify the mechanisms of the cross-linking reaction and the carbonization reaction.

The polymer conformations of three isomers of poly-[(phenylsilyllene)ethynylene phenyleneethynylene]s, which were optimized using molecular mechanics, are shown in Figure 12. The ortho- and para-isomers have a lumpy shape, so these two isomers would be difficult to intermolecularly cross-link. On the other hand, the meta-isomer is linear, so the isomer would be easy to intermolecularly cross-link. Only meta-isomer (MSP and polymer **a**) can be increased in cross-linking density and form the most thermally stable structure by the curing reaction.

A black, hard, and glassy material was obtained (specific gravity about 1.5) when MSP was heated at 1000 or 2000 °C under argon. Free carbon and SiC were found upon analysis. In the Raman spectrum, two bands were observed and the values of I_{1360}/I_{1580}, which indicate the ratio between the noncrystal part and crystal part, were 2.3 (1000 °C) and 1.4 (2000 °C),

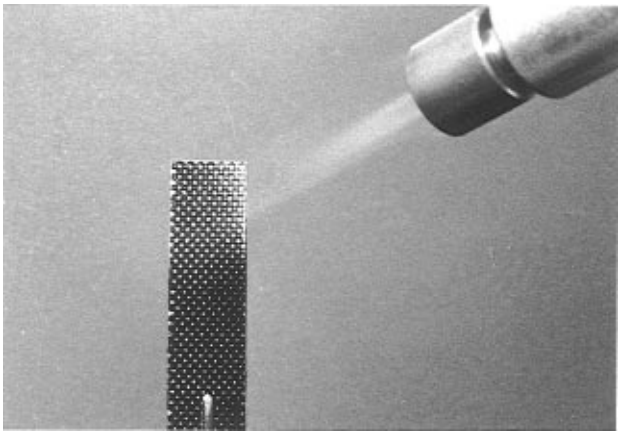


Figure 13. Combustion test of the carbon fiber reinforced MSP (Noncombustible and smokeless).

respectively. These values are larger than those of graphites prepared from an organic compound such as phenol resin (I_{1360}/I_{1580} = 0.2−1.5). A material of a peculiar structure, which is difficult to change into a crystal graphite, would be formed from MSP. MSP gives a ceramic (C−SiC), so a light and nonflamable material which consists of a ceramic on the surface and an organic polymer on the inner part could be prepared. Moreover, a very highly pure ceramic (C−SiC) could be prepared from the pure MSP. Many fine and functional C−SiC materials, such as fiber, film, and others, could be synthesized.[11] More details of the properties of the ceramics (C−SiC) will soon be reported.[12]

Many kinds of polyimides as the matrix resin for fiber-reinforced plastics (FRP) have been developed, and they are generally soluble in only a polar solvent of high boiling point, such as NMP, DMSO, and DMF. In the case of the polyimides of the condensation type, the polyamic acids are used as precursors for molding and cured for a long time at high temperature (usually 300−400 °C) accompanied by the generation of water. Therefore, it takes a long time to make FRP. As mentioned above, MSP is highly heat-resistant and nonflammable and has a reactive Si−H bond which would be able to make bonds with many reinforcing materials. Moreover, MSP is moldable, soluble in many solvents of low boiling point, and can be cured at low temperature with no generation of byproduct. When we use an oily oligomer, no solvent is needed in preparing the reinforced material. These characteristics are more advantageous than those of the polyimide in preparing the reinforced materials.

Three kinds of FRP were made using the SiC fiber, carbon fiber, and glass fiber. Prepregs were prepared by the molding or impregnation method and were pressed for 12 h at 150 °C at a pressure of 9.8×10^5 Pa to produce FRP. Bending strengths and modules at room temperature and 200 and 400 °C were almost equal, which suggests that the FRP prepared using MSP as a matrix resin could be used even at 400 °C, though further study of the mechanical properties at high temperature will be needed (polyimide of the addition type can be used under 300 °C). The FRP turned red but did not burn or smoke in the fire of a gas burner (Figure 13). When the burner was removed, the red FRP turned back to the original FRP.

MSP can be synthesized using the reactivity of the Si−H bond, and the excellent properties of MSP are determined by the Si−H bond. We propose a new highly heat-resistant polymer. We are now preparing MSP on

a large scale and many characteristics of MSP are being studied. Many challenges to make new functional materials using MSP are being examined. Moreover, the fact that poly(silyleneethynylenephenyleneethynylene)s have certain properties would be applied to many of the present polymers, that is, new polymers which have the Si(H)−C≡C unit could be designed. Further systematic studies would be required to clarify the features of the silicon-containing polymers which have the Si(H)−C≡C unit.

Summary

A series of silicon-containing polymers which have the Si(H)−C≡C unit in the molecule were studied. Six kinds of poly(silyleneethynylenephenyleneethynylene)s [−Si(R)H−C≡C−C_6H_4−C≡C−], wherein the phenylene group was the meta-, para-, or ortho-form and R represents a phenyl, methyl, or hydrogen atom, were prepared by two methods: (1) the dehydrogenative polymerization reaction between trihydrosilane ($RSiH_3$) and diethynylbenzene using magnesium oxide as a catalyst and (2) the condensation reactions using dichlorosilane ($RSiHCl_2$) and organic magnesium reagents.

Poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] (R = Ph), which was thermoset (curing temperature ca.150−210 °C), soluble in solvent, fusible, and moldable at 100−150 °C, showed high heat- and burning-resistant properties. The T_{d_5} (temperature of 5% weight loss) was 860 °C and the residue at 1000 °C was 94%. The melt viscoelasticity and dynamic modulus were measured. Poly(silyleneethynylene-1,3-phenyleneethynylene) (R = H) (T_{d_5} > 1000 °C) was more stable, while poly [(methylsilylene)ethynylene-1,3-phenyleneethynylene] (R = CH_3) (T_{d_5} 850 °C) was as stable as poly-[(phenylsilylene)ethynylene-1,3-phenyleneethynylene]. The two isomers of poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene], that is, the para-isomer (T_{d_5} 577 °C) and ortho-isomer (T_{d_5} 561 °C), were less stable. A cross-linking reaction mechanism concerning the Si−H and C≡C was proposed, and the correlation between the molecular structures and the thermal properties was discussed. From the polymer conformations, it was suggested that only the meta-isomer would be increased in cross-linking density and form the most thermally stable structure.

Fiber-reinforced plastics prepared using a glass, carbon, or SiC fiber showed sufficient mechanical strength even at 400 °C under air. A black, hard, and glassy material (C−SiC) was obtained when poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] was heated at above 1000 °C under argon.

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