Structural Study of Silyl−Carborane Hybrid Diethynylbenzene−Silylene Polymers by High-Resolution Solid-State ^{11}B, ^{13}C, and ^{29}Si NMR Spectroscopy

Hideaki Kimura,[†,§,||] Koichi Okita,[†] Motokuni Ichitani,[‡] Toshiya Sugimoto,[‡]
Shigeki Kuroki,[§] and Isao Ando*[,§]

Advanced Materials Laboratory, Japan Chemical Innovation Institute, 2-1-6 Sengen, Tsukuba, Ibaraki 305-0047, Japan, Minase Research Institute, Sekisui Chemical Co., Ltd., 2-1 Hyakuyama, Shimamoto-cho, Mishima-gun, Osaka 618-8589, Japan, and Department of Chemistry and Materials Science, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan

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The structure of silyl-carborane (1,7-$C_2B_{10}H_{10}$) hybrid diethynylbenzene-silylene polymers with thermal treatment over a wide range of temperatures has been characterized by using ^{11}B MQ-MAS NMR, and ^{13}C and ^{29}Si CP-MAS NMR methods. From the experimental results, the following was found: (1) naphthalene rings form by diene reaction between the Ph−C≡C group and C≡C group at temperatures from 250 to 500 °C; (2) three-dimensional network forms by addition reaction between the vinyl group and C≡C group at curing temperatures from 250 to 350 °C and addition reaction between *m*-carborane group and the vinyl group and/or the C≡C group at curing temperatures from 250 to 350 °C; (3) the hybrid polymers are decomposed by oxidation at curing temperature of 500 °C; and (4) structural change of the *m*-carborane hybrid polymer leads to desirable modification of the oxygen index, heat deflection temperature, and flexural strength.

1. Introduction

Icosahedral carboranes such as 1,2-, 1,7-, and 1,12-$C_2B_{10}H_{12}$ have remarkable thermal stability, resistance to attack by acids, and inactivity toward biological systems.[1−3] Particular attention has been paid to development of carborane-containing polymers with high thermal stability.[1,4] On the other hand, silicon-based polymers have thermal durability, mechanical toughness, easy processing, and low weight.[5−9] The polymers form a three-dimensional network structure by thermal hardening reaction, and then the thermally cured polymers are superior in their thermal stability, solvent resistance, form stability, and stiffness before thermal curing. New polymers containing both carboranes and silicons are anticipated. Some studies have been done to improve the thermal properties of polysiloxanes by combining them with *m*-carborane (1,7-carba-*closo*-dodecaborane).[10−12] Keller et al. have reported that a diacetylene−carborane−siloxane system that has very high stability compared to other silicon polymers.[13−16] Further, development of thermally stable and mechanically excellent carborane hybrid organosilicon polymers is sought.

In our previous paper,[17] we have reported that silyl−carborane hybrid diethynylbenzene−silylene polymer

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* Corresponding author. Tel: (+81)-3-5734-2139. Fax: (+81)-3-5734-2889. E-mail: iando@polymer.titech.ac.jp.

[†] Japan Chemical Innovation Institute.

[‡] Sekisui Chemical Co., Ltd.

[§] Tokyo Institute of Technology.

[||] Present address: Department of Chemistry and Materials Science, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro-ku, Tokyo 152-8552, Japan.

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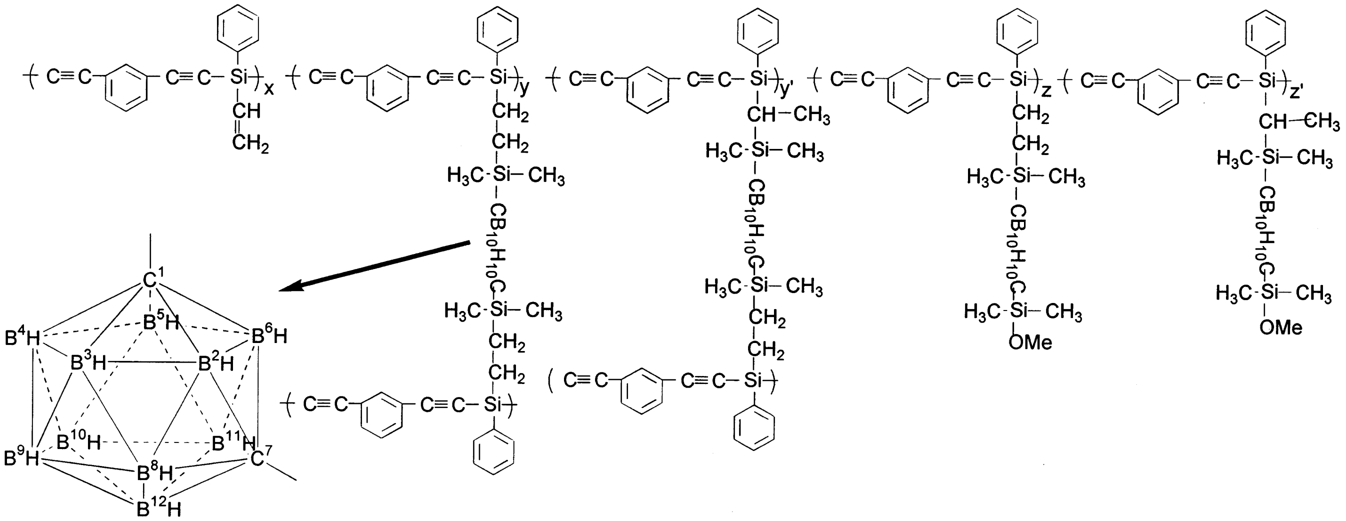

Figure 1. Chemical structure of silyl−carborane hybrid diethynylbenzene−silylene polymer considered in this work.

has very high thermal durability. The polymer contains the Si and C≡C group in the main chain, and the 1,7-dicarba-*closo*-dodecarborane group and the vinyl group in side chains. The fraction ratio of the silicon to the *m*-carborane group in the polymer can be controlled without changing the chemical structure of the main chain. The polymer exceeds other polymers in heat-resistance under air. The 5% weight loss temperature (Td_5) of the polymer cured at 350 °C under air is over 1000 °C as shown by thermogravimetric analysis (TGA). The oxygen concentration to burn the polymer cured at 350 °C (the oxygen index) is over 40%. We think that the polymer is heat-resistant enough to use as aerospace and construction materials. It is thought that very high thermal resistance of the polymer comes from cross-linked and oxidized carboranes generated by thermal curing. However, the relationship between the structure and curing temperature of carborane hybrid polymers is not yet clear.

It is supposed that there are some factors for improvement of mechanical toughness and nonflammability. First, structural analysis of the polymer is needed. The cross-linked structures of thermosetting resins can be characterized by the solid-state NMR method[18] because the polymers are insoluble and amorphous after curing.[19−22] The silyl−carborane hybrid diethynylbenzene−silylene polymer has four kinds of NMR-observable nuclei such as ^{1}H, ^{11}B, ^{13}C, and ^{29}Si. Multinuclear NMR study of polymers is very important for structural analysis of these materials because the NMR observations of individual nuclei lead to unique and different information about structures of the polymers studied here.

From such a background, we aim to characterize cross-linked silyl−carborane hybrid diethynylbenzene−silylene polymers by means of high-resolution solid-state ^{11}B, ^{13}C, and ^{29}Si NMR spectroscopy.

Table 1. Characteristics of Silyl−Carborane Hybrid Diethynylbenzene−Silylene Polymers

sample	curing condition	OI[a]	HDT[b] (°C)	FM[c] (GPa)
A-1	as received			
A-2	A-1 was molded and pressed at 250 °C[d]	34	132	2.28
A-4	A-2 was thermally cured at 350 °C[e]	40	>380[f]	2.66
A-500	A-2 was thermally cured at 500 °C[g]	>50	>380[f]	-[h]

[a] OI, the oxygen index. [b] HDT, heat deflection temperature. [c] FM, flexural modulus. [d] Molded for 6 min and pressed at 1795 kg/cm^2 under vacuity for 30 s. [e] Cured for 1 h. [f] More than 380 °C. [g] Cured for 30 min. [h] Too brittle.

2. Experimental Section

2.1. Materials. Silyl−carborane hybrid diethynylbenzene−silylene polymers are prepared by a hydrosilylation reaction between diethynylbenzene−silylene polymer with the reactive vinyl side group and the 1,7-bis(dimethylsilyl)carborane group in toluene as solvent (Figure 1).[17] Weight-average molecular weight of the polymer is determined to be 22 400 by using JASCO 802-SC gel permeation chromatography (GPC). The samples cured at 350 and 500 °C are molded at 250 °C for 6 min and pressed at 1795 kg/cm^2 under vacuum for 30 s. The curing condition and mechanical characteristics of these samples are summarized in Table 1, for which the flexural modulus is determined by use of a Shimazu Autograph AG-5000B.

2.2. Solid-State NMR Measurements. All of the NMR measurements are carried out by a Bruker Avance DSX-300 NMR spectrometer at 7.05 T at room temperature. The spectrometer is equipped with a 4-mm magic angle spinning (MAS) probehead capable of producing an MAS speed of 15 kHz. The molded samples are cut into small pieces to insert the polymer sample into an NMR rotor.

2.2.1. ^{13}C and ^{29}Si Cross Polarization (CP)-MAS NMR Measurements. The observation frequencies of ^{13}C and ^{29}Si nuclei are 75.6 and 59.6 MHz, respectively. The contact time is 4 ms for ^{13}C and 8 ms for ^{29}Si. The $\pi/2$ pulse width is 2.8 μs for both ^{13}C and ^{1}H and for both ^{29}Si and ^{1}H under CP conditions. Spectral width is 30 kHz (for ^{13}C) and 36 kHz (for ^{29}Si), and data points are 1 or 2 k. Two-pulse phase modulation (tppm) is used for ^{1}H decoupling. The MAS speed is set to 7 kHz for ^{13}C and 5 kHz for ^{29}Si. The recycle delay time is 5−8 s. The dipolar dephasing delay time is 60 μs for the ^{13}C dipolar

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dephased CP experiment. The ^{13}C chemical shifts are calibrated by using adamantane ($\delta = 29.5$ ppm) as an external standard relative to tetramethylsilane[$(CH_3)_4Si$] ($\delta = 0$ ppm). The ^{29}Si chemical shifts are calibrated by external poly(dimethylsilane) ($\delta = -33.8$ ppm) relative to tetramethylsilane.

2.2.2. ^{11}B MQ-MAS NMR with ^{1}H Dipolar Decoupling Measurements. Two-dimensional (2D) NMR experiments capable of averaging out the second-order quadrupolar interaction of half-integer spins are carried out by the multiquantum (MQ)-MAS method.[23−27] The observation frequency of ^{11}B nucleus (spin number $I = {}^{3}/_{2}$ and isotope natural abundance = 80.42%) is 96.3 MHz. The NMR rotor is spun at 12 kHz. Excitation of both the echo (−3Q) and anti-echo (+3Q) coherences is achieved by using a three-pulse sequence with zero quantum filter (z-filter). The widths of the first, second, and third pulses are 3.0−4.1 μs, 1.1−1.6 μs, and 19−28 μs, respectively. The z-filter is 20 μs. The recycle delay time is 6−15 s. The data point of the F1 (vertical) axis is 64 and for one of each the number of scans is 144. The total measurement time is 15−38 h. The phase cycling used in this experiment consists of 12 phases. Boron phosphate (BPO_4; $\delta = 0$ ppm) is used as an external standard for ^{11}B. The chemical shift value of BPO_4 is −3.60 ppm from $BF_3{\cdot}O(C_2H_5)_2$ which is used as standard reference in ^{11}B NMR in the liquid state. The transmitter frequency of ^{11}B is set on peak of BPO_4 for the trustworthy chemical shift after Fourier transform.[28, 29]

2.3. XPS Measurements. X-ray photoelectron spectra are obtained on a Kratos AXIS-165 equipped with a Mg anode X-ray source, hermi-spherical analyzer, and a multichannel detector. The operating pressure is approximately 1.6×10^{-10} Torr. Boron 1s core level spectra with valence bands are recorded in the fixed analyzer transmission (FAT) mode in the 180−200 eV range.

3. Results and Discussion

3.1. ^{29}Si CP-MAS NMR Spectral Analysis and Structural Characterization. Figure 2 shows 59.6 MHz ^{29}Si CP-MAS NMR spectra of silyl−carborane hybrid diethynylbenzene−silylene polymers ((a) polymer A-1 (before curing), (b) polymer A-2 (molded and pressed at 250 °C), (c) polymer A-4 (cured at 350 °C after molded and pressed at 250 °C), and (d) polymer A-500 (cured at 500 °C after molded and pressed at 250 °C)). The spectrum of polymer A-1 before curing has very resolved and narrow peaks, but the spectrum becomes very broad with an increase in curing temperature. From these experimental results, it is found that thermal curing leads to structural change. In ^{29}Si CP-MAS NMR spectrum 2(a) of polymer A-1, 6 highly resolved peaks with different chemical shifts appear. The six peaks are numbered from downfield by 1, 2, 3, 4, 5, and 6, respectively. The widths of peaks 1, 2, 3, and 6 are relatively narrow, and those of peaks 4 and 5 are broad. The peak assignment is made as follows. Peak 6 at −49.8 ppm in spectrum 2(a) can be assigned to the main chain $-Si(Ph)(CH{=}CH_2)-$ silicon according to our previous study,[21] and peaks 4 and 5 at −23.2 and −39.2 ppm are assigned to the $-Si(Ph)(CH(CH_3)-)-$ and $-Si(Ph)(CH_2-)-$ silicons of the main chain, respectively. Peaks 3, 2, and 1 at −12.5, − 2.2, and 8.1 ppm can be assigned to the $-CB_{10}H_{10}C-Si(CH_3)_2-OMe$, $CB_{10}H_{10}C-Si(CH_3)_2-CH_2$, and $-CB_{10}H_{10}C-Si(CH_3)_2-CH(CH_3)$ silicons of the side chains, respectively. A large amount of the vinyl groups exist in the hybrid polymer before thermal curing because peak 6 assigned to the main chain $-Si(Ph)(CH{=}CH_2)-$ silicon is relatively intense in spectrum 2(a).

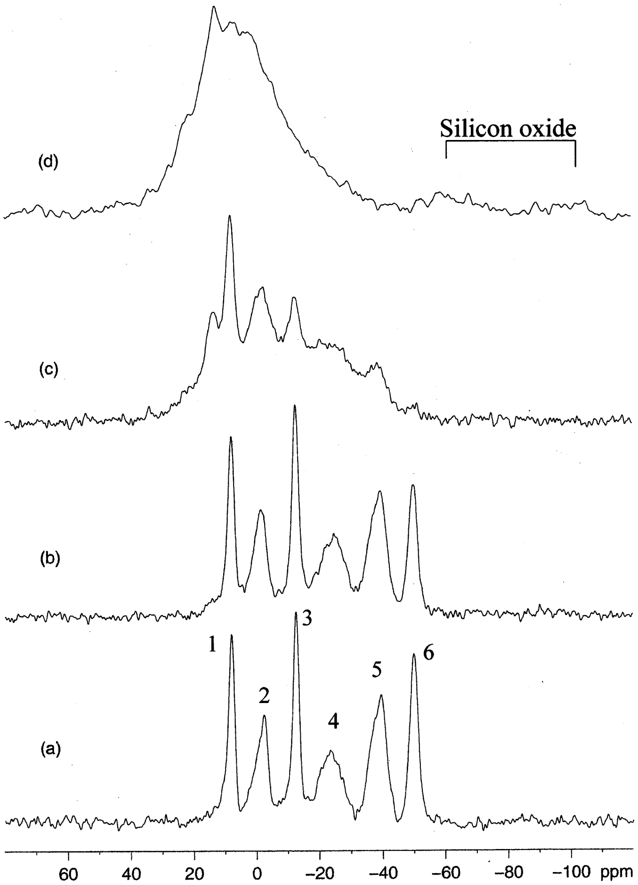

Figure 2. 59.6 MHz ^{29}Si CP-MAS NMR spectra of silyl−carborane hybrid diethynylbenzene−silylene polymers: (a) A-1 (before curing), (b) A-2 (molded and pressed at 250 °C), (c) A-4 (cured at 350 °C after molded and pressed at 250 °C), and (d) A-500 (cured at 500 °C after molded and pressed at 250 °C). Peak assignments: 1, $-CB_{10}H_{10}C-Si(CH_3)_2-CH(CH_3)$; 2, $CB_{10}H_{10}C-Si(CH_3)_2-CH_2$; 3, $-CB_{10}H_{10}C-Si(CH_3)_2-OMe$; 4, $-Si(Ph)(CH(CH_3)-)-$; 5, $-Si(Ph)(CH_2-)-$; and 6, $-Si(Ph)(CH{=}CH_2)-$.

Next, we are concerned with ^{29}Si CP-MAS NMR spectra of thermally cured polymers. Spectrum 2(b) of cured polymer after molding and pressing at 250 °C is very similar to spectrum 2(a) of uncured polymer. In comparison with spectrum 2(a) of uncured polymer, the intensity of peak 6 at − 49.8 ppm is slightly decreased in spectrum 2(b) of cured polymer after molding and pressing at 250 °C. As the curing temperature is further increased, peak 6 almost disappears at 350 °C as shown in spectrum 2(c). This shows that thermal hardening reaction of the vinyl group occurs at curing temperatures from 250 to 350 °C. The intensities of peaks 4 and 5 at −23.2 and −39.2 ppm are largely decreased at curing temperature of 350 °C, and almost disappear at 500 °C. In our previous paper, ^{29}Si CP-MAS NMR

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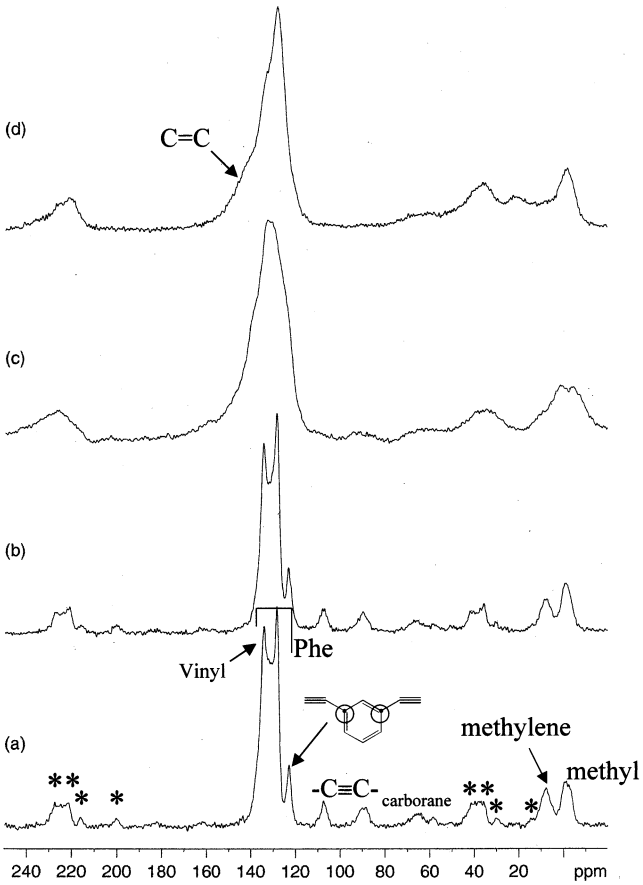

Figure 3. 75.6 MHz ^{13}C CP-MAS NMR spectra of silyl−carborane hybrid diethynylbenzene−silylene polymers: (a) A-1, (b) A-2, (c) A-4, and (d) A-500. The peaks marked with an asterisk are 350 °C spinning sidebands of the phenyl carbons and the C≡C carbons.

spectra of cured poly[(phenylvinylsilylene)ethynylene-1,3-phenylene-ethynylene], $(-C{\equiv}C-Ph-C{\equiv}C-Si(Ph)(CH{=}CH_2)-)_n$, in the curing temperature range of 250−450 °C are very broad in the range from 10 to −40 ppm. This spectral pattern is very similar to the patterns of spectra 2(c) and 2(d). We can look at some broad peaks ranged from 10 to −40 ppm as shown in spectrum 2(c), and three or four peaks centered at about 0 ppm in spectrum 2(d). The broad spectrum comes from the appearance of a variety of chemical structures in thermally cured *m*-carborane hybrid silicon-based polymer. Further, it is shown that structural change from the $-C{\equiv}C-Si-C{\equiv}C-$ group to the $-C{=}C-Si-C{\equiv}C-$ and $-C{=}C-Si-C{=}C-$ groups leads to the appearance of peaks centered at about 0 ppm. If we look at the upfield region of spectrum 2(d) carefully, there exist small and broad peaks at about −100 and −60 ppm. This suggests that a small amount of silicon oxides is produced at a curing temperature of 500 °C.

From the ^{29}Si NMR experimental results, the following was found: (1) thermal curing at temperatures from 250 to 500 °C leads to changes in structure of the silyl−carborane hybrid diethynylbenzene−silylene polymer, (2) thermal hardening reaction of the vinyl group occurs at curing temperatures from 250 to 350 °C, (3) the C≡C group changes into the C=C group by thermal hardening, and (4) a small amount of silicon oxides forms at curing temperature at 500 °C.

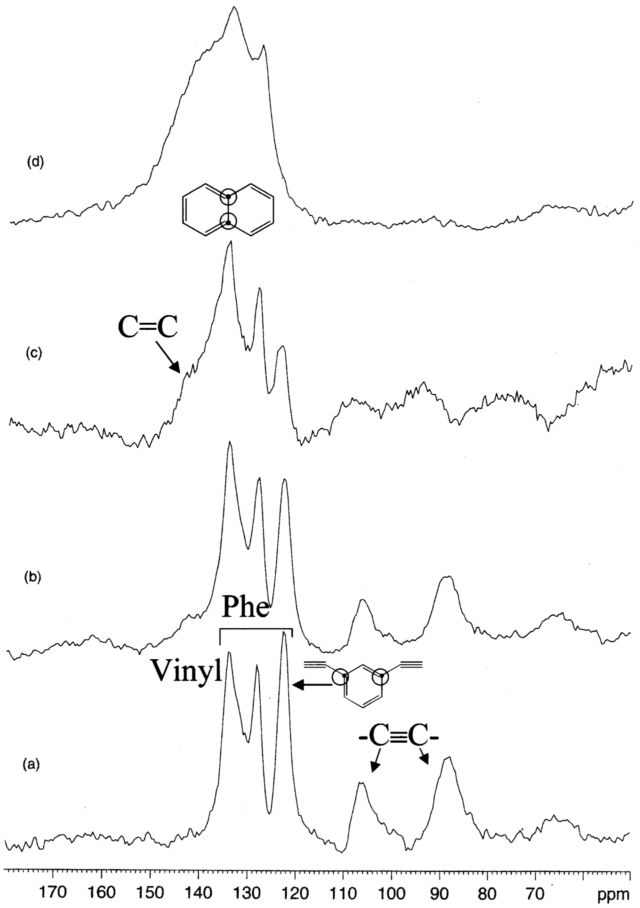

Figure 4. 75.6 MHz ^{13}C CP-MAS + DDph NMR spectra of silyl−carborane hybrid diethynylbenzene−silylene polymers: (a) A-1, (b) A-2, (c) A-4, and (d) A-500. The dipolar dephasing delay time was 60 μs.

3.2. ^{13}C CP-MAS NMR Spectral Analysis and Structural Characterization. To confirm that the acetylene group in the main chain and the vinyl group in the side chains play an important role in thermosetting reactions of the silyl−carborane hybrid diethynylbenzene−silylene polymers, the structures of the polymers are characterized by ^{13}C CP-MAS NMR as mentioned below. Figures 3 and 4 show 75.6 MHz ^{13}C CP-MAS NMR spectra and 75.6 MHz ^{13}C dipolar dephased CP MAS NMR spectra of the polymers ((a) A-1, (b) A-2, (c) A-4, and (d) A-500) used in section 3.1., where in ^{13}C dipolar dephased CP MAS NMR spectrum, the ^{13}C magnetization of a carbon bonded to proton is dephased by their dipolar couplings and then the ^{13}C signal disappears. The dipolar dephased CP MAS NMR naturally depends on the dipolar dephasing delay time. The dipolar dephasing delay time dependent experiments are carried out in the rage of 10−200 μs. As a result, signals of the phenyl carbons bonded to proton do not vanish at even a dipolar dephasing delay time of 200 μs. Then, we adopt the dipolar dephasing delay time of 60 μs.

At first, we are concerned with polymer A-1 before curing. ^{13}C CP-MAS spectrum 3(a) has relatively resolved and narrow peaks. The peak at 134.8 ppm and peaks at 108.0 and 90.0 ppm can be assigned to the vinyl group and the C≡C group according to our previous study in the ^{13}C CP-MAS NMR spectrum.[20−22] Peaks at 106.8 and 88.3 ppm can be assigned to the $Si-C{\equiv}C-$

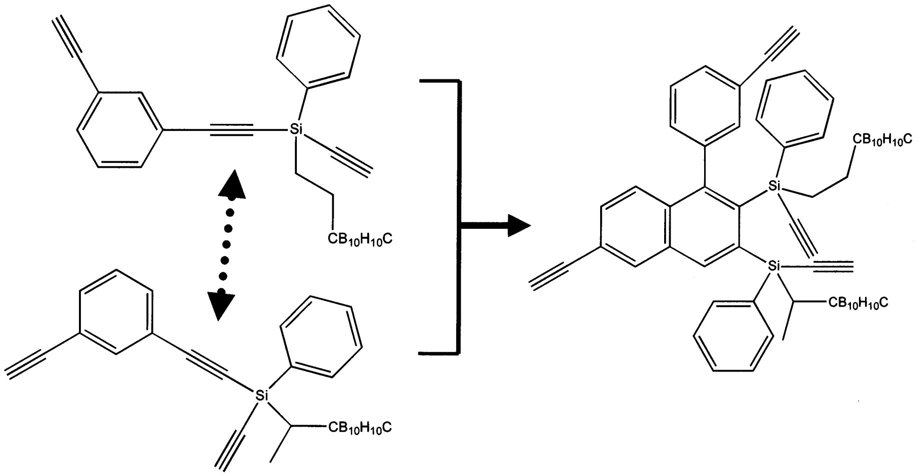

Figure 5. Thermosetting mechanism of silyl−carborane hybrid diethynylbenzene−silylene polymer by diene reaction between the C≡C group and Ph−C≡C group.

Ph carbons, and peaks at 122.8 and 134.1 ppm to the phenyl carbons in *ipso* position bonded to the C≡C group and the phenyl carbons in *ipso* position bonded to silicon, respectively, because as these carbons do not bond to proton, the corresponding carbons appear in the ^{13}C dipolar dephased CP MAS NMR spectra. A peak at 128.3 ppm can be assigned to the phenyl carbons bonded to proton because their dipolar interactions are greatly reduced by the fast flip-flop motion of the phenyl ring. Two peaks at ca. 10 and 15 ppm can be straightforwardly assigned to the methyl and methylene carbons, respectively, in the ^{13}C CP-MAS NMR spectra. Further, it can be said that two weak peaks in the 60−70 ppm range can be assigned to the carbonane carbons.

The structure of the polymer is significantly changed by thermal curing as mentioned in section 3.1. ^{13}C CP-MAS NMR spectrum of polymer A-2 cured at 250 °C is very similar to that of uncured polymer. On the other hand, as shown in ^{13}C dipolar dephased CP MAS NMR spectra 4(a) and 4(b), the intensity of peak at 122.8 ppm assigned to the phenyl carbons in *ipso* position bonded to the C═C group is somewhat decreased by thermal curing at 250 °C. This spectral change agrees with the ^{29}Si NMR results. It can be said that the structural change is very small at curing temperatures below 250 °C. As curing temperature is further increased, the intensity of the peak largely decreases. At curing temperature of 500 °C, the corresponding peak completely disappears. In cooperation with this, the peak intensity of the methylene carbons at ca. −10 ppm increases with an increase in curing temperature. This result suggests that the vinyl group converts to the methylene group by thermal hardening reactions. The intensities of corresponding peaks for the vinyl group gradually decrease with an increase in curing temperature, and then should completely disappear by curing at 500 °C according to our ^{29}Si NMR results. A broad peak at 140 ppm in spectrum 3(c) appears and its intensity increases with an increase in curing temperature. The peak can be assigned to the C═C group and the phenyl carbons bonded to proton. This is based on the finding of the ^{13}C dipolar dephased CP MAS NMR method that the ^{13}C magnetization of a carbon bonded to proton is dephased by their dipolar couplings and thus the ^{13}C signal does not appear.

The intensities of peaks from the C≡C carbons and the phenyl carbons bonded to the C≡C decrease with an increase in curing temperature, and then the peaks disappear by curing at 500 °C. A broad shoulder which comes from the C═C carbons appears at about 140 ppm in ^{13}C dipolar dephased CP spectrum 4(b) and its intensity increases with an increase in curing temperature. Therefore, it can be said that the C≡C bond changes to the C═C bond by thermal curing at temperatures from 250 to 500 °C. The intensity of the peak at 134.1 ppm in ^{13}C dipolar dephased CP spectrum 4(a) increases with an increase in curing temperature, and, on the other hand, that at 134.8 ppm in ^{13}C CP-MAS spectrum 3(a) decreases with an increase in curing temperature. Peaks in the range of 133.4−134.4 ppm come from the carbons which are not directly bonded to protons in ^{13}C dipolar dephased CP spectra, and the peak at 134.1 ppm corresponds to the 4a and 8a positioned carbons of the naphthalene ring ($\delta = 133.9$ ppm).[20−22] Kuroki et al. reported from ^{13}C NMR and the semiempirical MO method (MOPAC93/PM3) that the naphthalene ring forms by a Diels−Alder reaction between the Ph−C≡C group and the C≡C group because the hydrogen transfer reaction occurs easily.[20,21] The activation energy of the hydrogen transfer reaction calculated by Kuroki et al. was smaller than the activation energy of the Diels−Alder reaction. Therefore, it can be said that thermal curing of the silyl−carborane hybrid diethynylbenzene−silylene polymer leads to formation of the naphthalene rings (Figure 5). From these solid-state ^{13}C NMR results, it is found that (1) the naphthalene rings form by diene reaction between the Ph−C≡C group and the C≡C group at temperatures from 250 to 500 °C, (2) the −C≡C− group changes to the >C═C< group by another addition reaction, and (3) the vinyl group converts to the alkyl group by thermal hardening reactions at temperatures from 250 to 350 °C. Further, it is supposed that the vinyl group adds to the C≡C bond. The three-dimensional network may be formed by addition reactions between the vinyl group and the C≡C group as shown in Figure 6. Besides the main chain C≡C group, the vinyl group may add to the *m*-carborane group in the side chains.

3.3. ^{11}B MQ-MAS NMR Spectral Analysis and Structural Characterization. Figure 7 shows 96.3

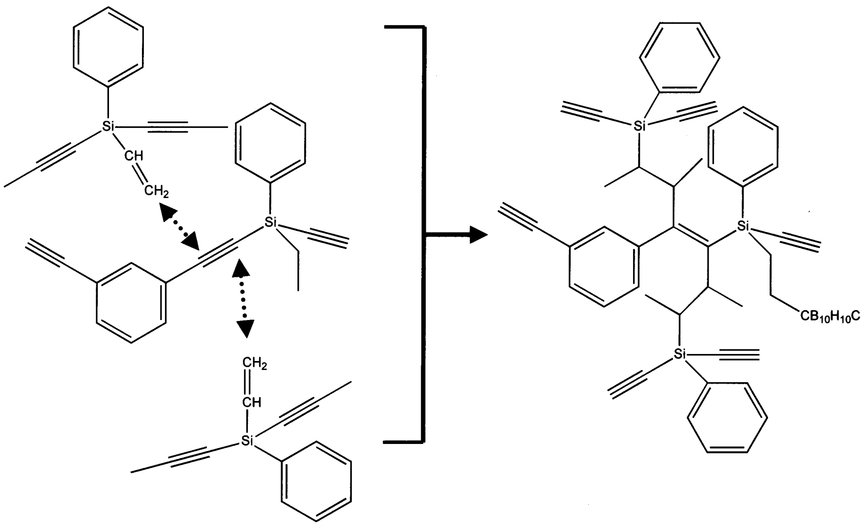

Figure 6. Thermosetting mechanism of silyl−carborane hybrid diethynylbenzene−silylene polymer by addition reaction between the C≡C group and vinyl group.

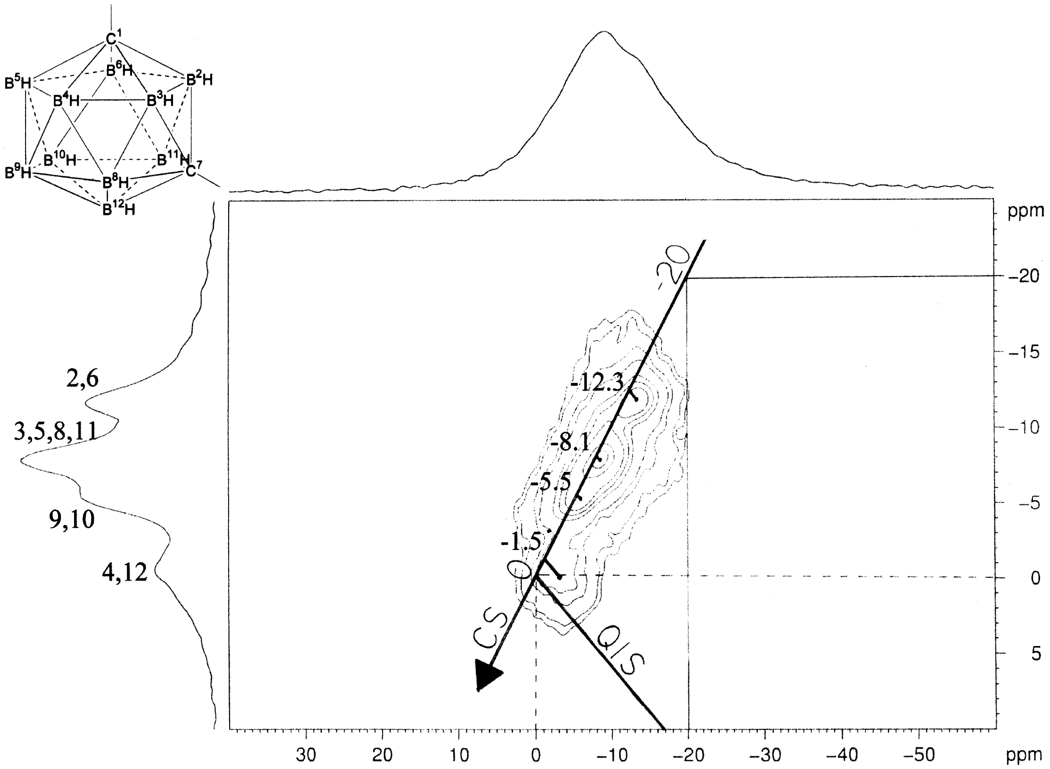

Figure 7. 96.3 MHz ^{11}B MQ-MAS NMR spectrum of silyl−carborane hybrid diethynylbenzene−silylene polymer (A-1) in the solid state. The chemical shift (CS) axis and the quadrupolar induced shift (QIS) axis are drawn as described in the text.

MHz 2D ^{11}B MQ-MAS NMR spectrum of the silyl−carborane hybrid diethynylbenzene−silylene polymer A-1 in the solid state. The F1 axis (the vertical axis) shows high-resolution ^{11}B NMR spectrum, and the F2 axis (the horizontal axis) is ^{11}B MAS NMR spectrum. Analysis and interpretation of this sheared spectrum are facilitated by introducing the chemical shift (CS) axis and the quadrupolar induced shift (QIS) axis because a shearing transformation places the anisotropic axis parallel to the F2 axis.[29] The QIS direction in the sheared spectrum has a constant slope of −10/17 and the CS axis has a constant slope of 1.[30] The resonance position differs from the frequencies observed in the spectrum due to the presence of the QIS. The isotropic chemical shifts are obtained as shown in Figure 7. In the high-resolution ^{11}B NMR spectrum, there are four peaks in the −10−0 ppm range. Each of the four peaks for the *m*-carborane group of the polymer can be easily assigned as shown in Figure 7 on the basis of ^{11}B NMR of pure *m*-carborane in the liquid state.[31] The ^{11}B NMR spectrum of the polymer in the solid state is very close to that in the liquid state. Peak assignment of the high-resolution ^{11}B NMR spectrum of the hybrid poly-

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[30] Amoureux, J.-P.; Pruski, M. In *Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K., Eds.; John Wiley & Sons: Chichester, 2002; Vol. 9, pp 226−251.

[31] Braun, S.; Kalinowski, H.; Berger, S. *100 and More Basic NMR Experiments*; VCH: Weinheim, 1996; pp 267−269.

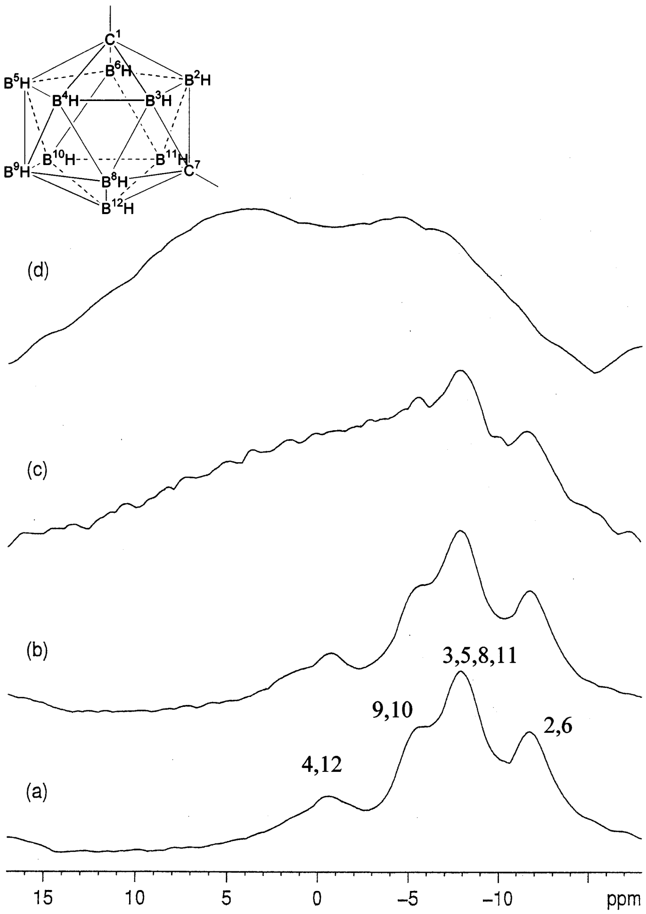

Figure 8. Isotropic projections of ^{11}B MQ-MAS NMR spectra of silyl–carborane hybrid diethynylbenzene–silylene polymers: (a) A-1, (b) A-2, (c) A-4, and (d) A-500.

mer is made as follows: $\delta = -12.3$ ppm, $B_{2,6}$; $\delta = -8.1$ ppm, $B_{3,5,8,11}$; $\delta = -5.5$ ppm, $B_{9,10}$; and $\delta = -1.5$ ppm, $B_{4,12}$.

Figure 8 shows isotropic projections of ^{11}B MQ-MAS NMR spectra of silyl–carborane hybrid diethynylbenzene–silylene polymers ((a) A-1, (b) A-2, (c) A-4, and (d) A-500). These spectra are from the F1 axis in ^{11}B MQ NMR ones. Spectrum 8(a) before curing is almost the same as spectrum 8(b) after molding and pressing at 250 °C. This shows that the structure of the carborane group is not affected by the molding and pressing at 250 °C. Structural changes of the carborane group occur at curing temperatures of 350 and 500 °C. In the spectrum of the carborane group at 350 °C, a large amount of the original carborane groups remain. On the other hand, the structural change of the carborane group at 500 °C is remarkable as seen from spectrum 8(d). The original carborane group does not remain. Such a structural change comes from oxidization of the carborane group as clarified by X-ray photoelectron spectroscopy (XPS) under air atmosphere.

Figure 9 shows B 1s core level spectra of silyl–carborane hybrid diethynylbenzene–silylene polymers cured at various temperatures. The binding energy of the B 1s core level for the polymer cured at 500 °C increases from 187 to 192 eV. Such a shift in the binding energy suggests a large change in the chemical bond of boron after 500 °C thermal curing. Peaks at 187 and 192 eV can be assigned to B–H and B–O, respectively. Therefore, it can be said that oxidization of the carborane group occurs by 500 °C thermal curing. There is a large amount of unreacted *m*-carborane groups in the polymer A-4 (350 °C thermal curing). These unreacted

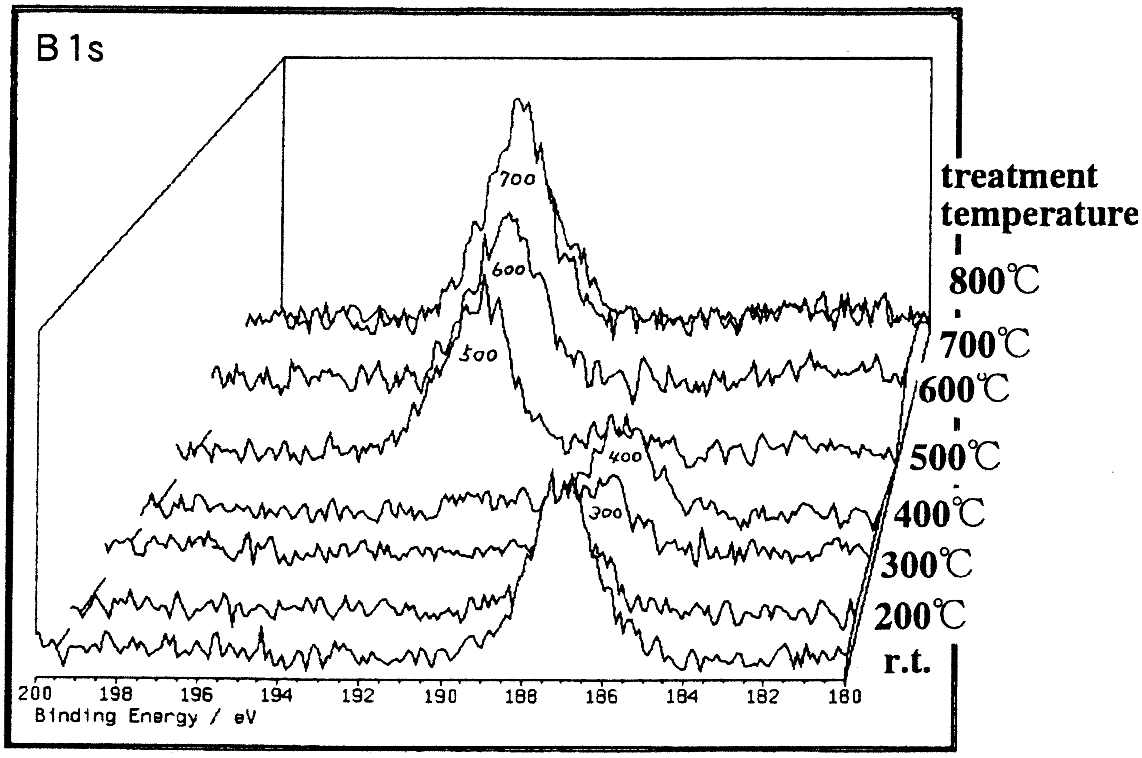

Figure 9. Boron 1s core level X-ray photoelectron spectra of silyl–carborane hybrid diethynylbenzene–silylene polymers cured at various temperatures.

carborane groups are completely oxidized by 500 °C thermal curing. And it can also be said that structural changes of the carborane group at 350 °C do not occur by oxidization. It is supposed that structural changes of the *m*-carborane group at 350 °C occur by cross-linking reactions. From ^{13}C and ^{29}Si NMR results, the C≡C group and the vinyl group are cross-linked by 350 °C thermal curing. Then, the *m*-carborane can be cross-linked to the C≡C group and the vinyl group.

3.4. Relationship Between Thermosetting Structure and Characteristics of Silyl−Carborane Hybrid Diethynylbenzene−Silylene Polymer. Structural changes of the *m*-carborane hybrid polymer seem to be related to characteristics of the polymer as shown in Table 1. The thermal durability of the polymer, such as the oxygen index and heat deflection temperature, is modified by thermal curing at temperatures from 350 to 500 °C. The oxygen index of polymer A-4 increases from 34 to 40. The increase of the flexural modulus of the polymer leads to the increase in temperature that is too high to measure. Modification of the thermal durability must be followed by formation of the thermal hardening structure. As the binding energy of the polymer is increased by the cross-linking reaction, structural change of the *m*-carborane group in the polymer and the formation of cross-linking structure lead to desirable thermal durability of the hybrid polymer.

The oxygen index of polymer A-500 is more than 50. This suggests that oxidization of the *m*-carborane group improves the desirable thermal durability of the hybrid polymer. The flexural modulus of polymer A-4 is higher than that of polymer A-2. The mechanical strength of polymer A-4 must be followed by the cross-linking reaction between the polymers. However, when the *m*-carborane hybrid silicon-based polymer is oxidized and decomposed by 500 °C thermal curing, the characteristic strength of the polymer is lost.

4. Conclusions

^{13}C and ^{29}Si CP-MAS spectra and ^{11}B MQ-MAS NMR spectra of silyl−carborane hybrid diethynylbenzene−silylene polymers have been successfully measured. It was found that (1) thermal curing leads to changes in the structure of the silyl−carborane hybrid diethynylbenzene−silylene polymer; (2) the naphthalene rings form by diene reaction between the Ph−C≡C group and the C≡C group at curing temperatures from ca. 250 to 500 °C; (3) the three-dimensional network forms by addition reaction between the vinyl group and C≡C bond at temperatures from 250 to 350 °C, and between the *m*-carborane group and the vinyl group and/or the C≡C group at temperatures from 250 to 350 °C; (4) silicon oxides and boron oxides are produced at a curing temperature of 500 °C and the polymer is decomposed; and (5) structural change of the *m*-carborane hybrid polymer is related to its characteristics such as the oxygen index, heat deflection temperature, and flexural strength. Further, it is demonstrated that high-resolution solid-state multinuclear NMR is a useful tool for doing structural analysis of materials with complicated chemical structures.

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