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Thermosetting Mechanism Study of Poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] by Solid-State NMR Spectroscopy and Computational Chemistry

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ABSTRACT: Poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] (abbreviated MSP) which contains Si−H and C≡C bonds, produces a very highly thermally stable polymer by curing above 150 °C. In this study, we determined the thermosetting mechanism of MSP using ^{13}C and ^{29}Si solid-state NMR methods and computational chemistry. From these results, we concluded that the intermolecular cross-linking reactions due to (1) the Diels−Alder reaction between Ph−C≡C and C≡C and (2) the hydrosilylation reaction between Si−H and C≡C proceed above 150 °C, and a very highly thermally stable structure is formed. Only the hydrosilylation reaction occurs above 300 °C.

Introduction

Recently, many studies of silicon-containing polymers composed of [$-SiR_2-C\equiv C-$] (R = alkyl or phenyl) units have been reported because of their potential applications in areas such as ceramic precursors and conducting materials.[1−9] 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] [$-Si(Ph)H-C\equiv C-C_6H_4-C\equiv C-]_n$,[1,2] poly [(phenylsilylene)diethynylene] [$-Si(Ph)H-C\equiv C-C\equiv C-]_n$,[4] and poly[methylsilylene]-ethynylene] [$-Si(CH_3)H-C\equiv C-]_n$[5] have been prepared, but there was almost no information about the properties of the polymers, expect for our previous reports.[1,2]

We found that poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] [$-Si(Ph)H-C\equiv C-C_6H_4-C\equiv C-]_n$(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 by curing.[1,2]

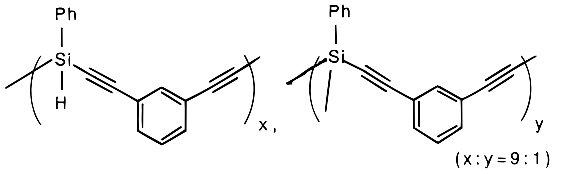
The thermosetting reaction of MSP occurred above 150 °C, and an exothermic peak at 210 °C was observed in the DSC curve.[1,2] From the TGA−DTA curves of MSP, there was no weight loss during curing under argon below 400 °C,[1,2] and the TG−MS results[10] showed that there was no evolution of a cracking product below 400 °C. It was found that the infrared absorption bands of the Si−H and C≡C bonds of MSP were gradually reduced by curing.[2] The values of elemental analysis[11] were not changed by curing. From these results, we assumed that an additional cross-linking reaction involving Si−H and C≡C bonds might have occurred to form a highly thermally stable structure. However, we could not show the concrete thermosetting structure and the cross-coupling reaction mechanism of MSP in our previous paper.[2]

On the other hand, a solid-state NMR method is a very useful tool for investigating the structure of insoluble materials, and many structural analyses of thermosetting polymers have been attempted by the solid-state NMR method.

In this study, we determined the thermosetting structure of MSP from the ^{13}C and ^{29}Si solid-state NMR methods. Moreover, we discussed the cross-linking reaction mechanism of MSP, which was concluded from the results of the solid-state NMR study and the computational chemistry study and clarified the relationship between the thermosetting structure of MSP and its high thermal stability.

Experimental Section

Preparation and Curing of MSP. MSP was prepared according to the same method previously reported by us.[1] The structure of the polymer was as follows.



(1)

We used MSP (M_w 4800, M_n 1900) sample for this study. MSP was cured at 150, 200, 300, or 400 °C for 2 h under argon.

Solid-State NMR Measurement. NMR spectra were recorded on a Bruker DSX-300 NMR spectrometer at room temperature. The observed frequencies of ^{13}C and ^{29}Si were 75.6 and 59.6 MHz, respectively. The 90° pulse of ^{1}H was 4.7 μs, and contact times of the cross polarization experiment were 2 ms for ^{13}C and 5 ms for ^{29}Si, respectively. The dipolar dephasing delay time was 200 μs for the ^{13}C CP+DDph (dipolar dephasing) experiment. The ^{13}C chemical shifts were calibrated indirectly through the adamantane peak observed at the upper field (29.5 ppm relative to tetramethylsilane), and the ^{29}Si chemical shifts were calibrated indirectly through the polydimethylsilane peak (33.8 ppm relative to tetramethylsilane).

Methods of Calculation. For silane compounds, calculations were performed using the Amsterdam density functional

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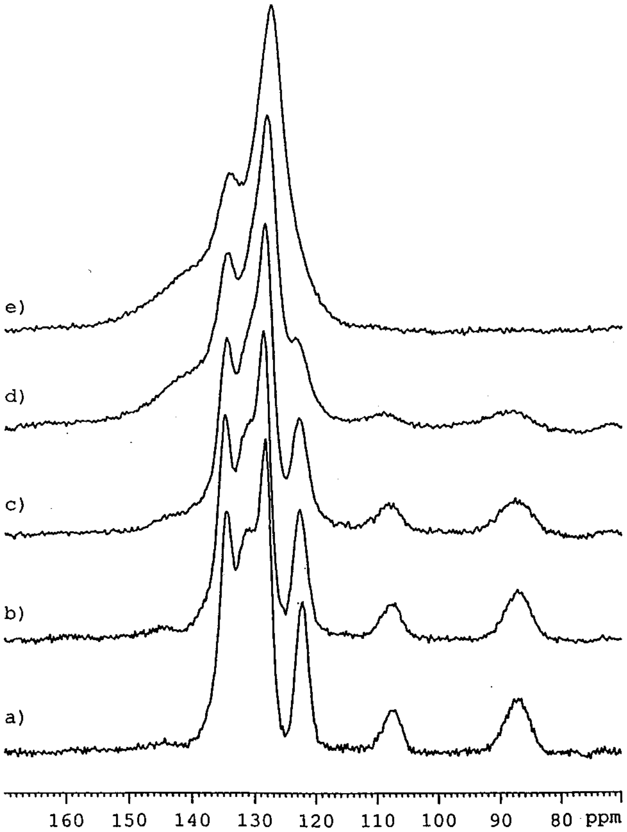


Figure 1. ^{13}C CP/MAS NMR spectra of MSP cured at various temperatures: (a) before curing; (b) at 150 °C; (c) at 200 °C; (d) at 300 °C; (e) at 400 °C.

(ADF) code.[12−14] The electronic configurations of molecular systems were described by an uncontracted DZP STO basis set on Si(3s,3p), C(2s,2p), and H(1s). These atoms were given an extra polarization function. Geometries were optimized within the local density approximation, Vosko−Wilk−Nusair, followed by single-point energy calculations using the gradient-corrected Becke exchange and Perdew correlation. For Diels−Alder reactions, PM3 calculations were carried out with the MOPAC (ver. 6) program system. All geometric variables were optimized and transition states were characterized via the force constant matrix.

Results and Discussion

(1) Thermosetting Structural Studies of MSP. The ^{13}C Solid-State NMR Results. Figure 1 shows the ^{13}C CP/MAS spectra of the MSP samples cured at various temperatures. The peaks at 87.1 and 107.6 ppm of the MSP sample before curing could be assigned to the C≡C carbons. These peaks decreased and broadened with the increase in curing temperature and vanished by curing at 400 °C. The peak at 122.3 ppm assigned to the phenylene carbons bonded to C≡C decreased and broadened with the increase in curing temperature and vanished by curing at 400 °C in the same way. Every peak broadened with the increase in curing temperature. This broadening of peaks would come from the conformational distribution of the products by a cross-coupling reaction. Any peak assigned to sp^3 carbons (which would appear from 0 to 100 ppm) was not observed on curing. The cured MSP samples had a new peak at 144 ppm, which increased and broadened with the increase in curing temperature. This peak can be assigned to the C=C carbons and the phenyl carbons bonded to the C=C bond from the literature data of ^{13}C chemical shifts.[15]

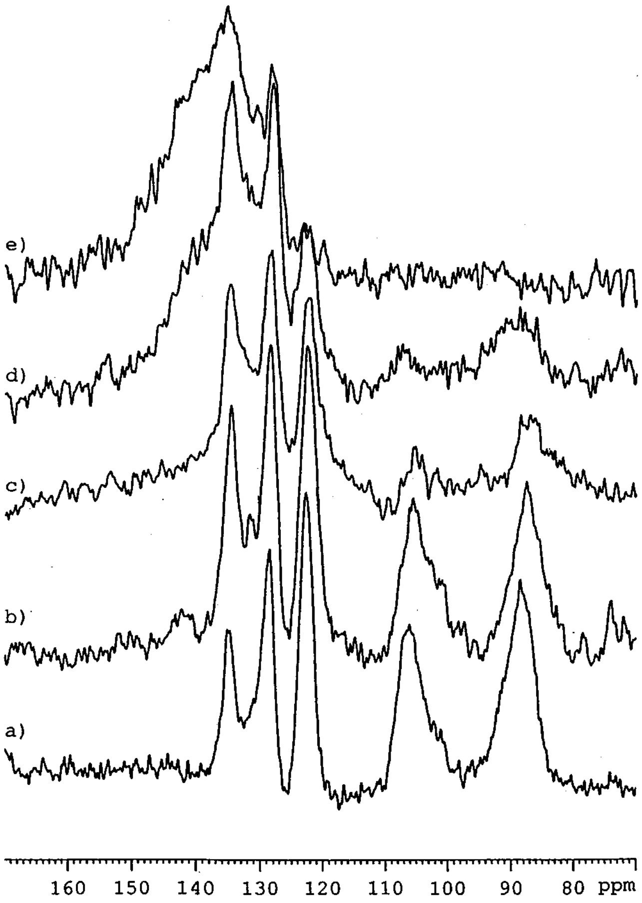


Figure 2. ^{13}C CP/MAS+DDph NMR spectra of MSP cured at various temperatures: (a) before curing; (b) at 150 °C; (c) at 200 °C; (d) at 300 °C; (e) at 400 °C.

Figure 2 shows the ^{13}C CP+DDph (dipolar dephasing)/MAS spectra of the MSP samples cured at various temperatures. The signals appearing in this experiment come from the carbons which coupled to ^{1}H weakly. On the other hand, the signals coming from the carbons which coupled with ^{1}H strongly disappear in this experiment. The peaks of the noncured MSP sample which were assigned to the C≡C carbons (87.1 and 107.6 ppm), the phenylene carbon bonded to C≡C (122.3 ppm), and the side-chain phenyl carbon(136.3 ppm) bonded to Si were observed. These carbons do not have directly attached ^{1}H. In addition, two peaks at 128.6 and 134.9 ppm, which can be assigned to the side-chain phenyl carbons, were observed. These carbons have directly attached ^{1}H. However, the dipole−dipole interaction with ^{1}H vanishes due to the flip-flop motion of the phenyl ring, so that these peaks could be observed.

The MSP sample cured at 150 °C showed two new peaks at 131.8 and 144 ppm. The peaks came from the carbons which do not have directly attached ^{1}H. Although there was no change in the intensity of the peak at 131.8 ppm, the peak at 144 ppm increased and broadened with the increase in curing temperature. The peak at 131.8 ppm corresponds to the 4a and 8a position carbons of the naphthalene ring, and the peak at 144 ppm corresponds to the C=C carbons and the phenyl carbons bonded to the C=C bond, and the biphenyl bond carbons based on the literature data for the ^{13}C chemical shifts.[15]

From the ^{13}C solid-state NMR results, it was suggested that the naphthalene rings would be formed and

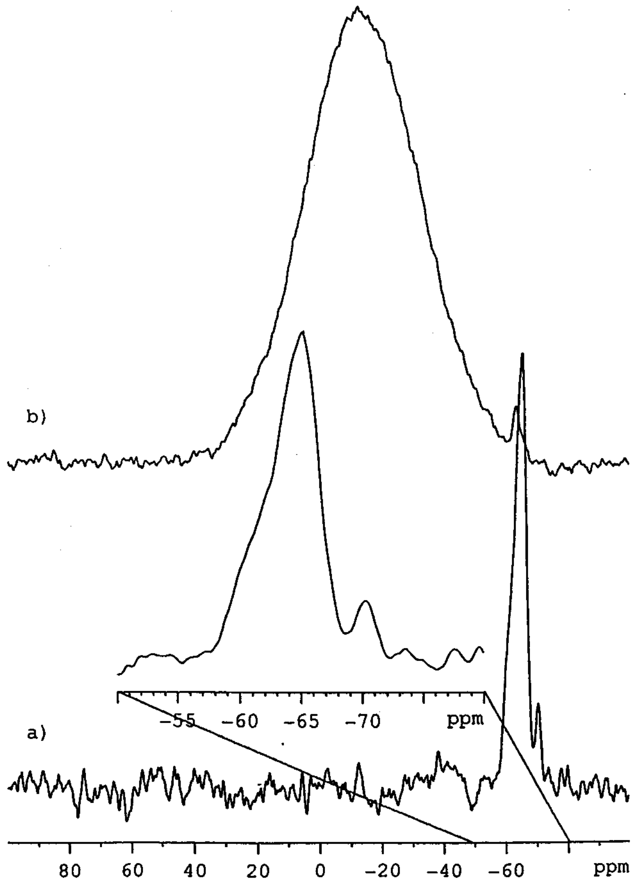


Figure 3. ^{29}Si CP/MAS NMR spectra of MSP: (a) before curing; (b) after curing at 400 °C.

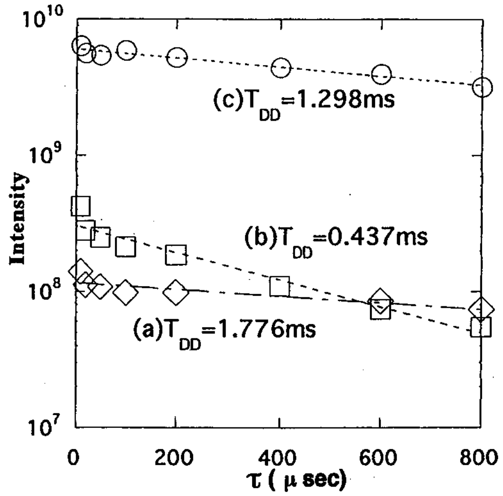


Figure 4. Dipolar dephasing decays of branched ^{29}Si signals which do not have directly attached protons (a), and ^{29}Si signals for directly attached protons (b) of MSP before curing, and ^{29}Si signals of MSP cured at 400 °C (c), respectively.

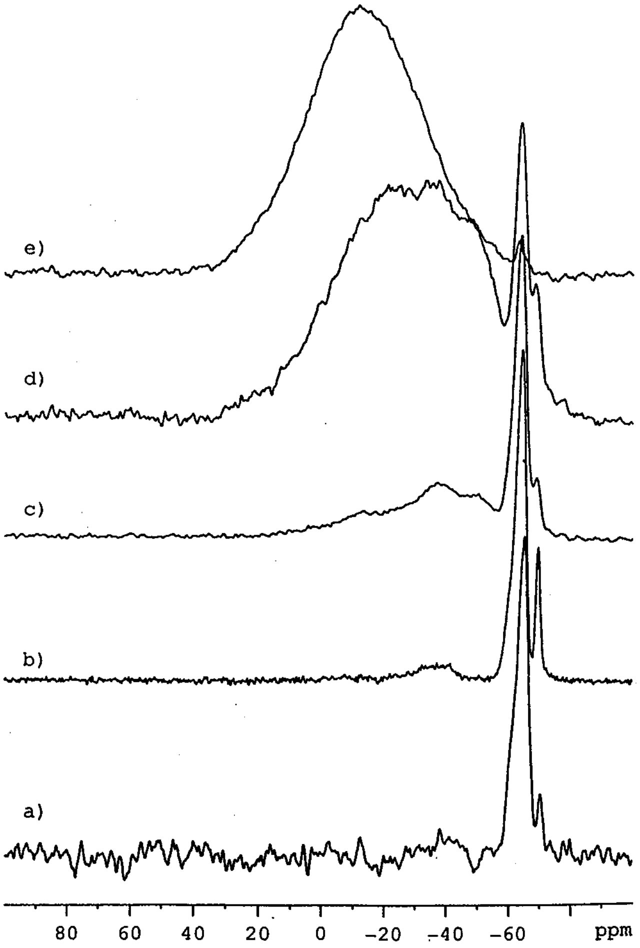


Figure 5. ^{29}Si CP/MAS NMR spectra of MSP cured at various temperatures: (a) before curing; (b) at 150 °C; (c) at 200 °C; (d) at 300 °C; (e) at 400 °C.

that the $C\equiv C$ bonds change into the $C=C$ bonds by curing. The naphthalene rings would be caused by the coupling reaction between two $C\equiv C$ bonds, and the $C=C$ bonds would be caused by the hydrosilylation reaction between $Si-H$ and $C\equiv C$ over a wide temperature range from 150 to 400 °C.

^{29}Si Solid-State NMR Results. The ^{29}Si CP/MAS spectra of the MSP sample before curing and cured at 400 °C are shown in Figure 3. ^{29}Si CP/MAS NMR spectra indicate that the MSP sample before curing has three peaks at −70.3, −65.0, and −60.8 ppm that are assigned to branched Si which do not have directly attached protons, SiH, and SiH_2 in the end-group, from solution state NMR results.[2] The MSP sample cured at 400 °C showed a very broad peak (half width = 2969 Hz) at −11.9 ppm. Figure 4 shows the dipolar dephasing decays of the branched ^{29}Si signal (−70.3 ppm) which do not have directly attached protons, and ^{29}Si signal (−65.0 ppm) directly attached protons of the MSP sample before curing, and the ^{29}Si signal (−11.9 ppm) of the MSP sample cured at 400 °C. T_{dd} (dipolar-dephasing relaxation time) of the Si directly attached protons of the MSP sample before curing was 0.437ms, and that of the branched Si was 1.776ms. T_{dd} of Si of the MSP sample cured at 400 °C was 1.298ms. This value was closed to the branched Si which do not have directly attached protons before curing. These results indicate that most of the Si atoms of cured MSP do not have directly attached protons.

Figure 5 shows the ^{29}Si CP/MAS spectra of the MSP sample cured at various temperatures. The MSP sample cured at 150 °C had a new peak at −37 ppm. T_{dd} of this peak is 0.685ms, so that this peak comes from Si atoms which have directly attached protons. From the ^{13}C NMR results, this peak would come from the $Si-H$ caused by the coupling reaction between two $C\equiv C$ bonds. The MSP sample cured at 200 °C showed two new peaks at −50 and −17 ppm, respectively. From the T_{dd} measurements of poly[(methylsilylene)ethynylene-1,3-phenyleneethynylene],[16] the peak at −50

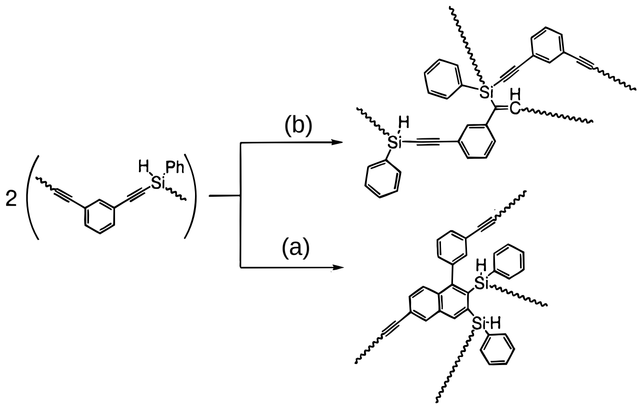


Figure 6. Thermosetting mechanism of MSP based on solid-state NMR results (a) the Diels–Alder reaction between Ph–C≡C and C≡C and (b) the hydrosilylation reaction between Si–H and C≡C.

Table 1. Bonding Energies of Si–H

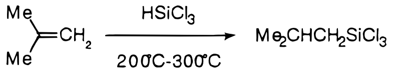
	bonding energy (kcal/mol	
compound	expt 1.[21]	calcd
$H_3Si{-}H$	90.3	97.8
$PhSiH_2{-}H$	88.2	95.3
$Cl_3Si{-}H$	91.3	
$HC{\equiv}CSiH_2{-}H$		95.1

ppm comes from Si atoms which have directly attached protons and the peak at −17 ppm comes from the Si atoms which do not have directly attached protons. Considering the ^{13}C NMR results, it seems that the peak at −50 ppm comes from Si–H and the peak at −17 ppm comes from the Si atoms which do not have directly attached protons formed by the hydrosilylation reaction. In the spectrum of the MSP sample cured at 300 °C, in particular the intensity of the peak at −17 ppm, which comes from the Si atoms that have directly attached protons, increased. As we noted, the MSP sample cured at 400 °C showed a very broad resonance at −11.9 ppm.

From the solid state ^{13}C and ^{29}Si NMR results, it follows from what has been said that the thermosetting reaction of MSP is due to (1) the Diels–Alder reaction between Ph–C≡C and C≡C and (2) the hydrosilylation reaction between Si–H and C≡C (Figure 6).

It seems that a new peak at −37 ppm of the MSP sample cured at 150 °C can be assigned to Si–H formed by the Diels–Alder reaction. Finally, every Si of MSP cured at 400 °C would change into Si atoms which do not have directly attached protons by the hydrosilylation reaction. In the next section, we will consider these two reactions by computational chemistry.

(2) Analysis of the Thermosetting Mechanism. The Hydrosilylation Reaction. It is well-known that the hydrosilylation reaction occurs radically at 250 °C-300 °C with no catalyst (eq 2)[17] Table 1 shows the Si–H bonding energies of silane compounds by experiments[21] and the density functional method calculations. Each Si–H bonding energy is about 90 kcal/mol. The bonding energy of the nearby Si–H on the phenyl group is lower by 2 kcal/mol than that of the nonsubstituted Si–H. Further, the bonding energy of the nearby Si–H on the C≡C group is lower than that of the nonsubstituted Si–H. Because the Si–H of MSP is near these two substituted groups, the Si–H of MSP has high reactivity compared with the nonsubstituted Si–H.



(2)

Table 2. Orbital Energy Levels of Ethynyl Compounds

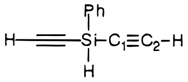
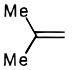
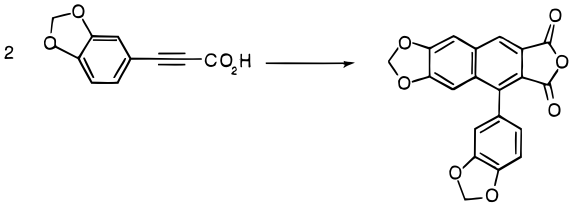
	HOMO level	LUMO level
$H{-}C_1{\equiv}C_2{-}H$	-11.61 eV	2.01 eV
 $\mathrm{H{-}C{\equiv}C{-}Si(Ph)(H){-}C_1{\equiv}C_2{-}H}$	-9.09 eV	-0.03 eV
	-9.721 eV	1.098 eV

Table 3. Energies (kcal/mol) of Diels–Alder Type Reactions

	transition state	intermediate	product	activation energy	heat of formation
anti–in	345.39	301.13	219.01	71.65	−54.73
anti–out	342.94	296.06	211.10	69.20	−62.64
syn–in	332.65	295.29	213.48	58.91	−60.26
syn–out	331.71	293.19	206.52	57.97	−67.22

Table 2 shows the orbital energy levels of the ethynyl compounds calculated by the semiempirical MO method (MOPAC93/PM3). The difference between the HOMO and LUMO energy levels suggests the high reactivity of the C≡C bonded to Si and the phenyl group compared with the nonsubstituted C≡C. These results suggest that the hydrosilylation reaction proceeds between Si–H and C≡C in MSP as shown in eq 2.

The Diels–Alder Reaction. There are some examples of the Diels–Alder reaction between Ph–C≡C and C≡C.[18–20] The Diels–Alder reaction of [3,4-(methylenedioxy)phenyl]propionic acid (eq 3) in the solid state reported by Desiraju et al.[20] is a notable example. This Diels–Alder reaction progressed below 70 °C, and the reaction proceeded to 25% in 30 days at 120 °C.



(3)

In this chapter, we used the monomer unit model of MSP and calculated the energies of the transition state, the intermediate, and the product in the Diels–Alder reaction by the semiempirical MO method (MOPAC93/PM3) and will discuss the reactivity of the C≡C of MSP. There are considered to be four structural isomeric products obtainable by the Diels–Alder reaction: (1) each substituent group of Si is syn-oriented and the reacting phenyl group is between the two ethynyl groups (in), (2) each substituent group of Si is syn-oriented and the reacting phenyl group is not between the two ethynyl groups (out), (3) each substituent group of Si is anti-oriented and the reacting phenyl group is between the two ethynyl groups (in), and (4) each substituent group of Si is anti-oriented and the reacting phenyl group is not between the two ethynyl groups (out). The calculation results are presented in Table 3. Figure 7 shows the chemical reaction scheme of case 4, syn–out.

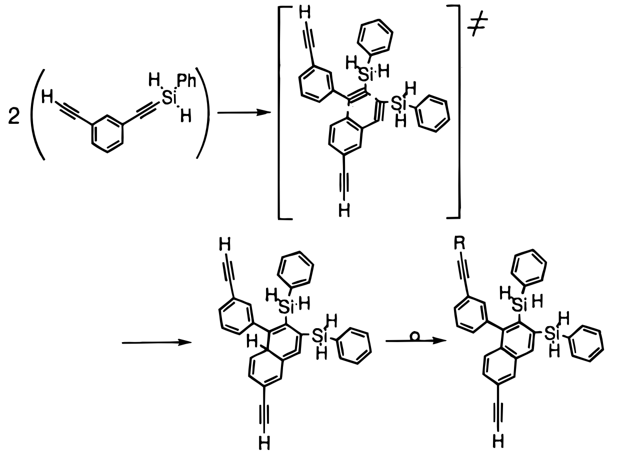


Figure 7. Diels–Alder reaction scheme of case 4, syn–out.

From the calculation results, case 4, syn–out, is the best route for the Diels–Alder reaction of MSP, because the activation energy of case 4 is the smallest and the heat of formation is the biggest of these four cases. The activation energy of this reaction is 57.97 kcal/mol. The calculated activation energy in the same way for eq 3 is 49.15 kcal/mol. From the fact that the reaction of eq 3 occurred at 120 °C, we may state that the Diels–Alder reaction of MSP occurs at 210 °C.

After the Diels–Alder reaction between Ph–C≡C and C≡C, the hydrogen transfer occurs and the naphthalene ring is formed. Next we calculated the activation energy of the hydrogen transfer reaction of MSP using the product of the Diels–Alder reaction model between acetylene and ethynylbenzene. The calculated activation energy of the hydrogen transfer reaction is 22.6 kcal/mol which is smaller than the activation energy (57.97 kcal/mol) of the Diels–Alder reaction, which was calculated previously. This fact says that the hydrogen transfer reaction occurs easily and that the naphthalene ring is formed after the Diels–Alder reaction between Ph–C≡C and C≡C.

Summary

Based on the results of the ^{13}C and ^{29}Si solid-state NMR methods and computational chemistry, we concluded that the intermolecular cross-linking reactions of MSP due to (1) the Diels–Alder reaction between Ph–C≡C and C≡C and (2) the hydrosilylation reaction between Si–H and C≡C proceed at 150–200 °C, and a very highly thermally stable structure is formed. Above 300 °C, only the hydrosilylation reaction occurs and the intermolecular cross-linking proceeds further.

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