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A study on pyrolysis and cross-link formation of poly(*p*-phenylene butadiyne) by thermoanalysis and spectroscopy

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Abstract

In this study, we prepared a type of arylacetylene, poly(*p*-phenylene butadiynylene), PPPB, and studied its pyrolysis behavior. A pellet of PPPB maintained its shape and provided a carbonization yield of 94% by heat-treatment at 1000 °C, although it experienced exothermal reaction and partial fusion at approximately 200 °C. It was also found that PPPB did not show graphitization even when it was heat-treated at 3000 °C. X-ray diffraction (XRD) study revealed the breakdown of the initial crystal structure of PPPB at 200 °C and a formation of the carbon structure at above 650 °C. By combining the results of TG–MS, FT-IR, and ^{13}C NMR, a mechanism for pyrolysis of PPPB including the cross-link formation was proposed, which included a Diels–Alder type reaction between the terminal acetylene and the diene structure comprising of diacetylene and phenyl groups, which is facilitated by increased mobility due to the partial fusion and the presence of the terminal acetylene groups.

Keywords: Glass-like carbon; Carbonization; Infrared spectroscopy; Nuclear magnetic resonance; Carbon yield

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1. Introduction

Carbon materials are prepared by pyrolyzing organic substances under inert atmospheric conditions. During the pyrolysis, the organic compounds are changed into carbons, by the elimination of low molecular weight compounds, the cyclization and the aromatization of the carbon atoms, and the extension of the aromatic rings. The carbonization yield usually depends on the types of the precursors used, and it exerts significant influence on the physicochemical properties of the prepared carbons such as porosity, and shrinkage in dimensions. Controlling the pyrolysis process and selecting the precursors are quite important factors in order to obtain carbon materials with desired properties.

Weight loss during carbonization is not desirable for manufacturing carbon materials from the viewpoints of both saving resources and costs. The smaller weight loss on carbonization is favored particularly in the production of glass-like carbons, because the larger weight loss results in either the decrease of the density, or in large shrinkage or cracks. The organic compounds that contain carbon–carbon triple bonds are known to provide higher carbonization yields than compounds containing only single or double bonds. There are three categories of these kinds of organic compounds: (i) substituted monomers [1], (ii) acetylene terminated resins (ATRs) [2,3], and (iii) arylacetylenes [4,5]. All of these compounds have been proven to provide higher carbonization yields of more than 80%.

Arylacetylenes are organic substances that include aromatic diacetylene units in their backbone structures, which were first synthesized by Hay [6]. Economy et al. proposed a one-pot synthesis of a C/C composite by employing arylacetylenes, such as 1,3- or 1,4-diethynyl benzene oligomers as a matrix resin, since the oligomers showed carbon yields as high as 97% at a carbonization temperature of 650 °C [7]. Kijima et al. synthesized three types of arylacetylenes with *p*-, *m*-, and *o*-

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configurations on their phenyl rings, and reported extremely high carbonization yields, such as 92%, 96%, and 90% for *p*-, *m*-, and *o*-polymers, respectively [8].

The formation of a cross-linking structure is commonly recognized by these authors as an important step that provides high carbonization yields. It is also revealed that the arylacetylene compounds aforementioned showed exothermal reactions at approximately 200 °C in DTA measurements, where cross-linking reactions were considered to occur. Economy et al. and Kijima et al. proposed different mechanisms for the formation of cross-linking, i.e., Diels–Alder reactions including triple-bonds and topochemical 1,4-addition reaction between the adjacent diacetylene structure. However, these mechanisms seemed to not be the conclusions that have been drawn from sufficient analysis of the pyrolysis process in detail.

In the present study, we prepared an arylacetylene compound, poly(*p*-phenylene butadiynylene), PPPB, according to Kijima's preparation, and conducted detailed analyses by combining thermal analysis, electron microscopy and spectroscopy in order to understand the details of the pyrolysis mechanism, paying special attention to the cross-linking formation in the material.

2. Experimental

Poly(*p*-phenylene butadiynylene), PPPB was synthesized by an oxidative coupling reaction of *p*-diethynylbenzene [8] as shown in Scheme 1 of Fig. 1. A catalyst solution, which was prepared by passing oxygen through an acetone solution of copper chloride (I) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine, was added to an acetone solution of the monomer, *p*-diethynylbenzene. The polymerization was continued for 1 day by passing oxygen through the solution at room temperature. The product was thoroughly washed with a HClaq/MeOH mixed solution with the volume ratio of 1/10, an ammonia aqueous solution, water, and methanol in this order. The product yield was 84%.

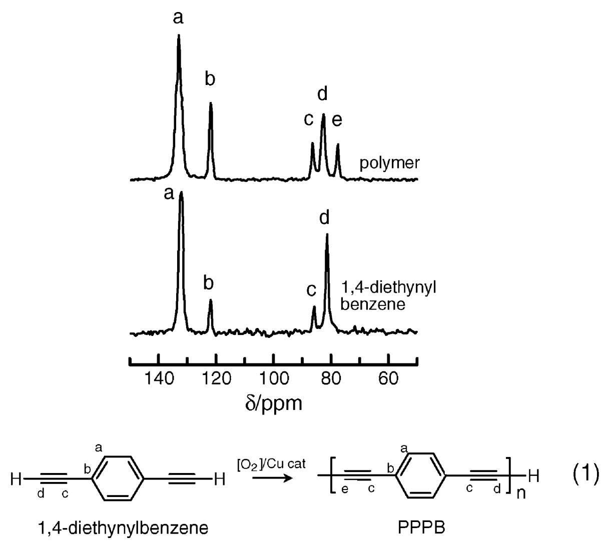

Fig. 1. ^{13}C NMR spectra of 1,4-diethynylbenzene and its polymer. Scheme 1 shows the synthesis of the PPPB.

The product was formed into pellets with a diameter of 10 mm and a thickness of 1 mm by applying 0.4 MPa with a pelletizer, and was subjected to heat-treatment by placing the pellets between two glass-like carbon plates. This operation was required in order to avoid explosion of the pellets during the heat-treatments [7,8]. The pelletized compound was heat-treated in a nitrogen flow at predetermined temperatures between 150 and 1000 °C for 1 h, at a heating rate of 10 °C min^{-1}. Hereafter, the samples are referred to by their heat-treatment temperatures, for example, PPPB180 represents the sample prepared at 180 °C. High temperature treatment was also conducted in order to observe the graphitizability of the compound, i.e., the sample carbonized at 1000 °C was heated in an argon stream at 3000 °C using a graphite furnace.

Characterization of the heat-treated samples was performed by FT-IR and solid-state ^{13}C NMR measurements after crushing the pellets into powder. The FT-IR spectra were obtained by the diffuse reflectance method using an FT-IR spectrometer (Magna560, Nicolet). ^{13}C NMR spectra were obtained using the CPMAS technique (spinning rate = 6 kHz) using an NMR spectrometer (AVANCE DSX300, Bruker). External adamantane was used as a chemical shift reference ($\delta = 2.95$ ppm for the high field resonance). The fractured surfaces of the pellets were studied by scanning electron microscopy (SEM).

3. Results and discussion

3.1. Chemical structure of the product

The ^{13}C NMR spectra of 1,4-diethynylbenzene and the product obtained are presented in Fig. 1. Two sp^2-peaks at 133 ppm (a) and 122 ppm (b), and two sp-peaks at 86 ppm (c) and 83 ppm (d) were observed in the spectrum of 1,4-diethynylbenzene. The product possessed an additional peak at 78 ppm (e), which was confirmed to be due to a quarternary carbon by using the dipolar dephasing method, indicating the introduction of carbons connecting two 1,4-diethynylbenzene moieties. The peak at 83 ppm remained in the product, which indicated the presence of a considerable amount of terminal acetylene groups even after the coupling reaction.

The FT-IR spectra and the list of the peaks are presented in Fig. 2 and Table 1, respectively. The C–H vibrations of the terminal acetylene groups were observed at 3265 cm^{-1} ($\nu_{-C\equiv C-H}$), 637 cm^{-1}, and 1263 cm^{-1} ($\delta_{-C\equiv C-H}$) [9], which agreed with the result of ^{13}C NMR mentioned above. The peak at 1915 cm^{-1} was assigned to the diacetylene band that was affected by the conjugation with the phenyl groups [10], because it was located at an intermediate wavenumber between isolated acetylene (2209 cm^{-1}) [5] and diacetylene (2070 cm^{-1}) [11], and allene (1887 cm^{-1}) [12] and butatriene (1880 cm^{-1}) [13]. The peaks at 544 and 833 cm^{-1} were the out-of-plane deformation vibrations of the aromatic C–H pertaining to the two adjacent hydrogen atoms attached to the phenyl ring of PPPB [8,9].

According to the chemical analysis, the H/C atomic ratio of the product was 0.52. The H/C ratio of the monomer was 0.6, and that of the ideal dimer should be 0.5. A simple calculation

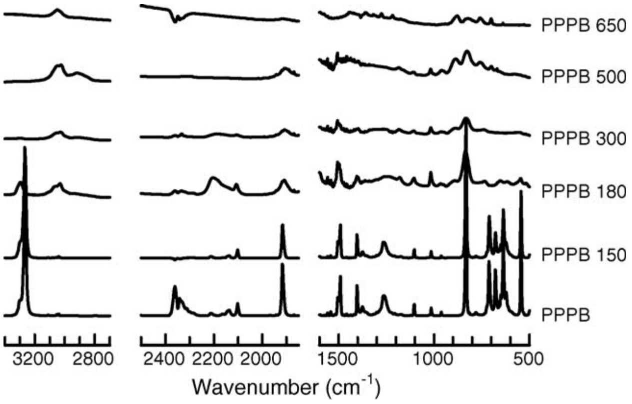

Fig. 2. FT-IR spectra of PPPB heat-treated at different temperatures.

Table 1
Peak assignments of FT-IR spectra

Wavenumber (cm)	Mode
544, 833	C–H out-of-plane of two adjacent hydrogen atoms on aromatic ring
637, 1263	=C–H deformation and its overtone
1491, 1504	C=C skeletal vibrations
1915	Diacetylene conjugated with phenyl groups in PPPB
2102	Diacetylene
2209	Isolated C=C
2922	Aliphatic C–H
3034	Aromatic C–H
3265	=C–H affected by conjugation
3298	=C–H

concluded that 80% of the total number of molecules was in the dimer and the rest in the monomer. Hence, the product could be identified as a mixture containing dimers and monomers of 1,4-diethynylbenzene. This conclusion is consistent with the ^{13}C NMR and FT-IR results that indicated the presence of the terminal acetylene C–H groups. From this consideration, the polymerization did not proceed sufficiently to produce a 'polymer'. In the previous report by Kijima et al., there is no description on the elemental analysis of PPPB nor on the degree of polymerization, however, the results of TG–DTA, FT-IR, and XRD in that paper were similar to those obtained in the present study, as described below. Thus, we identified our sample as PPPB.

3.2. Carbonization behavior of PPPB

The pelletized compound was mechanically stable since it did not show any signs of disintegration even by heat-treatment at 1000 °C. It only displayed a slight shrinkage of 7.7% in diameter and 7% in thickness of the pellet. This indicated that strong cross-links were formed in the material.

A drastic change in the microscopic structure of the PPPB with the heat-treatment was found in the SEM observation of the fractured surfaces of the pellets, as shown in Fig. 3. Initially, the pellet showed a fractured surface that was characteristic of a lump made of powdery material, of which the appearance was maintained up to 150 °C. When the sample was heat-treated above 250 °C, the aforementioned feature was changed into a uniform and smoothed surface. The change in the appearance of the fractured surface of the pellet is an indication of the occurrence of the partial fusion of PPPB during the heat-treatment at above 250 °C. As shown in the next paragraph, this is the temperature just above the exothermal reaction detected by DTA. Fig. 3 also shows the SEM photograph of PPPB heat-treated at 850 °C, PPPB850. Small differences in the appearance are observed between PPPB250 and PPPB850.

Two weight losses were observed for PPPB by TG–DTA measurement, as shown in Fig. 4(a): one at approximately

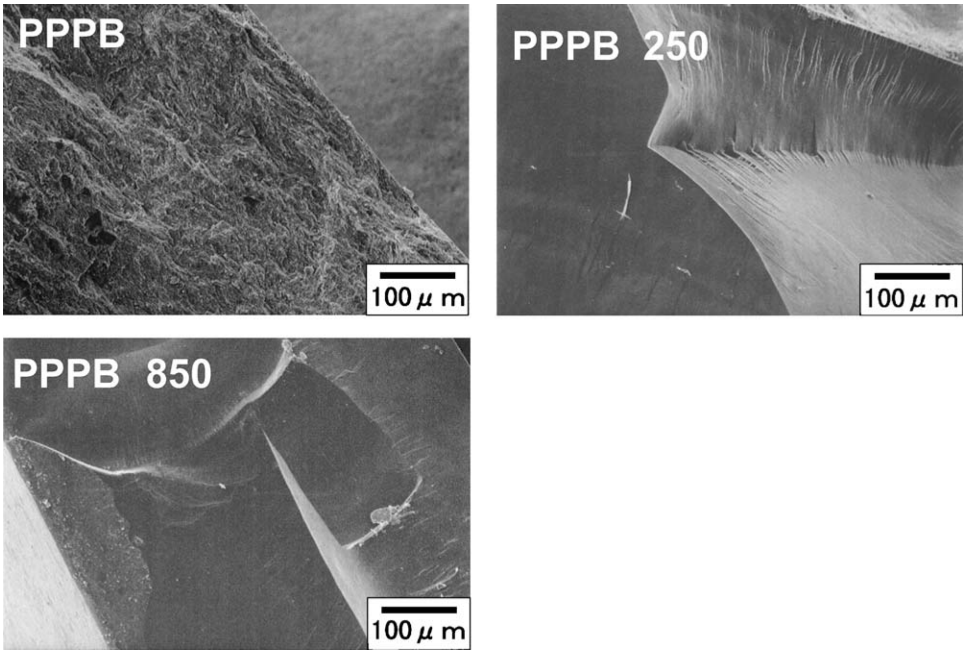

Fig. 3. SEM images of the fractured surfaces of the PPPB pellets.

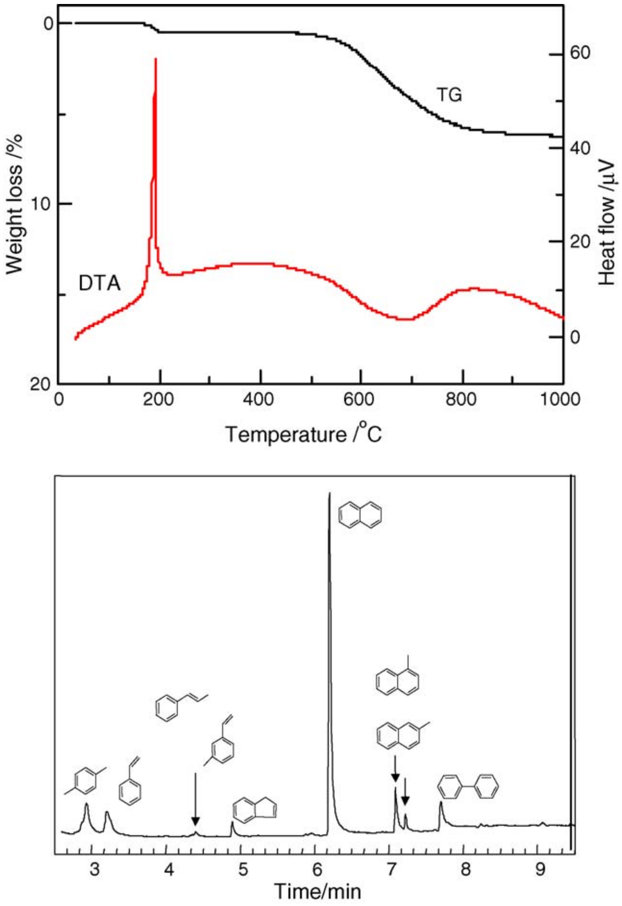

Fig. 4. (a) TG–DTA diagrams of PPPB. (b) Gas chromatogram of the gas collected during pyrolysis at 665–675 °C.

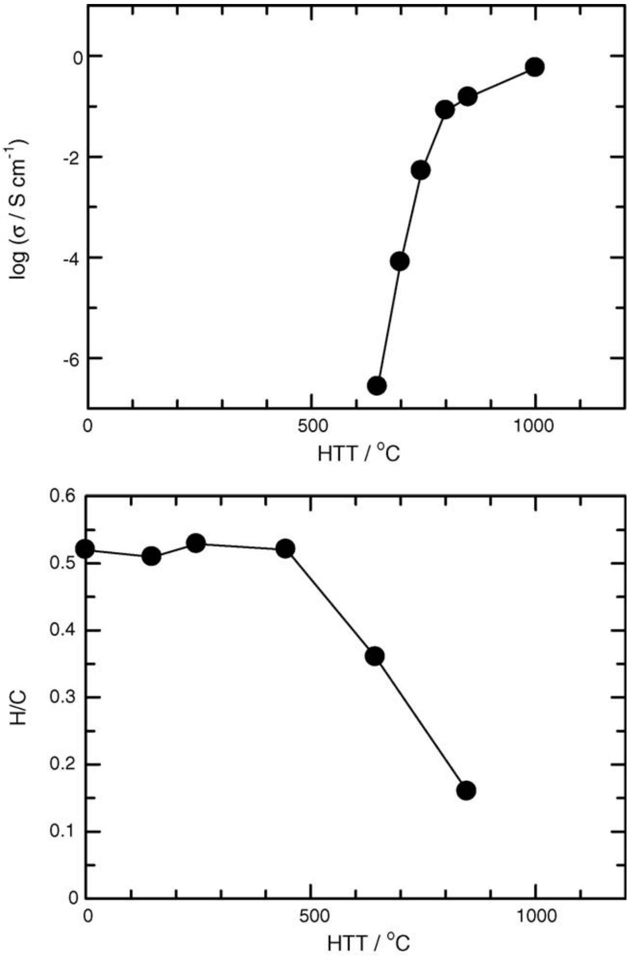

Fig. 5. Changes in electrical conductivity (a) and in H/C atomic ratio (b), with the heat-treatment temperature.

200 °C and the other at approximately 600 °C. It is also observed that the first weight loss accompanied a large exothermal peak in DTA, where a direct TG–MS study revealed that the emitted gaseous product was acetone, the solvent used in the synthesis, which was probably trapped in the crystals of PPPB. The gaseous products in the second weight loss were collected by using a liquid-nitrogen trap, and they were subjected to an analysis by GC–MS. Fig. 4(b) presents a chromatogram of the gaseous products emitted at 665–675 °C. The major substance was naphthalene, which was not included in the original precursor, PPPB. Therefore, ring formation and aromatization reactions occurred within the temperature range. The carbonization mechanism of this compound should also include these chemical processes. Finally, the compound gave a considerably high carbonization yield of 94% at 1000 °C.

Electrical conductivities of the heat-treated samples are plotted in Fig. 5(a), as a function of the heat-treatment temperature, HTT. The conductivity rapidly increased in the temperature range of 650–800 °C, indicating the formation of a carbon structure, i.e., extended π-electron systems. The enlargement of the aromatic system was inferred to take place from the rapid decrease in the H/C atomic ratios in the same HTT range, as shown in Fig. 5(b). From these observations, the actual carbonization took place at approximately just above 600 °C. The rapid development in the electrical conductivity can be understood as an example of the metal-insulator transition found by Carmona and Delhaés [14].

The changes in the X-ray diffraction (XRD) patterns are presented in Fig. 6. The original crystalline pattern of PPPB was maintained up to 150 °C. However, when the sample was heat-treated at 180 °C, where the exothermal reaction and the change in the appearance of the fractured surface occurred, the sharp crystalline peaks completely disappeared. Thus, these three observations, i.e., the large exothermal reaction, partial fusion of crystal, and losing crystallinity of PPPB, are closely related to each other. Of course, the partial fusion should give an endothermal peak rather than an exothermal peak. As we will explain in Section 3.4, the exothermal peak is considered to be caused by the chemical reaction involving triple bonds. The reason that only exothermal peak was observed would be the occurrence of both exothermal and endothermal reactions at the same temperature range, where the caloric value of the exothermal reaction was overwhelmingly large. With increasing the heat-treatment temperature above 650 °C, development of two characteristic bands were observed at approximately 23° and 43°, which were assigned as the (0 0 2) and the (10) diffractions of carbon, respectively. The *d*(0 0 2) spacing values were: 0.4 nm for PPPB650 and PPPB700, 0.38 nm for

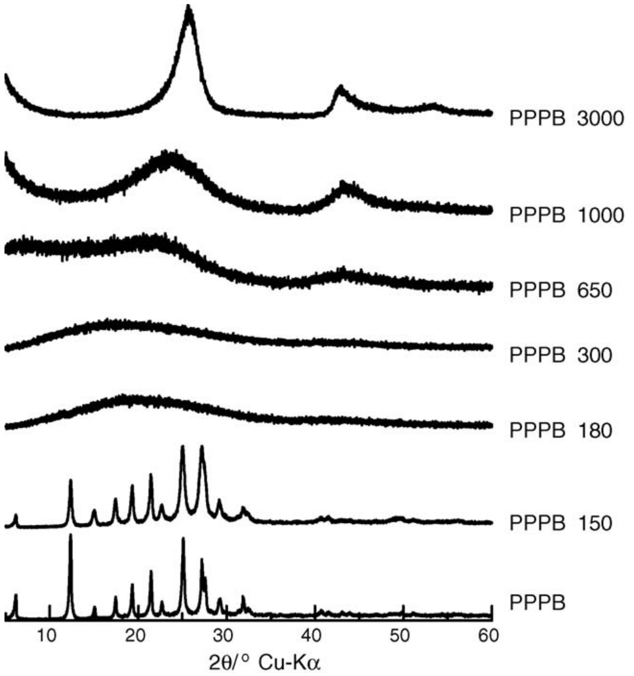

Fig. 6. Changes in the XRD patterns by heat-treatment of PPPB.

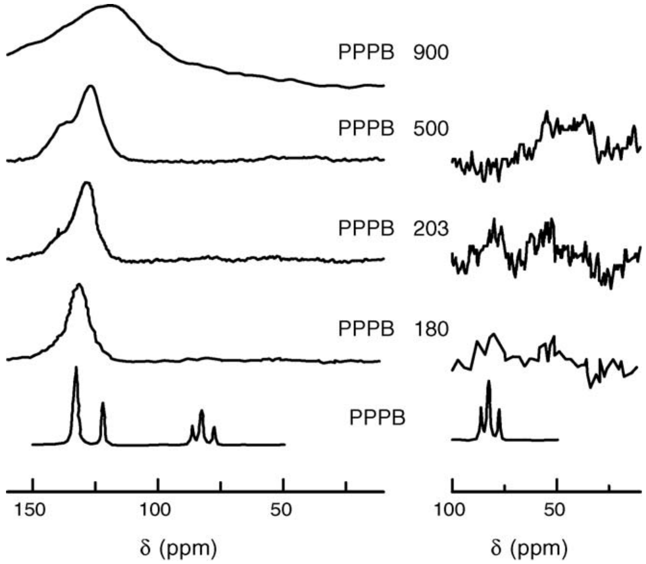

Fig. 7. Changes in ^{13}C NMR spectra by heat-treatment of PPPB.

PPPB850, respectively. In the same figure, the XRD pattern of the sample that had been heat-treated at 3000 °C is given. The sample showed no tendency of graphitization, since it provided only broad diffractions that are characteristic of turbostratic carbons and a larger $d(0\,0\,2)$ spacing of 0.34 nm than graphite, of which the $d(0\,0\,2)$ spacing is 0.3354 nm. The lack of graphitizability indicated that the material before the heat-treatment at 3000 °C included a highly cross-linked structure. This is also evidence of the occurrence of cross-linking formation in the present compound during heat-treatment.

It should be mentioned that the polymer we used in the present study consists of a phenyl group and a butadiyne structure. Baughman et al. predicted an interesting planar molecule, graphyne, that also consists of sp^2 and sp carbon atoms [15]. According to their quantum chemical calculation, graphynes were expected to have band gaps in their band structure, donor–acceptor interaction with potassium, for example. The most striking differences between our present molecule and graphyne are the sequence of the carbon atoms with different conjugation and the substitution number on the phenyl ring, i.e., the sequence of graphyne is sp^2-sp-sp-sp^2, while that of PPPB is sp^2-sp-sp-sp-sp-sp^2, and the number of substitution of graphyne is 6, while that of PPPB is 2. These differences may give non-planar structures to the carbonized PPPB.

3.3. Chemical changes studied by ^{13}C NMR and FT-IR

3.3.1. Changes in sp-carbons

The sp-carbons of PPPB were found to be chemically changed by the heat treatment at 180 °C, which was evidenced by the changes in the intensity of the sp^2-carbon signals in ^{13}C NMR, which were located between 75 and 90 ppm in δ, as shown in Fig. 7. Although only poorly resolved peaks with low S/N ratios were obtained, we can certainly observe the changes in the chemical environment around the sp-carbon moieties in the exothermal stage.

The FT-IR spectroscopy could provide more detailed information on the sp-carbon moieties than ^{13}C NMR did. The intensities of the absorptions concerning the triple bonds decreased in the exothermal stage as shown in Fig. 2. The ≡C–H deformation bands at 637 cm^{-1} and its overtone at 1263 cm^{-1} completely disappeared by the heat treatment at 300 °C. Simultaneously, the stretching band at 3265 cm^{-1} almost disappeared instead of the appearance of an aromatic C–H stretching band at 3034 cm^{-1}. The formation of an isolated triple bond was demonstrated by the appearance of absorption at 2210 cm^{-1} [5,9]. This seems to be formed at the expense of a diacetylene unit that was conjugated with the phenyl group in PPPB, and was represented by a band at 1915 cm^{-1} [10].

In short, by the heat-treatments up to 180 °C, the following events took place: the disappearance of the terminal acetylenic C–H, and the conversion of the Ph–C≡C–C≡C unit in PPPB to an isolated C≡C bond.

3.3.2. Changes in sp^2-carbons

The heat-treatment at 180 °C also induced remarkable changes in the environment of the sp^2-carbons as evidenced by the changes in the sp^2-carbon signal of the ^{13}C NMR, i.e., the two characteristic absorptions at 122 and 133 ppm of PPPB completely changed into a broad absorption with a peak position of 130 ppm. The formation of the broad absorption band indicated the generation of various types of sp^2-carbons, which is commonly observed in the carbonization of organic substances [16]. Such broadening is considered to be due to the overlapping of unresolved lines of a cross-linked material that has become structurally more diverse [17]. An undulation on the main peak appeared at approximately 144 ppm in PPPB180, showing an increase in the intensity with the heat treatment-temperature, and was assigned as the carbons included in C=C or in the phenyl group, which attached to the phenyl ring [18].

The aromatic vibrations in FT-IR shown in Fig. 2, showed an occurrence of substitution reactions on the phenyl group of the compound. The three bands at 544, 833, and 1491 cm^{-1} disappeared by the heat treatment at above 180 °C. The first and the second peaks are the out-of-plane deformations of C–H, and the third peak is aromatic skeletal vibration, which is known to disappear by substitution reactions of the phenyl ring by alkyl groups [9]. The findings on sp^2-carbons both in ^{13}C NMR and FT-IR indicated the occurrence of substitution reactions of the phenyl ring in PPPB.

3.3.3. Formation of *sp^3-carbons*

The formation of sp^3-carbons was found both in ^{13}C NMR and FT-IR during pyrolysis, which were not included in PPPB. In the FT-IR spectra, the formation of an absorption at 2922 cm^{-1} was observed at the temperatures ranging 180–500 °C, which was assigned as a C–H stretching mode of aliphatic groups. The formation of the sp^3-band was also evidenced by the increase in the relative intensity of the absorption at 20–60 ppm.

3.4. *Mechanism for cross-link formation and carbonisation*

Before discussing the chemical process occurring in the pyrolysis, we would like to summarize the experimental findings of this study: (1) partial fusion of PPPB during the exothermal stage, (2) conversion of the terminal acetylene group to aromatic and aliphatic C–H, (3) conversion of the diacetylene unit to an isolated triple bond unit, (4) substitution of hydrogen on the phenyl group by alkyl or alkenyl groups, and (5) introduction of diversity into the sp^2-carbons. Results (2)–(5) probably become good clues in considering the cross-linking mechanism.

Topochemical 1,4-addition is known to be a preparation method for polydiacetylenes from diacetylenes [19,20], where only minimal crystalline structural change occurs during polymerization [10]. Kijima et al. considered that the 1,4-addition was the reaction responsible for the cross-link formation in PPPB [8]. This mechanism was also applied to the cross-link formation in poly[(dimethylsilylene)diacetylene] by Corriu et al. [11]. Both authors evidenced the occurrence of 1,4-addition by the appearance of ene-yne structure peaks in IR spectra. In general, the ene-yne structure has two absorption bands in the acetylene region (2130 cm^{-1}) and in the allene region (1900 cm^{-1}) [11–13]. In the present study, two FT-IR peaks at 1915 and 2200 cm^{-1} were observed. However, these peaks cannot be taken as evidence of the occurrence of the topochemical 1,4-addition, for the following reasons: (1) the band at 1915 cm^{-1} already existed in PPPB, and its intensity decreased with the heat treatment, (2) 1,4-addition polymerization could not give a mechanism including the substitution on the phenyl ring of PPPB, and (3) the cross-link formation accompanied a considerable change in the crystalline state, as shown by the XRD in Fig. 6.

Another possibility of the cross-link formation mechanism is Diels–Alder reactions. Economy et al. considered that the Diels–Alder type reactions were responsible for the cross-link formation in their compounds, 1,3- and 1,4-diethynylbenzene oligomers [7]. However, we consider that the Diels–Alder type reaction between diacetylenes would be difficult, because the diacetylene unit is extremely rigid and hence cannot react with the C≡C part in another diacetylene unit.

Kuroki et al. synthesized a silicon-containing polymer that comprised a backbone of –Si–C≡C–Ph–, MSP-1, and studied its mechanism for the cross-link formation [18]. Based on the spectroscopic analyses and quantum chemical calculations, they concluded that both hydrosilylation and a Diels–Alder type reaction were responsible for the cross-link formation. In the Diels–Alder type reaction mechanism, the diene-like

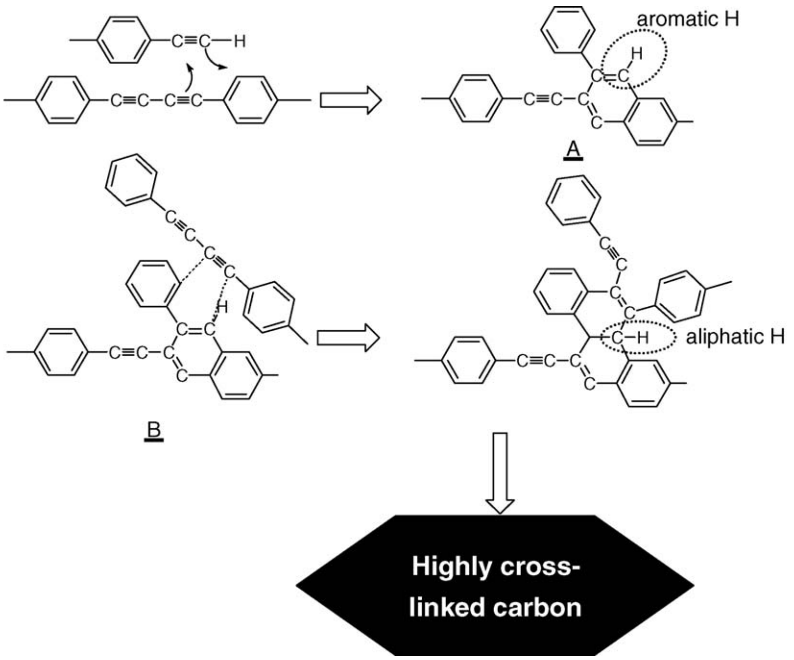

Fig. 8. Proposed mechanism for cross-link formation in the exothermic region and pyrolysis of PPPB.

structure that was formed with the phenyl group and the acetylene group, reacted with an acetylene group on the other molecular chains.

Fig. 8 shows our proposed model for the cross-link formation in PPPB. In constructing this model, we applied Kuroki's mechanism to our case, because PPPB also includes a diene-like structure similar to MSP-1, i.e., the presence of a combined structure of phenyl and diacetylene groups. In this case, the terminal acetylene group was considered to be a dienophile. Taking into account his model, we submit one possible model for the formation of cross-linking in PPPB. When the sample was heat-treated at approximately 180–200 °C, the access of the terminal acetylene group on PPPB to the diene-like structure would be facilitated, because of the increased mobility due to the partial fusion near the temperature. The first scheme is one possible reaction, which resulted in the formation of structure A. Structure A also includes a different diene site enabling the occurrence of another type of cross-link formation as shown by formula B. During these chemical changes, we also observe the formation of aromatic and aliphatic protons as indicated by circles in Fig. 8. Such types of reactions would continuously occur at the temperatures ranging from 180 to 500 °C, judging from the IR and ^{13}C NMR as mentioned in Section 3.3.3. The formation of polynuclear aromatic structures can also be explained by this mechanism. If the cross-links connecting the polynuclear aromatic rings and the body of the pyrolyzed polymer were weak, the unstably connected aromatic molecules would be thermally liberated, which would explain the formation of naphthalene at approximately 600 °C that was detected by GC–MS analysis shown in Fig. 4(b). Finally, such inter-connected polynuclear aromatic structures would result in the formation of non-graphitzing carbons, since they prevent the reorganization of the formed graphenes. Thus, we could present a plausible mechanism for the carbonization of PPPB that satisfactorily explained the experimental results obtained in this study.

4. Conclusion

In this paper we described the results of a study on the cross-link formation and carbonization of PPPB, of which the carbonization yield was as high as 94%. The analyses of the physical and chemical changes of PPPB with the heat-treatment temperature studied by SEM, XRD, ^{13}C NMR and FT-IR provided the following findings:

(1) A large exothermal reaction occurred approximately at 200 °C, and a partial fusion and degradation of crystal structure of PPPB were also observed at the same temperature range.
(2) Around the temperature region mentioned above, the diacetylene structure included in PPPB was converted to isolated triple bonds.
(3) The formations of sp^3 and sp^2 carbons were detected by the heat-treatment temperature of 500 °C.
(4) The actual carbonization of PPPB was found to take place above 600 °C.

Finally we proposed a tentative mechanism for the cross-link formation in PPPB, which is a cause of lesser graphitization by the heat-treatment at 3000 °C.

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