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Thermal analysis and solid-state ^{13}C NMR study of crosslink in polyimides containing acetylene groups in the main chain

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Abstract

Three kinds of aromatic poly(amic acid)s that contain acetylene groups in the main chain were cured in air at temperatures up to 400°C to give intermolecular crosslinked polyimides. The crosslink reactions occurred at the internal acetylene units and the chemical structures thus generated have been investigated by thermal analyses (thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC)) and high resolution solid-state ^{13}C cross polarization (CP)/magic angle spinning (MAS) NMR. The thermal analyses indicated that broad exotherms are observed above 300°C for all the polyimides cured at 200, 300, and 350°C, and the exothermal reactions do not eliminate volatile components from the polyimide structure. The ^{13}C CP/MAS NMR spectra of pyromellitic dianhydride/3,3′-diaminodiphenylacetylene (PMDA/*m*-intA) polyimides show that the signal intensities of the acetylene carbons and the phenyl carbons directly bonded to the acetylene units significantly decrease after curing above 300°C, which indicates that crosslink reactions occurred during curing. In addition, a signal that can be assigned to the C1-carbon of biphenyl structure newly appears after curing, and it grows as the curing temperature increases from 350 to 400°C. From the examination of the chemical shift of the new signal, the most probable crosslink mechanism is the Diels–Alder cycloaddition that occurs between two phenylethynyl groups and provides polycyclic aromatic structures containing biphenyl linkages. The DSC, TGA, and NMR spectra suggest that the same crosslink reactions occur in the other two polyimides, although they occur in the different temperatures ranges. The signal intensities in the NMR spectra indicate that 40–55% of the acetylene carbons remained unreacted even after curing at 400°C. This situation significantly differs from the cases of acetylene- and phenylethynyl-terminated polyimides, in which almost no acetylene units remained after curing as a result of a variety of crosslink reactions. The crosslink reactions occurring at the internal acetylene units are more selective and uniform due to the preferred layer packing of the diphenylacetylene groups and the restricted molecular motion in the solid state. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: ^{13}C cross polarization/magic angle spinning nuclear magnetic resonance; Crosslink; Diels–Alder cycloaddition

1. Introduction

Aromatic polyimides have been used in a wide range of applications in electronic and aerospace industries because of their very high thermal stability and mechanical durability. However, the insoluble and infusible nature of polyimides sometimes results in defects in the manufacturing processes. The development of soluble or thermoplastic polyimides has been attracting major research interests, although such polyimides would have drawbacks such as lower thermal stability and lower solvent resistance. There has been a strong demand for polyimides having good processing ability, high thermal stability, and high solvent resistance. One promising approach is to use crosslink sites that react by thermal curing during processing or after processing. The precursors are soluble in polar organic solvents but the cured products are insoluble and exhibit high thermally stability. The crosslink sites have to be carefully chosen not to deteriorate the inherent high-temperature performance of polyimides. Meyer et al. [1] have reported that the 5 wt%-loss temperature of an imide compound synthesized from 4-phenylethyneylphthalic anhydride and 3-phenylethynyl aniline was improved from 380 to 584°C by thermal curing at 380°C for 30 min. Hou et al. [2] have developed a phenylethynyl-terminated imide (PETI) oligomer using 4-phenylethynylphthalic anhydride as the endcapper. They reported that the glass transition temperature (T_g) was increased from 210 to 352°C by curing at 350°C for 1 h. On the other hand, we have synthesized polyimides containing an acetylene moiety in the internal repeating unit using 3,3′-diaminodiphenylacetylene (*m*-intA) as a diamine [3–9]. The polyimide derived from 2,2′-bis(3,4-dicarboxyphenyl) hexafluoropropane dianhydride (6FDA)

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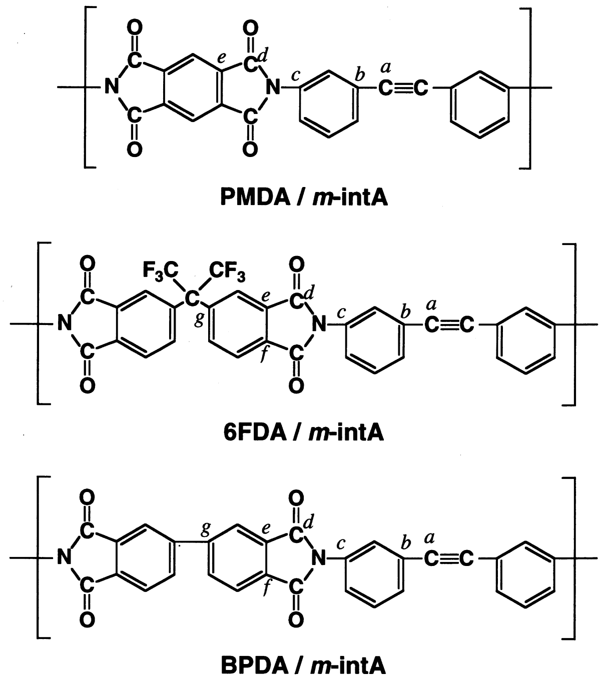


Scheme 1.

and *m*-intA is soluble in several polar organic solvents but it turns out to be insoluble and its T_g is considerably increased from 237 to 330°C after curing at 350°C for 1 h [7]. The cure mechanism of acetylene groups in polyimides has been analyzed using model compounds or acetylene- or phenylethynyl-terminated polyimides [10–16]. The thermal polymerization of arylacetylenes (monofunctional model compounds) and their linear dimers has been studied using chromatography and spectrometry techniques [10,11] and the variations of the chemical structures caused by curing for acetylene-terminated imide oligomers have been investigated using solid-state ^{13}C cross polarization (CP)/magic angle spinning (MAS) NMR [12]. The solid-state ethynyl cure products were reported to contain aromatic structures, condensed polycyclic aromatic structures, backbone addition, and bridge structures. Fang et al. [16] recently examined the cure reactions of phenylethynyl end-capped polyimides and they observed a weak broad signal that is due to a single-bonded structure after cure in addition to double-bonded carbon structures. The former can be derived from polyene structures by intra- and intermolecular Diels–Alder reaction to form cycloolefinic ring or branched structures. In the present study, we investigate the solid-state crosslink reactions of the acetylene groups incorporated into the main chain of polyimides using thermal analyses (thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC)) and solid-state ^{13}C CP/MAS NMR. To our knowledge, this is the first investigation of the cure products of the internal acetylene units in aromatic polyimides using solid-state ^{13}C NMR. Although it has been reported that cure mechanisms occurring at acetylene termini of polyimide are complicated, more uniform and selective mechanisms are expected to occur for the internal acetylene groups because the polyimide chains have more ordered structures, and the molecular motion at the internal acetylene groups should be more restricted than at the termini.

2. Experimental

2.1. Materials

Pyromellitic dianhydride (PMDA) and 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) purchased from Wako Chemical Co. and 6FDA obtained from Hoechst Japan were recrystallized from acetic anhydride and then sublimated under reduced pressure. *N*-methyl-2-pyrrolidone (NMP) was purified by distillation and used as a solvent for the preparation of poly(amic acid). *m*-intA was prepared and purified according to the reported procedure [17].

2.2. Sample preparation

All polyimides were prepared by the conventional two-step synthesis through poly(amic acid)s utilizing corresponding diamine and dianhydride. The preparation of PMDA/*m*-intA is explained below as an example. In a three-necked flask, 0.416 g of *m*-intA (2.0 mmol) was dissolved in 5 g of NMP under nitrogen. An equimolar amount of PMDA (0.436 g) was added and another 4.1 g of NMP was added to control the concentration of the polymer solution to 10 wt%. This mixture was stirred at room temperature for several hours to give a viscous poly(amic acid) solution. The solution thus obtained was dried in vacuo at 50°C for 24 h, and then cured stepwise at 100°C for 1 h and 200°C for 1 h in air to give an uncrosslinked polyimide of PMDA/*m*-intA. Subsequently, the sample was further treated stepwise at 300°C for 1 h, 350°C for 1 h, and 400°C for 30 min in air to give closslinked polyimides. The other two polyimides derived from 6FDA and BPDA were prepared in the same manner.

2.3. DSC and TGA measurements

DSC thermograms were measured with a Seiko DSC-22. Samples of ca. 5 mg in weight were heated from 30 to 500°C at a heating rate of 10°C/min. TGA measurements were performed with a Shimadzu TGA-50. Samples of ca. 10 mg in weight were heated from 30 to 600°C at a heating rate of 5°C/min.

2.4. Solid-state NMR measurements

Solid-state ^{13}C CP/MAS NMR spectra were recorded at 67.8 MHz at ambient probe temperature with a JEOL GSX-270 spectrometer. The strength of the r.f. field used for spin-locking the proton nuclei was equivalent to 45–50 kHz. The

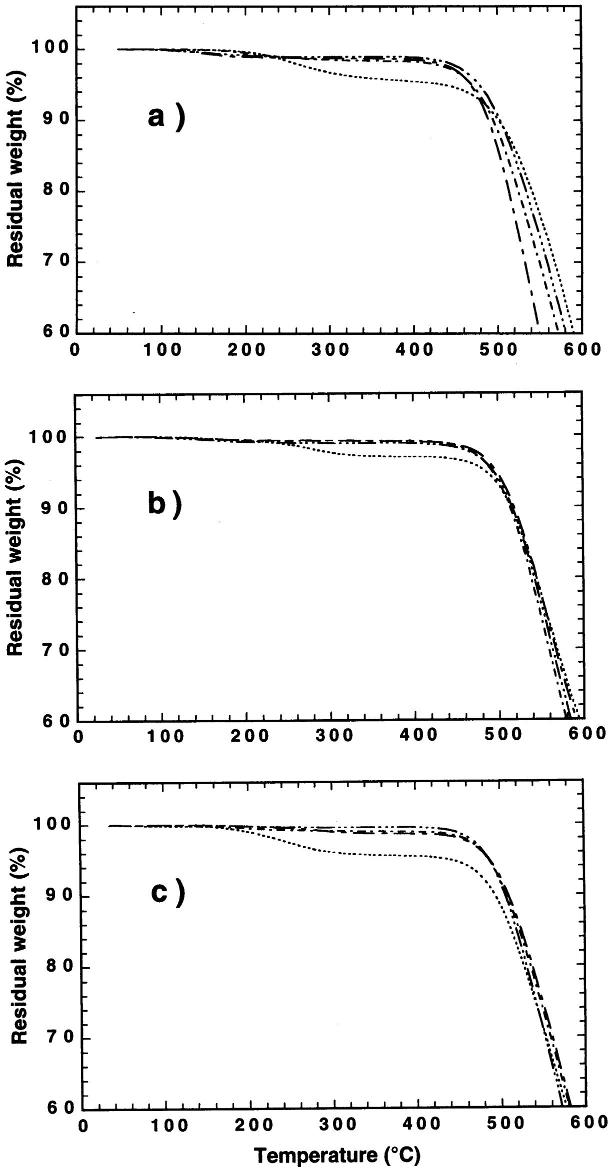


Fig. 1. TGA curves of polyimides: (a) PMDA/*m*-intA; (b) 6FDA/*m*-intA; and (c) BPDA/*m*-intA, cured at (- - - -), 200°C for 1 h; (— - —), 300°C for 1 h; (— ··· —), 350°C for 1 h; and (- ·- · -), 400°C for 30 min.

π/2 pulse duration, the contact time, and the relaxation delay were 5.0–5.5 μs, 2 ms, and 3–4 s, respectively. The spectral width was 20 kHz and the number of data points was 8 K. Free induction decays were accumulated 4000–6400 times for each spectrum to achieve reasonable signal-to-noise ratio. Samples were packed in a cylindrical rotor and spun at the magic angle (54.74°) at rates of 3.0–3.2 kHz. The pulse techniques of total suppression of spinning sidebands (TOSS) and dipolar dephasing (DD) were used to suppress the spinning sidebands and the signals from protonated carbons. ^{13}C chemical shifts were measured via replacement with a sample of adamantane (the lower frequency peak: 29.5 ppm) and were quoted with respect to tetramethylsilane ($(CH_3)_4Si$)).

Table 1
5 wt%-loss temperatures (°C) of polyimides

Polyimide	Curing temperature (°C)			
	200	300	350	400
PMDA/*m*-intA	441	478	485	478
6FDA/*m*-intA	495	506	503	502
BPDA/*m*-intA	450	496	494	494

3. Results and discussion

3.1. Thermal analysis

The TGA curves of PMDA/*m*-intA, 6FDA/*m*-intA, and BPDA/*m*-intA polyimides cured at 200, 300, 350, and 400°C are shown in Fig. 1 and the 5 wt%-loss temperatures are listed in Table 1. The significant decreases in weight between 200 and 300°C, which were observed for the polyimides cured at 200°C, were caused by the elimination of the residual solvent (NMP) and water accompanied by the subsequent imidization reaction. The solvent could not be completely evaporated by curing at 200°C because the boiling temperature of NMP is 202°C, and it forms strong complexes with poly(amic acid) [18,19]. In addition, the imidization of conventional aromatic poly(amic acid) films is reported to proceed toward 300°C [20]. A decrease

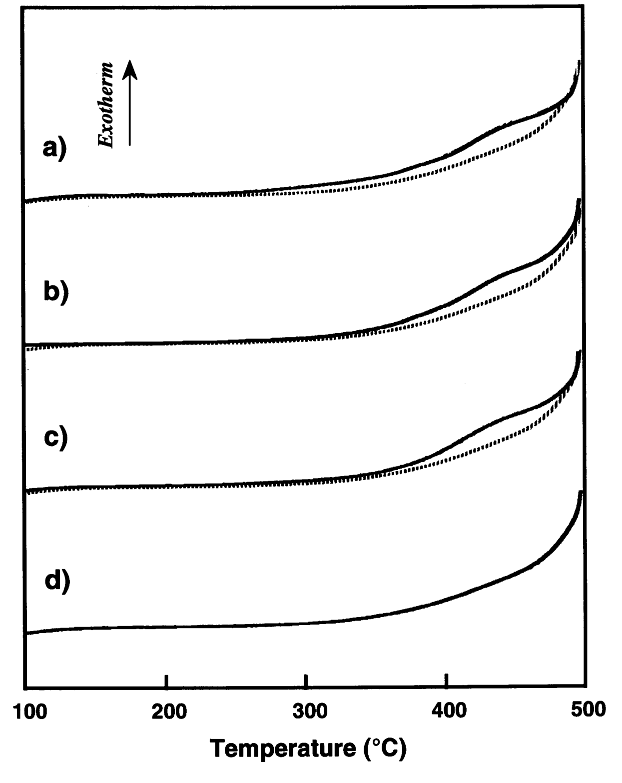


Fig. 2. DSC thermograms of PMDA/*m*-intA polyimide cured at: (a) 200°C; (b) 300°C; (c) 350°C; and (d) 400°C. The thermogram at 400°C is attached to the other thermograms by dotted lines for comparison.

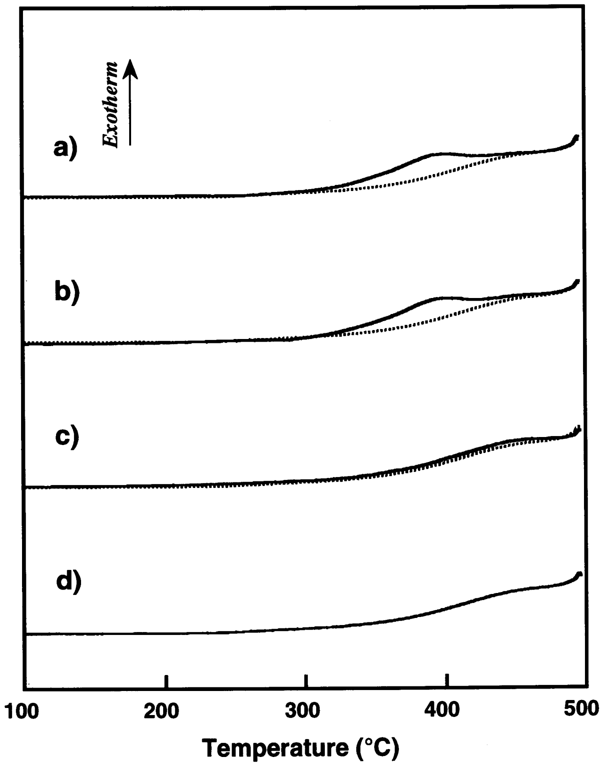


Fig. 3. DSC thermograms of 6FDA/*m*-intA polyimide cured at: (a) 200°C; (b) 300°C; (c) 350°C; and (d) 400°C.

in weight between 200 and 300°C observed for 6FDA/*m*-intA (1.8%) is smaller than that observed for PMDA/*m*-intA (3.1%) and BPDA/*m*-intA (3.1%). This suggests that the imidization reaction occurs at lower temperatures in 6FDA/*m*-intA than in the other polyimides. A solution-state ^{13}C NMR study revealed that the imidization reaction of a polyimide derived from 6FDA and a rod-like fluorinated diamine was almost completed at 200°C [21]. In contrast, the polyimides cured at 300°C and higher temperatures show very similar TGA curves to each other. No significant weight loss was observed between 200 and 400°C but the weights gradually decrease above 400°C for PMDA/*m*-intA, and 420°C for 6FDA/*m*-intA and BPDA/*m*-intA. These weight losses can be attributed to the thermal degradation of the main chain of polyimides. Note that the 5 wt%-loss temperatures of these samples show little dependence on the curing temperature when they were cured above 300°C (Table 1). This will be considered later in relation to the NMR results.

Figs. 2–4 show the DSC thermograms of the three polyimides cured at 200, 300, 350, and 400°C. The DSC thermograms of each polyimide cured at 400°C are attached to the other thermograms by dotted lines for comparison. The gradual ascent of the baselines above 400°C, which is observed in Figs. 2(d) and 4(d), is caused by thermal degradation of the polyimides as observed in the TGA curves. It is clearly shown that additional broad exotherms are observed for all the polyimides cured at 200, 300, and 350°C. For the PMDA/*m*-intA polyimide, a broad exotherm is observed between 250 and 490°C in Fig. 2(a), and between 350 and 490°C in Fig. 2(b) and (c). The exotherms become vigorous at ca. 350°C and reach a maximum at ca. 430°C under a heating rate of 10°C/min, and the amounts of exotherms gradually decrease as the cure temperature increases. These phenomena indicate that a part of the exothermal reactions had already occurred during curing, and it restarts when the DSC temperature passes the curing temperature. However, it is difficult to determine the termination temperatures of the exothermal reactions because the weight loss and accompanying exotherms caused by thermal degradation become vigorous above 400°C. On the other hand, the absence of additional exotherms below 400°C for the polyimides cured at 400°C for 30 min indicates that most of the reactions were completed after curing. Since the endothermal imidization reaction was almost completed at 300°C, the exotherms can be attributed to crosslink reactions that occur at the internal acetylene group of the *m*-intA moiety as has been proposed [22,23]. Furthermore, the absence of a significant weight loss between 350 and 400°C in the TGA curves (Fig. 1) indicates that the crosslink reactions do not eliminate any volatile components from the polyimide structure.

In the DSC thermograms of the 6FDA/*m*-intA polyimide, broad exotherms are also observed in Fig. 3(a) and (b), which start at ca. 300°C, reach a maximum at 390°C, and then almost terminate at 430°C. The exotherm

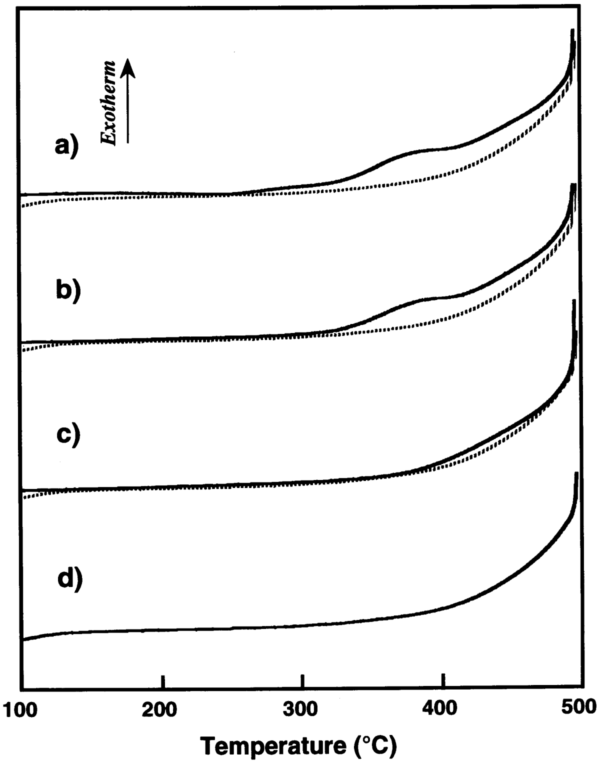


Fig. 4. DSC thermograms of BPDA/*m*-intA polyimide cured at: (a) 200°C; (b) 300°C; (c) 350°C; and (d) 400°C.

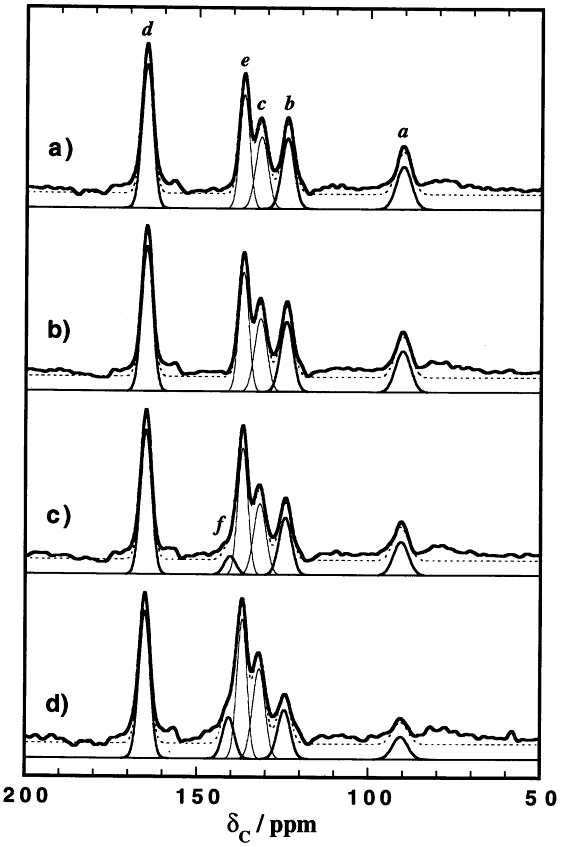


Fig. 5. Solid-state ^{13}C TOSS-DD CP/MAS NMR spectra of PMDA/*m*-intA polyimides cured at: (a) 200°C; (b) 300°C; (c) 350°C; and (d) 400°C. The alphabets over each peak in the spectra correspond to the carbons marked in Scheme 1.

begins in the same temperature range as for PMDA/*m*-intA, but the exotherm in 6FDA/*m*-intA terminates at much lower temperatures. In addition, the DSC of 6FDA/*m*-intA cured at 350°C (Fig. 3(c)) is very similar to that cured at 400°C (Fig. 3(d)), which indicates that the exothermal reactions terminate after curing at 350°C for 1 h. This narrow temperature range of the exotherms shown in Fig. 3(a) and (b) and the disappearance of the exotherm in Fig. 3(c) indicate that the crosslink reactions efficiently occur at lower temperatures in 6FDA/*m*-intA. This is also supported by the fact that the 6FDA/*m*-intA cured at 200°C is soluble in *N*,*N*-dimetylacetoamide (DMAc) and dimethlsulfoxide (DMSO), and that cured at 300°C is partially soluble in the solvents, but became insoluble after curing at 350 and 400°C [7]. The solubility at lower curing temperatures can be ascribed to the absence of intermolecular crosslink structure and the low degree of intermolecular packing originating from the low polarizable hexafluoroisopropylidene ($-C(CF_3)_2-$) groups. In contrast, the insolubility at higher curing temperatures is straightforwardly ascribed to the intermolecular crosslink structures formed between the acetylene groups in the main chain.

In the DSC thermograms of the BPDA/*m*-intA polyimide, a broad exotherm is observed between 250 and 500°C in Fig. 4(a), and a similar exotherm is observed between 310 and 500°C in Fig. 4(b). The magnitude of the exotherm observed for the polyimide cured at 350°C (Fig. 4(c)) is much smaller than that at 300°C. The amounts of the exotherms gradually decrease as the cure temperature increases, and no exotherm is observed in Fig. 4(d). Hence, the exothermal reaction becomes vigorous below 300°C and reaches a maximum at 370–385°C. The exotherms are in the same temperature range as for PMDA/*m*-intA. However, the maximum temperature of the exotherm is displaced to lower temperatures, by 35–50°C, than PMDA/*m*-intA and the sample cured at 350°C shows a similar DSC behavior to that cured at 400°C. Hence, the crosslink reactions in BPDA/*m*-intA occur at lower temperatures than in PMDA/*m*-intA, which coincides with the intermediate DSC behaviors between those of PMDA/*m*-intA and 6FDA/*m*-intA. This is understandable in terms of molecular rigidity and intermolecular interactions. BPDA/*m*-intA has a degree of freedom of bond rotation at the biphenyl linkage of BPDA moiety but it has no $-CF_3$ groups that considerably weaken the intermolecular interactions. Hence, a dianhydride having a higher degree of internal rotation and a lower degree of intermolecular interaction (6FDA > BPDA > PMDA) exhibits a lower maximum temperature of the crosslink reactions.

3.2. ^{13}C CP/MAS NMR and the nature of crosslink reactions

The main object of this work is to investigate the nature of the crosslink reactions at the internal acetylene units using solid-state NMR. Fig. 5 shows the ^{13}C CP/MAS NMR spectra of the PMDA/*m*-intA polyimide cured at 200, 300, 350, and 400°C, together with the signal assignments and the

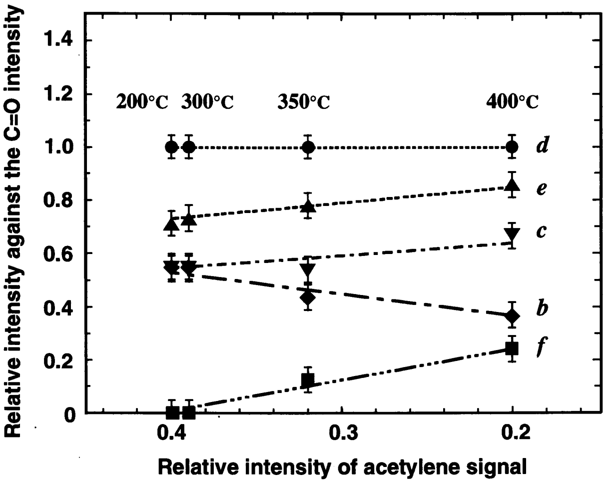
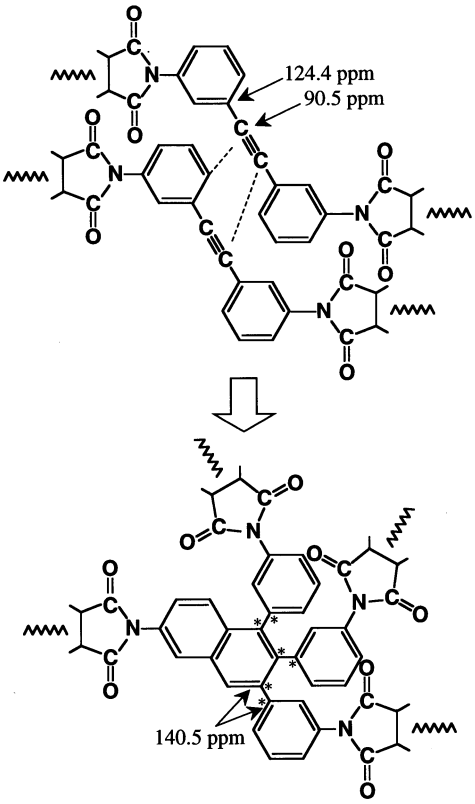


Fig. 6. Comparison of the relative intensities of the NMR signals between the acetylene peak and those of other characteristic peaks: (●), *d*; (▲), *e*; (▼), *c*; (◆), *b*; and (■), *f* of PMDA/*m*-intA polyimide. The signal intensity of the carbonyl carbon (peak *d*) is taken as unity for normalizing the signal intensities of the other peaks.



Scheme 2.

spectral deconvolution using Gaussian functions. The alphabets over each peak in the spectra correspond to the carbons marked in Scheme 1, which gives the structures of the polyimides containing internal acetylene units. The DD (selective observation of quaternary and methyl carbons) pulse sequence was used for the measurements to avoid signal overlapping of protonated and unprotonated carbons. In addition, the TOSS pulse sequence was utilized so that no overlap of spinning sidebands is expected. The peak intensities of the acetylene carbon (peak *a*, 90.5 ppm) and the carbon directly connected to the acetylene group (peak *b*, 124.4 ppm) show significant decreases in Fig. 5(c) and (d) compared with those in Fig. 5(a) and (b). This readily indicates that the acetylene groups in the main chain were changed to other structures by crosslink reactions occurring at temperatures higher than 300°C. In addition, note that a new peak appears at 140.5 ppm (peak *f*) in the spectra of PMDA/*m*-intA and 6FDA/*m*-intA cured above 350°C. This signal is hopefully assigned to a certain carbon in the crosslinked products. No other significant changes are observed in the spectra of the polyimides cured at 350 and 400°C. The relatively low spectral resolution in Fig. 5(d) can be related to the progress in the crosslink reactions, in which the intensity of the new signal is increased and that of the acetylene signal is decreased.

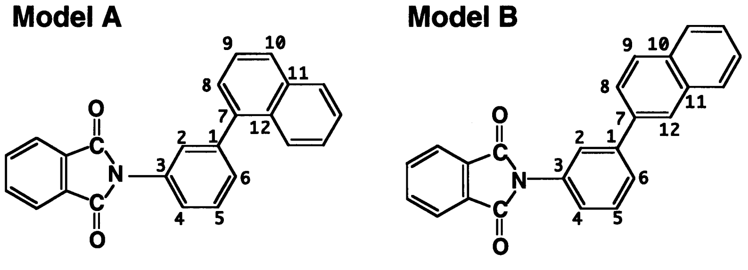
Quantitative estimation of the NMR signal intensities should be helpful for further investigation of the crosslink reactions. Swanson et al. [12] have reported the useful finding that the signal intensities of the carbonyl group in acetylene-terminated polyimides remain unchanged in the cure products, so that it is reasonable to adopt the same assumption for the polyimides in this study. Fig. 6 shows the relationships between the relative intensities of the acetylene peak (*a*) and those of other peaks for the PMDA/*m*-intA polyimide. Signal intensity of each peak was calculated as the integral of the fitted Gaussian function and the signal intensity of the carbonyl carbon peak (*d*) was taken as unity for all the spectra in Fig. 5. One can see the following tendencies as the relative intensity of the acetylene peak decreases. Firstly, the signal assigned to the carbon directly bonded to the acetylene groups (peak *b*) exhibits a linear decrease in intensity. Secondly, the signal intensity of the newly appearing signal (peak *f*) exhibits a linear increase. Thirdly, the signal intensities of peaks *c* and *e* show slight increases. The fact that the relative intensity of the acetylene peak for the polyimide cured at 200°C is very close to that at 300°C indicates that the crosslink does not essentially occur at temperatures below 300°C. Further, the decrease in the intensities of peaks *a* and *b* at higher curing temperatures indicates that the crosslinking becomes vigorous between 350 and 400°C, which agrees well with the characteristic features observed in the DSC measurements. The slight increase in the signal intensities of peaks *c* and *e* may indicate generations of novel aromatic structures. The linear increase in signal *f* against the decrease in *a* supports this view.

The assignment of the signal newly appearing at 140.5 ppm is a key to infer the products of the crosslink reactions. When the Diels–Alder cycloaddition is assumed to occur in the polyimides of this study, one of the most probable crosslink reactions occurring between the internal acetylene units of the polyimides is shown in Scheme 2 (PMDA/*m*-intA is used as a model). According to this scheme, the signal intensity of the C1-carbons (indicated by asterisks) at the biphenyl linkages newly generated by

Table 2

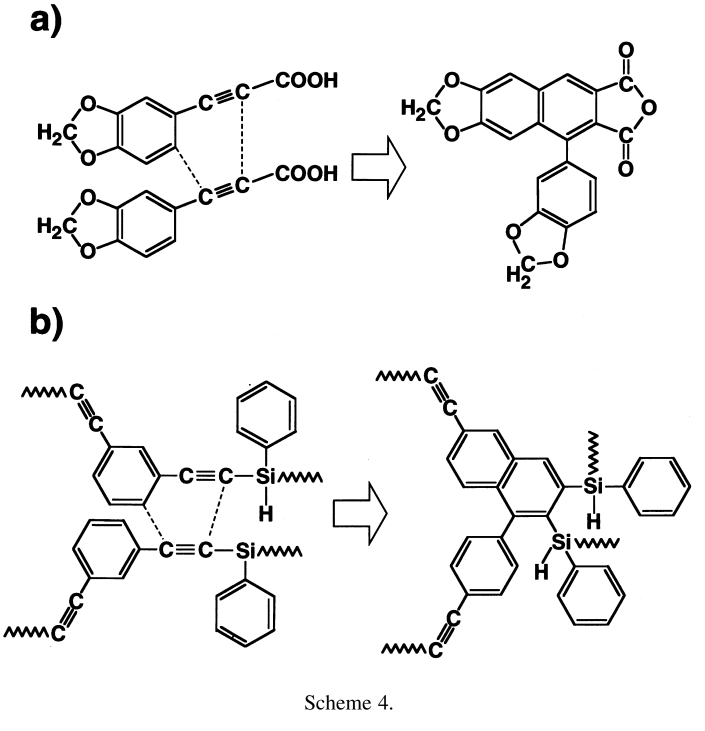
Calculated ^{13}C NMR chemical shifts of the model compounds shown in Scheme 3 (ppm from $Si(CH_3)_4$, errors: ±0.5 ppm). The substituent shielding effects deduced from aromatic compounds [24,25] were used for the calculation (see text). The chemical shifts of the C1-carbons at the biphenyl linkages are in italics

Carbon	Model A	Model B
1	*141.1*	*141.3*
2	124.5	125.9
3	131.8	132.4
4	125.7	126.1
5	128.4	129.0
6	125.3	126.1
7	*140.3*	*138.5*
8	126.9	125.5
9	125.3	128.4
10	127.6	127.4
11	133.8	132.6
12	131.7	133.7



Scheme 3.

the Diels–Alder cycloaddition should be increased with a progress of the reaction. For estimating the ^{13}C NMR chemical shifts (δ_c) of these carbons, we calculated the δ_c of the model compounds (for the products of the Diels–Alder cycloaddition reactions) shown in Scheme 3. (Table 2).The substituent shielding parameters, which were deduced from naphthalene, α- and β-phenylnaphthalene, and *N*-phenylphthalimide, were used for the calculations [24,25]. Note that the calculated δ_c of C1-carbons at the biphenyl linkages in the models (carbons 1 and 7) are located between 138.5 and 141.3 ppm. Hence, the NMR resonance at 140.5 ppm can be presumably assigned to the C1-carbons at the biphenyl linkages incorporated into the newly generated aromatic structures. Kishan and Deiraju [26] have reported that the Diels–Alder cycloaddition reaction of [3,4-(methylenedioxy)phenyl]-propionic acid occurs below 70°C in the solid state and proceeds topochemically to 25% after 30 days at 120°C. Scheme 4(a) shows the Diels–Alder cycloaddition reactions proposed by them. Kuroki and Okita [27] have recently proposed a thermosetting mechanism of poly[(phenylsilylene)ethynylene-1,3-phenyleneethynylene] using solid-state ^{13}C and ^{29}Si NMR. They reported that a thermally stable structure is formed by the Diels–Alder cycloaddition reaction between Ph–C≡C– and –C≡C– components. The Diels–Alder cycloaddition reactions proposed by them are shown in Scheme 4(b). Swanson et al. [12] have reported that the polymerization of acetylene-terminated imide oligomers could occur according to different mechanisms: cyclotrimerization, biradical mechanism, Glaser and Straus coupling, and Friedel–Craft alkenylation. They have reported that the peaks newly appearing in the ^{13}C CP/MAS NMR spectrum can be assigned to the proposed cure products, phenylnaphthalene structures and trisubstituted benzenes, but more than one coupling mechanism are required to form such cure products for the acetylene-terminated imide oligomers. In contrast, the Diels–Alder cycloaddition between the two diphenylacetylene units in *m*-intA diamine moieties, which are incorporated into the polyimides of this study, can readily give such products including biphenyl linkages by one-step reaction as shown in Scheme 2. In addition, the fact that the



Scheme 4.

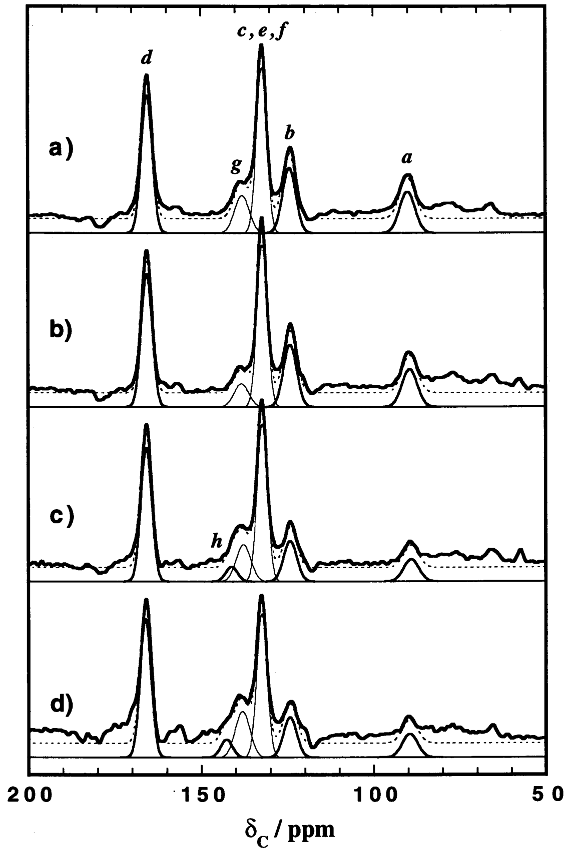


Fig. 7. ^{13}C TOSS-DD CP/MAS NMR spectra of 6FDA/*m*-intA polyimides cured at: (a) 200°C; (b) 300°C; (c) 350°C; and (d) 400°C.

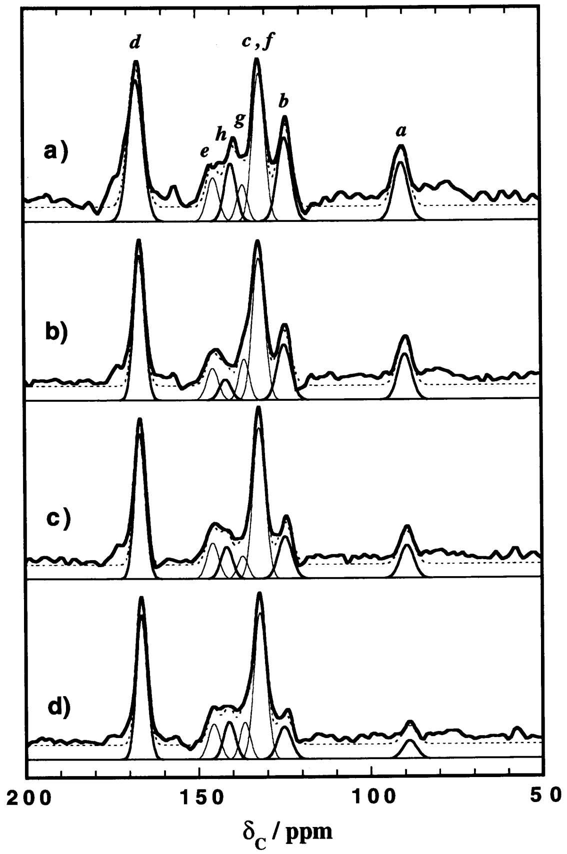


Fig. 8. ^{13}C TOSS-DD CP/MAS NMR spectra of BPDA/*m*-intA polyimides cured at: (a) 200°C; (b) 300°C; (c) 350°C; and (d) 400°C.

Diels–Alder mechanism does not eliminate any volatile components coincides with the TGA results.

^{13}C CP/MAS NMR spectra of 6FDA/*m*-intA and BPDA/*m*-intA polyimides cured at 200, 300, 350, and 400°C are shown in Figs. 7 and 8. The peak intensities of the peaks *a* and *b* also show significant decreases in Figs. 7(c), (d) and 8(c), (d). The relationships between the relative intensities of the acetylene peak (*a*) and those of other peaks for these polyimides are shown in Figs. 9 and 10 in the same manner as in Fig. 6. The NMR spectra (Fig. 8) show that the cross-link reactions in 6FDA/*m*-intA significantly proceed between 300 and 350°C, and the signal of C1-carbons at the biphenyl linkages resonating at 142.0 ppm (*h*) grows in inverse proportion to the decrease of the acetylene peak *a*. In addition, the signal intensity of a resonance at 138.0 ppm (*g*) also shows a gradual increase with increasing curing temperature but the assignment of this signal is unclear. On the other hand, smaller and gradual changes are observed in the magnitude of the acetylene signals between 200 and 300°C for BPDA/*m*-intA polyimides despite the considerable spectral changes between 135 and 150 ppm. As the curing temperature is increased from 200 to 300°C, the half-height-width of the carbonyl signal (*d*) significantly decreases, the signal intensity of the peak at 132.1 ppm (*c*,*f*) increases, and that of the peak at 141.5 ppm (*h*) decreases. Although the assignment of peak *h* in Fig. 8(a) is unclear, the significant decrease in intensity caused by the succeeding imidization reaction suggests that this peak originates from the C1-carbon at the biphenyl linkage of poly(amic acid). A drastic conformational change may

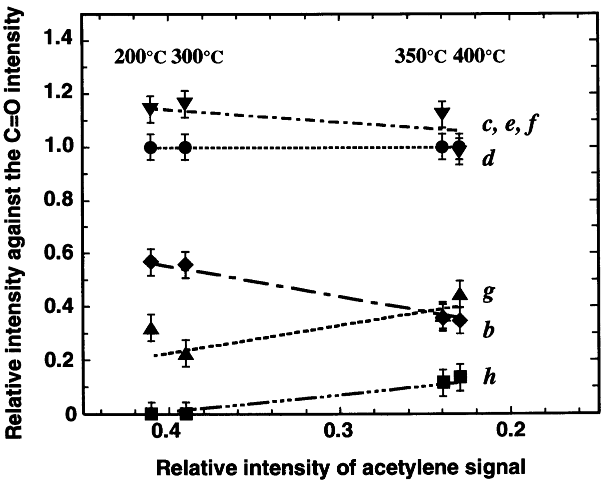


Fig. 9. Comparison of the relative intensities of NMR signals between the acetylene peak and those of other characteristic peaks: (▼), *c*, *e*, *f*; (●), *d*; (▲), *g*; (◆), *b*; and (■), *h* of 6FDA/*m*-intA polyimide.

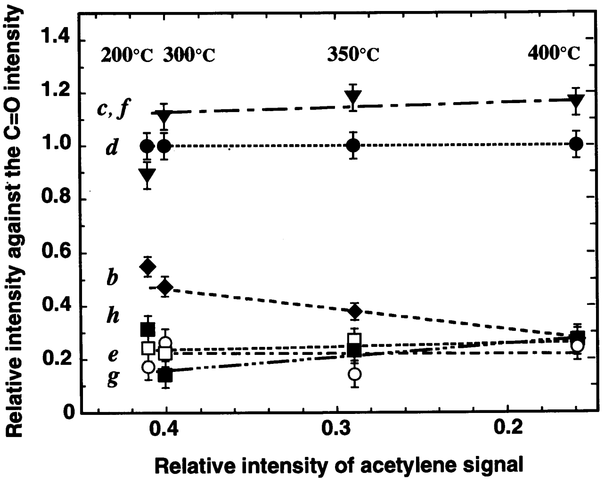


Fig. 10. Comparison of the relative intensities of NMR signals between the acetylene peak and those of other characteristic peaks: (▼), *c*; (●), *d*; (◆), *b*; (□), *e*; (○), *g*; and (■), *h* of BPDA/*m*-intA polyimide.

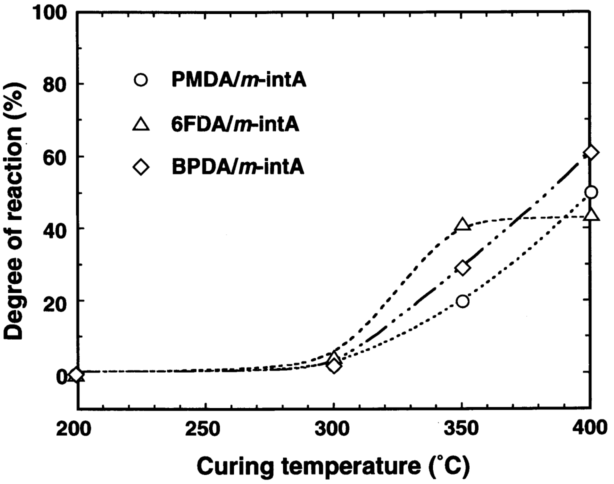


Fig. 11. Curing temperature dependence of the degree of crosslink reactions at the internal acetylene units.

occur at BPDA moiety during imidization and it displaces the peak position. In contrast, the signal intensity of peak *h* gradually increases after curing above 300°C. Hence, the origin of this peak at the initial stage should be different from those observed above 300°C. Since the chemical shift (141.5 ppm) of peak *h* is close to those of the newly appearing peaks in PMDA/*m*-intA (140.5 ppm) and 6FDA/*m*-intA (142.0 ppm) cured at 350 and 400°C, the increase in intensity can be interpreted by the generation and growth of a new peak. In addition, the signal intensity of the phenyl carbon directly bonded to the acetylene group (*b*) gradually decreases in proportion to the magnitude of the acetylene peak above 300°C. Considering these results, the Diels–Alder cycloaddition is also the most probable crosslink mechanism for 6FDA/*m*-intA and BPDA/*m*-intA polyimides.

3.3. The degree of reaction at the acetylene units

^{13}C CP/MAS NMR spectra of the polyimides clearly show that significant amounts of the acetylene carbons remained unreacted even after curing at 400°C for 30 min (Figs. 5(d), 7(d), 8(d)). Fig. 11 shows the dependence of the degree of crosslink reactions at the internal acetylene units on the curing temperature. They were calculated from the signal intensities of the residual acetylene carbons in the ^{13}C CP/MAS spectra. The signal intensities of the polyimides cured at 200°C were taken as references because no crosslink reactions occur at this temperature. It is clearly shown that the crosslink reactions in the PMDA/*m*-intA and BPDA/*m*-intA polyimides begin above 300°C, become vigorous around 350°C, and continue until 400°C. On the other hand, the crosslink reactions in 6FDA/*m*-intA occur more vigorously between 300 and 350°C, and almost terminate at 350°C. These facts agree well with the DSC data as stated above and the crosslink reactions of this polyimide occur within a narrow temperature range, suggesting more selective and uniform reactions than the other two polyimides. Moreover, even after curing at 400°C, 50, 55, and 40% of the acetylene carbons remained unreacted in PMDA/*m*-intA, 6FDA/*m*-intA, and BPDA/*m*-intA, respectively. These low degrees of crosslink reactions can be ascribed to the inherent molecular rigidity of the fully aromatic polyimides and the rigid intermolecular network structures generated by the crosslink reactions between the acetylene units in the main chain. This situation significantly differs from the cases of acetylene- and phenylethynyl-terminated polyimides, in which almost no acetylene units remained after curing as a result of a variety of crosslink reactions [10–12]. Although crystal structures of polyimides derived from *m*-intA diamine have never been reported, the face-to-face arrangement of the diamine moieties of polyimides, which is called ‘preferred layer packing’, has been reported for the crystal structures of a rigid-rod polyimide [28] and imide oligomers [29]. The same situation is likely to occur in the molecular packing of the polyimides of this study. Although the polyimides have fully aromatic rigid structures and exhibit no glass transition, the preferred layer packing can facilitate intermolecular crosslink reactions because minimal motions are required for the initiation of the reaction. The rigid intermolecular network structures thus generated should strictly hinder the subsequent reactions of unreacted acetylene units located in the neighborhood. Hence, these situations can explain the selective and uniform crosslink reactions occurring between the acetylene units incorporated into the main chain. The reactions may not proceed to the complicated chemical reactions as it has been proposed for acetylene- and phenylethynyl-terminated polyimides [10–12]. Furthermore, the 5 wt%-loss temperatures of the polyimides cured at 300, 350, and 400°C are almost the same (Table 1), indicating that the extent of intermolecular crosslink reactions does not affect the final stability of the polyimides against thermal degradation. This also suggests that the unreacted internal acetylene units are preserved after curing and the post cure above 400°C causes structural degradation of the main chain because of the difficulty in the subsequent crosslink reactions.

4. Conclusions

The thermal curing behaviors and crosslink reactions occurring for the three kinds of fully aromatic polyimide containing internal acetylene units have been investigated using TGA, DSC, and solid-state ^{13}C NMR. No significant weight loss was observed between 300 and 400°C by TGA but distinct exotherms were observed above the curing temperatures by DSC for the polyimide cured at 200, 300, and 350°C. In contrast, such exotherms were not observed for the polyimides cured at 400°C. The exothermal crosslink reactions occurring at the internal acetylene units begin above 300°C and almost terminate after curing at 350°C for 6FDA/*m*-intA, and at 400°C for PMDA/*m*-intA and BPDA/*m*-intA. They do not eliminate any volatile components from the polyimide chains. The order of the maximum temperatures of the crosslink reactions observed by DSC is 6FDA/*m*-intA < BPDA/*m*-intA < PMDA/*m*-intA, which indicates that a dianhydride having a higher degree of internal rotation and a lower degree of intermolecular interactions (6FDA > BPDA > PMDA) decreases the maximum temperature. As the curing temperature increases, the signal intensities of the acetylene carbons and the phenyl carbons bonded to the acetylene unit decrease, and that of the C1-carbon at the biphenyl linkage increases. These observed phenomena are well expained by the Diels–Alder cycloaddition reaction (Scheme 2) that provides a variety of biphenyl linkages and naphthalene-ring structures. The ^{13}C CP/MAS NMR spectra show that almost half of the acetylene carbons remained unreacted even after curing at 400°C for 30 min. The face-to-face arrangement of the diamine moieties of polyimides (preferred layer packing), which has been observed for a rigid polyimide, can facilitate the selective and uniform crosslink reactions between the acetylene units incorporated into the main chain.

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