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# Thermal crosslinking of acetylene-containing polymers obtained by radical polymerization of aromatic enynes

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## Abstract

Acetylene-containing polymers, obtained by the radical polymerization of 4-substituted aromatic enynes, were subjected to the thermal crosslinking reaction on the basis of the reactivity of the acetylene moieties. The crosslinking occurred from ca. 140°C to give an insoluble product. The crosslinking was supposed to be the irreversible reaction of the acetylene moieties to give new conjugated structure from the IR and UV–vis spectra. The steric bulkiness of the substituents tend to restrain the crosslinking and decline the decomposition temperature of the polymers. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords*: Enyne; Radical polymerization; Thermosetting resin

## 1. Introduction

Since acetylene-containing polymers are attractive candidates as reactive and functional polymers based on the characteristics of the acetylene moieties, many synthetic approaches such as polycondensation [1–3] and vinyl polymerization [4–12] of acetylene containing monomers have been made to obtain these polymers. Among the possible applications of acetylene-containing polymers, that based on the thermal oligomerization of the acetylene moieties providing crosslinked materials [1–5,7] is of importance because it proceeds without producing volatile by-products [13–15]. In the cases of polymers having arylethynyl groups, this feature has been applied to realize composites with excellent mechanical performance [1–3].

As we reported previously, the radical polymerization of 4-phenyl-1-buten-3-yne (**1**) and its derivatives gives polymers consisting of the specific 1,2-polymerized units (i.e. the units having arylethynyl groups in the side chain) (Scheme 1) [7,8]. The thermal analysis of poly(**1**) (**P1**) indicated that **P1** undergoes thermal crosslinking reaction at ca. 140°C giving rise an insoluble polymer [7].

Because the decomposition temperature of **P1** is higher than the conventional polymers having analogous structure, **P1** and its derivatives may serve as novel thermosetting resins. To explore this possibility and to clarify the origin of this higher thermal stability, we describe herein the details of thermal crosslinking behavior of **P1** and other polyenynes bearing aromatic substituents.

## 2. Experimental part

### 2.1. Materials and instruments

Polymers (**P1**–**P4**) were prepared by the radical polymerization of **1**, 4-(4-methoxyphenyl)-1-buten-3-yne (**2**), 4-(4-chlorophenyl)-1-buten-3-yne (**3**), and 4-(4-methylphenyl)-1-buten-3-yne (**4**), respectively, as previously reported [7,8]. Other reagents were used as received.

$^1$H- and $^{13}$C nuclear magnetic resonance (NMR) spectra were measured on a JEOL EX-400 instrument using tetramethylsilane as an internal standard (400 and 100 MHz for $^1$H- and $^{13}$C NMR, respectively). Fourier transform infrared (FT-IR) spectra were measured on a JASCO FT/IR-5300 instrument. Gel permeation chromatography (GPC) measurements were performed on a Tosoh TSK-gel G2500HXL and G3000HXL or G4000HXL and G5000HXL tandem columns using tetrahydrofuran (THF) as an eluent at 30°C. Polystyrene standards were used for

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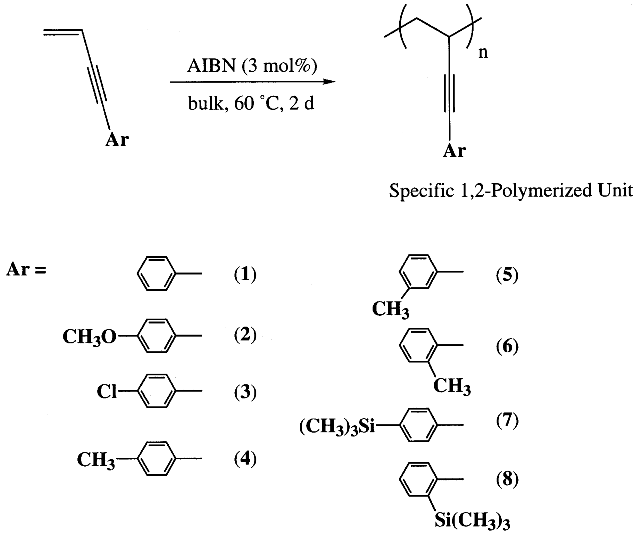

Scheme 1.

calibration. Thermogravimetry (TG) measurements were performed on a Shimadzu TGA-50 instrument. Differential scanning calorimetry (DSC) measurements were performed on a Shimadzu DSC-60 instrument. TG and DSC measurements were performed under $N_2$ at the scan rate of 10°C/min. UV–vis spectrum of thin film of **P1** was measured by a Shimadzu UV-2100 instrument. The film was cast on a glass plate from 0.02 M solution of **P1** in chloroform and measured before and after curing under air at 270°C for 2 h.

### *2.2. Monomer syntheses*

#### *2.2.1. Synthesis of 4-(3-methylphenyl)-1-buten-3-yne (**5**)*

In a 300-ml three-neck round bottom flask equipped with a Dimroth condenser and a dropping funnel, $PdCl_2$ (26 mg, 0.15 mmol), $PPh_3$ (79 mg, 0.3 mmol), CuI (57 mg, 0.3 mmol), vinyl bromide (5.72 g, 54 mmol) were dissolved in 120 ml of diethylamine under nitrogen atmosphere. Then (3-methylphenyl)acetylene (4.15 g, 36 mmol) was added dropwise from the dropping funnel and stirred for 1 day. The resulting suspension was filtrated and the solvent was evaporated. The remaining organic layer was dried over $CaCl_2$ and distilled over $CaH_2$ (43°C/0.6 mm Hg). Yield 84% (4.26 g, 30 mmol). $^1$H NMR ($CDCl_3$): $\delta$ 2.33 (s, 3H, C*H*$_3$–), 5.53 (dd, $J = 2.0$, 11.1 Hz, 1H, *Z*-C*H*$_2$=C), 5.72 (dd, $J = 2.4$, 17.7 Hz, 1H, *E*-C*H*$_2$=C), 5.98 (dd, $J = 11.4$, 17.7 Hz, 1H, CH$_2$=C*H*R), 7.26–7.41 (4H, –C$_6$*H*$_4$–) ppm; $^{13}$C NMR ($CDCl_3$): $\delta$ 21.2 (*C*H$_3$–), 87.7 (–*C*≡C–Ar), 90.1 (–C≡*C*–Ar), 117.2 (*C*H$_2$=C), 122.9, 126.7, 128.2, 129.2, 132.1, 138.0 (–*C*$_6$H$_4$–), 128.6 (CH$_2$=*C*) ppm; IR (neat): 3100, 3040, 3011, 2922, 2860, 2203, 1942, 1846, 1784, 1609, 1580, 1485, 1451, 1381, 1290, 1181, 1096, 1042, 970, 918, 880, 835, 783, 691 cm$^{-1}$.

#### *2.2.2. Synthesis of 4-(2-methylphenyl)-1-buten-3-yne (**6**)*

The same procedure was followed as described for **5** using (2-methylphenyl)acetylene (4.31 g, 37 mmol) in place of (3-methylphenyl)acetylene. Distillation from $CaH_2$ gave pure **6** in 62% yield (40°C/1.0 mm Hg). $^1$H NMR ($CDCl_3$): $\delta$ 2.43 (s, 3H, C*H*$_3$–), 5.52 (dd, $J = 1.6$, 10.6 Hz, 1H, *Z*-C*H*$_2$=C), 5.72 (dd, $J = 1.5$, 16.1 Hz, 1H, *E*-C*H*$_2$=C), 6.05 (dd, $J = 11.0$, 17.4 Hz, 1H, CH$_2$=C*H*R), 7.26–7.41 (4H, –C$_6$*H*$_4$–) ppm; $^{13}$C NMR ($CDCl_3$): $\delta$ 20.6 (*C*H$_3$–), 88.9 (–*C*≡C–Ar), 92.0 (–C≡*C*–Ar), 117.3 (*C*H$_2$≡C), 122.2, 125.5, 126.5, 129.4, 131.9, 140.1 (–*C*$_6$H$_4$–), 128.3 (CH$_2$=*C*) ppm; IR (neat): 3100, 3063, 3011, 2949, 2922, 2861, 2213, 2182, 1952, 1919, 1844, 1802, 1734, 1701, 1605, 1541, 1485, 1456, 1410, 1379, 1290, 1260, 1198, 1159, 1117, 1076, 1042, 970, 918, 864, 756, 716 cm$^{-1}$.

#### *2.2.3. Synthesis of 4-(4-trimethylsilylphenyl)-1-buten-3-yne (**7**)*

The same procedure was followed as described for **5** using (4-trimethylsilylphenyl)acetylene (0.25 g, 1.4 mmol) in place of (3-methylphenyl)acetylene. Pure **7** was isolated by silica gel column chromatography (eluent:hexane) in 73% yield ($R_f = 0.5$). $^1$H NMR ($CDCl_3$): $\delta$ 0.26 (s, 9H, C*H*$_3$–), 5.45 (dd, $J = 2.0$, 11.1 Hz, 1H, *Z*-C*H*$_2$=C), 5.73 (dd, $J = 2.0$, 17.6 Hz, 1H, *E*-C*H*$_2$=C), 6.01 (dd, $J = 11.2$, 17.5 Hz, 1H, CH$_2$=C*H*R), 7.38–7.49 (4H, –C$_6$*H*$_4$–) ppm; $^{13}$C NMR ($CDCl_3$): $\delta$ −1.3 (*C*H$_3$–), 88.4 (–*C*≡C–Ar), 90.1 (–C≡*C*–Ar), 117.2 (*C*H$_2$=C), 123.4, 130.6, 133.2, 141.1 (–*C*$_6$H$_4$–), 126.9 (CH$_2$=*C*) ppm; IR (neat): 3102, 3065, 3013, 2957, 2897, 2857, 2218, 1917, 1844, 1736, 1719, 1655, 1609, 1534, 1499, 1410, 1391, 1306, 1290, 1250, 1190, 1109, 1020, 970, 918, 867, 820, 758, 735, 716, 693, 631 cm$^{-1}$.

#### *2.2.4. Synthesis of 4-(2-trimethylsilylphenyl)-1-buten-3-yne (**8**)*

The same procedure was followed as described for **5** using (2-trimethylsilylphenyl)acetylene [16] (5.22 g, 30 mmol) in place of (3-methylphenyl)acetylene. Distillation from $CaH_2$ gave pure **8** in 84% yield (47°C/0.5 mm Hg). $^1$H NMR ($CDCl_3$): $\delta$ 0.28 (s, 9H, C*H*$_3$–), 5.45 (dd, $J = 2.0$, 11.2 Hz, 1H, *Z*-C*H*$_2$=C), 5.62 (dd, $J = 2.0$, 17.6 Hz, 1H, *E*-C*H*$_2$=C), 5.95 (dd, $J = 11.6$, 17.6 Hz, 1H, CH$_2$=C*H*R), 7.26–7.41 (4H, –C$_6$*H*$_4$–) ppm; $^{13}$C NMR ($CDCl_3$): $\delta$ −1.1 (*C*H$_3$–), 90.8 (–*C*≡C–Ar), 91.7 (–C≡*C*–Ar), 117.4 (*C*H$_2$=C), 126.4, 127.4, 128.7, 132.3, 133.9, 142.5 (–*C*$_6$H$_4$–), 128.3 (CH$_2$≡*C*) ppm; IR (neat): 3102, 3075, 3052, 3009, 2955, 2899, 2216, 1931, 1838, 1726, 1709, 1659, 1607, 1588, 1555, 1462, 1429, 1408, 1290, 1248, 1161, 1126, 1090, 1067, 1038, 968, 916, 841, 756, 713, 696, 667 cm$^{-1}$.

### *2.3. Synthesis of polymers*

#### *2.3.1. Radical polymerization of **5***

A mixture of **5** (0.713 g, 5.0 mmol) and 2,2′-azobis(isobutyronitrile) (AIBN, 0.025 g, 0.15 mmol) was heated at 60°C for 2 days in a degassed sealed tube. After the reaction, the resulting glassy solid was dissolved in THF and the

Table 1
Radical polymerization of 4-substituted enynes (the polymerization was carried out in bulk at 60°C for 2 days using 3 mol% of AIBN)

| Run | Monomer | Yield (%)[a] | $M_n$[b] | $M_W/M_n$[b] |
|---|---|---|---|---|
| 1 | **1**[c] | 71 | 3,400 | 1.49 |
| 2 | **2**[c] | 80 | 5,400 | 1.61 |
| 3 | **3**[c] | 62 | 5,100 | 1.28 |
| 4 | **4**[c] | 41 | 5,900 | 1.26 |
| 5 | **5** | 28 | 6,400 | 1.25 |
| 6 | **6** | 37 | 5,500 | 1.30 |
| 7 | **7** | 51 | 4,900 | 1.26 |
| 8 | **8** | 19 | 3,800 | 1.24 |

[a] Isolated yield after precipitation with methanol.
[b] Estimated by GPC (THF, polystyrene standard).
[c] See Ref. [8].

solution was poured into methanol to precipitate the polymer. The methanol-insoluble product was collected by filtration and dried under vacuum (yield 0.265 g, 37%). $^1$H NMR (CDCl$_3$): $\delta$ 0.4–4.3 (C$H_3$–, –C$H_2$–, –C$H$–), 6.0–7.8 (–C$_6H_4$–) ppm; $^{13}$C NMR (CDCl$_3$): $\delta$ 21.2–23.0 ($C$H$_3$–), 25.0–35.0 (–$C$H$_2$–), 35.0–48.5 (–$C$H–), 79.2–83.8 (–$C$≡C–Ar), 89.0–96.0 (–C≡$C$–Ar), 120.0–138.5 (–C$_6$H$_4$–) ppm; IR (film): 3034, 2920, 2859, 2733, 2226, 1941, 1873, 1784, 1688, 1601, 1580, 1485, 1449, 1377, 1350, 1310, 1217, 1167, 1092, 1040, 999, 972, 905, 880, 783, 758, 690, 667 cm$^{-1}$.

### *2.3.2. Radical polymerization of **6***

The same procedure was followed as described for **5** using **6** (0.707 g, 5.0 mmol) in place of **5**. Yield 28% (0.196 g). $^1$H NMR (CDCl$_3$): $\delta$ 0.5–4.2 (C$H_3$–, –C$H_2$–, –C$H$–), 5.8–8.1 (–C$_6H_4$–) ppm; $^{13}$C NMR (CDCl$_3$): $\delta$ 18.0–22.7 ($C$H$_3$–), 25.0–35.0 (–$C$H$_2$–), 35.0–48.3 (–$C$H–), 78.6–83.2 (–$C$≡C–Ar), 94.6–99.7 (–C≡$C$–Ar), 123.6–145.0 (–C$_6$H$_4$–) ppm; IR (film): 3061, 3019, 2922, 2855, 2222, 1948, 1914, 1881, 1802, 1723, 1599, 1572, 1485, 1454, 1377, 1350, 1217, 1159, 1115, 1044, 941, 862, 756, 716 cm$^{-1}$.

Table 2
Decomposition temperature of polyenynes (determined by thermogravimetric analyses (10°C/min, under nitrogen))

| Polymer ($M_n$) | $T_d$ (°C)[a] | $T_{d10}$ (°C)[b] |
|---|---|---|
| **P1** (3,400) | 382 | 401 |
| **P2** (5,400) | 374 | 394 |
| **P3** (5,100) | 366 | 393 |
| **P4** (5,900) | 373 | 387 |
| **P5** (6,400) | 388 | 404 |
| **P6** (5,500) | 365 | 388 |
| **P7** (4,900) | 338 | 366 |
| **P8** (3,800) | 285 | 290 |

[a] Decomposition temperature.
[b] Temperature for 10 wt% loss.

### *2.3.3. Radical polymerization of **7***

The same procedure was followed as described for **5** using **7** (0.185 g, 0.9 mmol) in place of **7**. Yield 51% (0.094 g). $^1$H NMR (CDCl$_3$): $\delta$ −0.4–0.6 (C$H_3$–), 0.7–3.8 (–C$H_2$–, –C$H$–), 6.2–7.9 (–C$_6H_4$–) ppm; $^{13}$C NMR (CDCl$_3$): $\delta$ −1.6–1.1 ($C$H$_3$–), 22.3–34.0 (–$C$H$_2$–), 34.0–47.5 (–$C$H–), 80.9–85.7 (–$C$≡C–Ar), 91.0–96.9 (–C≡$C$–Ar), 123.6–147.5 (–C$_6$H$_4$–) ppm; IR (film): 3063, 3015, 2955, 2897, 2855, 2226, 1914, 1869, 1802, 1655, 1595, 1535, 1501, 1449, 1391, 1306, 1250, 1188, 1109, 1020, 951, 841, 820, 756, 716, 693, 669, 629 cm$^{-1}$.

### *2.3.4. Radical polymerization of **8***

The same procedure was followed as described for **5** using **8** (0.398 g, 2.0 mmol) in place of **8**. Yield 19% (0.076 g); $^1$H NMR (CDCl$_3$): $\delta$ −0.5–0.6 (C$H_3$–), 0.7–4.0 (–C$H_2$–, –C$H$–), 6.0–7.6 (–C$_6H_4$–) ppm; $^{13}$C NMR (CDCl$_3$): $\delta$ −2.1–3.8 ($C$H$_3$–), 24.0–35.0 (–$C$H$_2$–), 35.0–47.5 (–$C$H–), 81.5–85.8 (–$C$≡C–Ar), 92.5–97.1 (–C≡$C$–Ar), 123.3–148.5 (–$C_6$H$_4$–) ppm; IR (film): 3409, 3052, 2955, 2897, 2222, 1930, 1726, 1709, 1692, 1659, 1584, 1530, 1462, 1427, 1350, 1309, 1248, 1217, 1126, 1076, 839, 758, 721, 689 cm$^{-1}$.

## 3. Results and discussion

### *3.1. Polymer synthesis*

The acetylene-containing polymers (**P5**–**P8**) were obtained by the radical polymerization of 4-substituted enynes (**5**–**8**) in bulk at 60°C for 2 days using AIBN as an initiator in same manners with other polyenynes previously reported (Scheme 1, Table 1) [7,8]. The polymers (**P5**–**P8**) consisted of the specific 1,2-polymerized units as were the cases of other polyenynes, which was confirmed by $^1$H NMR, $^{13}$C NMR, and IR spectra. The molecular weights of **P5**–**P8** ranged from 3800 to 6400, being in the range to that of polymers from aromatic enynes. The details of the radical polymerization of **1**–**4** have been described in Ref. [8].

### *3.2. Thermal decomposition of polyenynes*

TG measurement of **P1** indicated that the decomposition temperature of **P1** ($T_{d10} = 401$°C) was significantly higher than that of polymers having aromatic substituents such as polystyrene ($T_{d10} = 343$°C [17]). The TG analyses of various polyenynes were performed to evaluate the substituent effect and to understand the reason for higher thermal stability of polyenynes (Table 2). As a result, the polymers with sterically less hindered aromatic moieties (**P2**–**P7**) proved to have higher decomposition temperature regardless of the electronic character of the substituent (e.g. **P2** having an electron-donating group exhibited $T_d =$ 374°C and **P3** having an electron-withdrawing group exhibited $T_d = 366$°C). On the other hand, **P8** having bulky

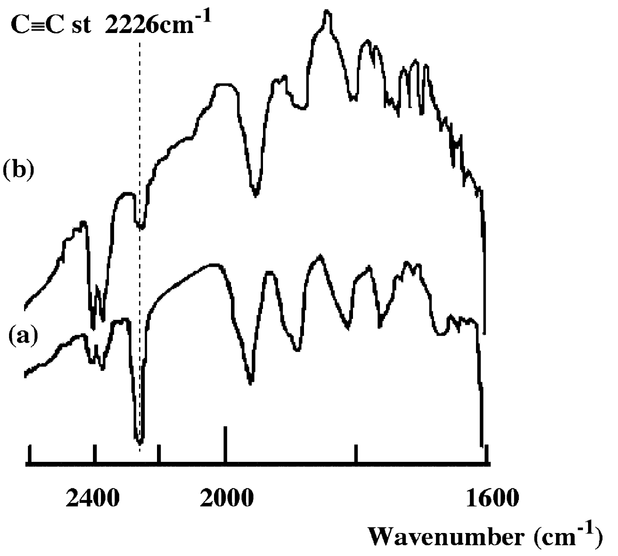

Fig. 1. DSC curves of **P1** at the first (a) and the second (b) scans (under $N_2$, scan rate 10°C/min).

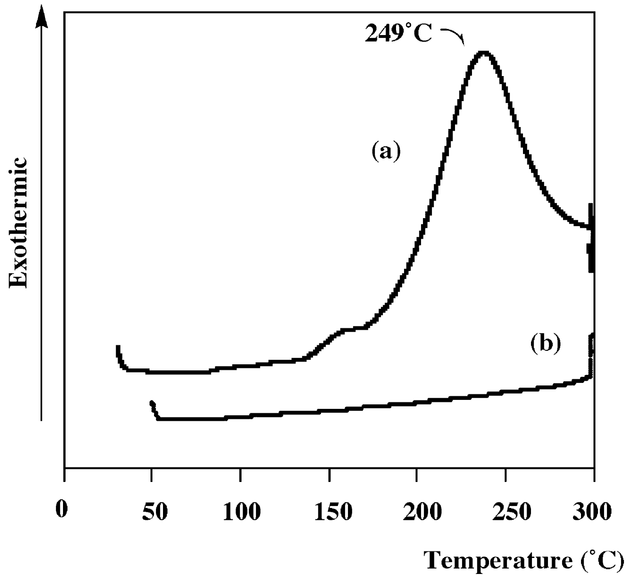

Fig. 3. UV–vis spectra of **P1** film before (a) and after (b) curing at 270°C for 2 h under air.

trimethylsilyl moieties at the *ortho*-position exhibited lower decomposition temperature ($T_d = 285$°C, vide infra).

### 3.3. Thermal crosslinking of polyenynes

As communicated previously, **P1** undergoes thermal crosslinking reaction to turn into an insoluble polymer. The irreversible crosslinking is supposed to take place by means of the reaction of the triple bond moieties in the side chain of **P1**. To clarify the nature of the thermal crosslinking of polyenynes, the thermal behavior of **P1** was examined in detail. When **P1** was heated at 270°C in a degassed sealed tube for 2 h, **P1** turned into insoluble product. The IR spectra of the starting and the cured **P1** revealed that the peak at 2226 cm$^{-1}$, attributable to C≡C stretching vibration, decreased by ca. 90% after the heating process (Fig. 1). This result indicates that the thermal crosslinking of **P1** is caused by the reaction of the acetylene moieties. The nature of the crosslinking reaction was investigated from the UV–vis spectra of thin film of **P1** before and after the curing (under air, 270°C, 2 h). After the curing, the pale yellow colored film of **P1** turned to red keeping its transparency. The UV–vis spectrum of the cured film showed a red-shift from that of the starting film, indicating the production of new π-conjugated structure (Fig. 2). The thermal reactions of aromatic acetylenes have been reported to give various π-conjugated products, such as fused aromatic rings, by means of their inter- or intra-molecular cyclization [13–15]. Accordingly, the present curing process may involve analogous reactions to produce crosslinked polymers, although the detailed structural units formed in the present system have not been clarified yet.

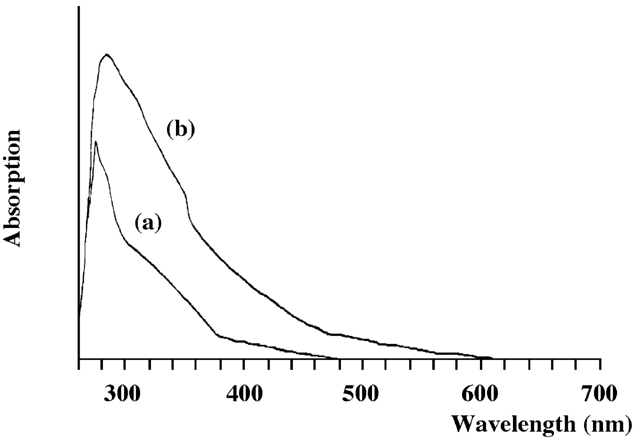

Fig. 2. IR spectra of **P1** (KBr disk) before (a) and after (b) DSC measurement.

In the DSC thermogram of **P1** (Fig. 3, taken under $N_2$, at a scan rate of 10°C/min), an exothermic peak, which started from ca. 140°C and reached to its maximum at ca. 240°C, was observed. The slope of the peak became steep after the glass transition temperature (157°C). The TG analysis revealed that no weight loss has occurred within this temperature range. Since this exothermic peak was not observable in the second scan, it should originate from the irreversible process, most probably the crosslinking reaction. The DSC thermograms of other poly(aromatic enyne)s (**P2**–**P8**) also exhibit exothermic peaks as was the case of **P1**, indicating that these polymers might also undertake the crosslinking reactions.

The polymer having bulky trimethylsilyl group at the *ortho*-position of the benzene ring (**P8**) exhibited a lower decomposition temperature (vide supra), which was not

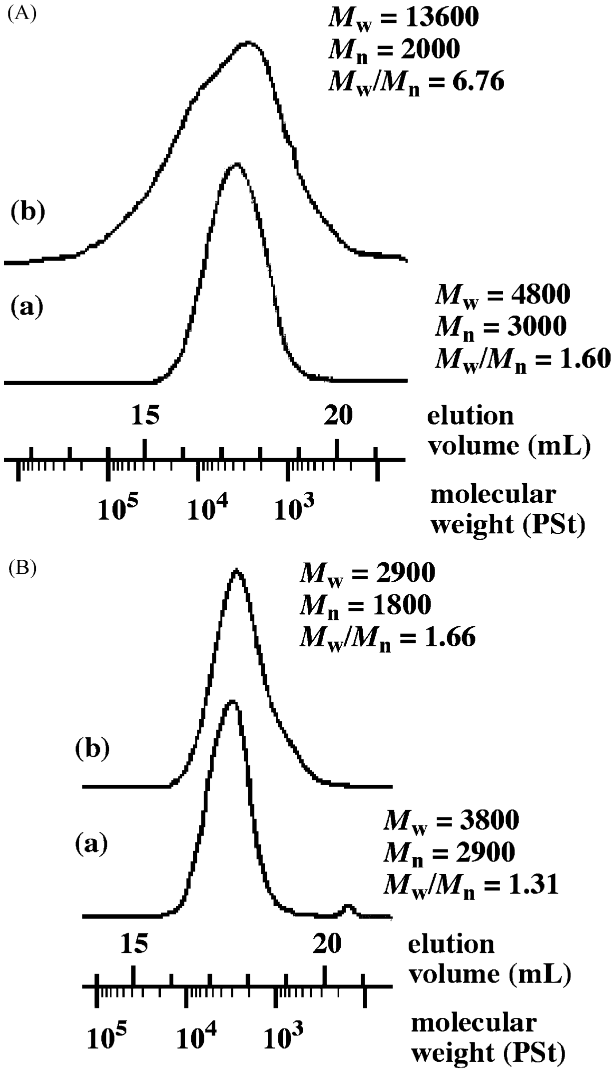

Fig. 4. (A) GPC trace of **P1** before (a) and after (b) curing ($CHCl_3$-soluble part). (B) GPC trace of **P8** before (a) and after (b) curing.

ascribable to the difference in the conversion of the acetylene moieties. To investigate the difference in the thermal behavior of **P1** and **P8**, conversions of acetylene moieties and molecular weight of **P1** and **P8** was compared before and after heating from 30 to 270°C at a heating rate of 10°C/min under nitrogen. The conversion of acetylene moieties in **P1** and **P8** was estimated from the IR spectra to be 64 and 61%, respectively. In spite of the similar conversion of the acetylene moieties in **P1** and **P8**, it is of note that there is a significant difference in the change in the molecular weight. After the thermal treatment, **P1** became partly insoluble in any organic solvents (ca. 50%), while **P8** was completely soluble in, for instance, chloroform. The GPC trace of the chloroform-soluble fraction of **P1** exhibited a shoulder elution peak in the higher molecular weight region after the heating process, although the presence of the crosslinked product might make it less meaning to compare the molecular weight (Fig. 4A). Meanwhile, that of **P8** shifted slightly to the lower molecular weight region after the heating process (Fig. 4B). These results can be taken to mean that the intermolecular reactions of the acetylene moieties leading to the crosslinked product, which occurred in the thermal treatment of **P1**, were suppressed in the case of **P8**. Instead, the intramolecular reactions of the acetylene moieties took place in the thermal treatment of **P8** which did not involve the crosslinking reaction. As was the case of other acetylene-containing polymers [1–5], the crosslinking reaction seems to be important to improve the thermal stability of the polymers. That is, polyenynes with sterically less hindered aromatic substituents (e.g. **P1**) undertake thermal crosslinking of their acetylene moieties and, consequently, have higher decomposition temperature than thermally uncrosslinkable polyenynes such as **P8**.

## 4. Conclusions

The polymers having acetylene moieties in the side chain, prepared by the radical polymerization of aromatic enynes, were subjected to the thermal crosslinking reaction. The crosslinking reaction occurred from ca. 140°C to give insoluble polymers where the irreversible reaction of the acetylene moieties to give a new conjugated structure was supposed to take place as confirmed by the IR and UV–vis spectra. The steric bulkiness rather than the electronic character of the substituents affects the crosslinking degree and, consequently, the decomposition temperature of the polymers.

## Acknowledgements

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