# High-Pressure Synthesis of Cyclic Mesitylacetylene Oligomer

#### YOSHITSUGU KOJIMA, TAKAAKI MATSUOKA, HIDEROH TAKAHASHI

Toyota Central Research & Development Laboratories, Inc., Nagakute-cho, Aichi-gun, Aichi 480-1192, Japan

Received 14 August 1997; accepted 2 November 1998

ABSTRACT: Reaction of mesitylacetylene was carried out by annealing under high pressure (0.13 and 0.52 GPa). The products obtained were classified into soluble and insoluble products in chloroform. The insoluble product reacted under 0.13 GPa was the mesitylacetylene polymer. The soluble product reacted under 0.13 GPa was classified as the monomer and the oligomer [number-average molecular weight  $(\bar{M}_n)$ : 390, weight-average molecular weight  $(\bar{M}_w)$ : 453, Oligomer yield  $(O_y)$ : 36%]. The oligomer yield was accelerated by pressure [pressure: 0.13–0.52 GPa,  $\bar{M}_n$ : 390–315,  $\bar{M}_w$ : 453–968,  $O_y$ : 36–98%]. Field desorption mass spectrum showed that the oligomer had cyclic structure. The result of the elementary analysis revealed that the insoluble product reacted under 0.52 GPa was a polycyclic aromatic compound. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1539–1542, 1999

**Key words:** high pressure; cyclic structure; mesitylacetylene; oligomer; field desorption mass spectrum

### **INTRODUCTION**

Polyacetylene is an insoluble conjugated polymer that can be obtained by using conventional Ziegler-Natta catalysts.<sup>1–3</sup> Substituted acetylenes such as phenylacetylene, having bulky phenyl groups on the sp hybridized carbons produces oligomers not exceeding a number-average molecular weight of 7500 and insoluble products by use of the Ziegler-Natta catalysts.<sup>4,5</sup> Masuda et al. found in 1974 that Group 5 and 6 transition metal catalysts (W and Mo catalysts) are effective for substituted acetylene polymerization.<sup>4,6</sup> These polyacetylenes and polyacetylenes with substituents have attracted much attention as electrical and nonlinear optical materials.<sup>7–9</sup>

In general, the polymerization of unsaturated compounds start from initiator or catalyst and a

Correspondence to: Y. Kojima.

linear polymer is formed.<sup>4,10</sup> In previous articles, new cyclic oligomers were synthesized, in the absence of initiator or catalyst, by high-pressure oligomerization of diphenyldiacetylene and phenylacetylene.<sup>11,12</sup>

In this study, the reaction of mesitylacetylene under high pressure was carried out using a high hydrostatic pressure reactor. The structure of the product was evaluated by elemental analysis, FTIR, size exclusion chromatography (SEC), <sup>13</sup>C-NMR spectra and field desorption mass (FDMS) spectra.

#### **EXPERIMENTAL**

#### Materials

Reactions of mesitylacetylene in the form  $H-C=C-C_9H_{11}$  under high-pressure were carried out using a high hydrostatic pressure reactor, as shown in the previous article.<sup>11</sup> The spec-

Journal of Applied Polymer Science, Vol. 72, 1539–1542 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/121539-04

imen (about 1 g) was packed into a polytetrafluoroethylene cell (inside diameter: 8 mm, length: 23 mm). After closing the cell, it was introduced into the high-pressure vessel. The specimen was compressed at 0.13 and 0.52 GPa by hand oil pump, substantially annealed at 150°C for a constant time of 5 h, with a pressure transmitting medium (silicone oil). The specimens were annealed at a heating rate of  $10^{\circ}$ C/min. After reaction under high pressure, the product was cooled to room temperature, decompressed, and removed from the cell.

#### Characterization

Elemental analysis was conducted using an instrument for combustion analysis (Perkin-Elmer Elemental Analyzer 240C) for carbon and hydrogen. A Fourier transform infrared spectrophotometer (Japan Spectroscopic Co., Ltd. FT/IR-5M) was used for infrared studies. Specimens in powder form were mixed with KBr (0.5 mg of specimen with 200 mg of KBr), and were formed into tablets by applying pressure. The molecular weight of the product was determined by SEC with a liquid chromatograph (Japan Analytical Industry Co., Ltd. LC-908) consisting of a refractive index detector and a polystyrene preparative column (exclusion limit: 70,000). Chloroform was used as a mobile phase at a flow rate of 3 mL/min on the column. It was also used as a solvent, and the concentration of the product solution was 3% (wt/vol). A carbon-13 (<sup>13</sup>C)-NMR spectrum of the specimen was obtained on a spectrometer (Japan Electron Optics Laboratory JNM-FX90Q) at 22.53 MHz ( $^{13}$ C). The conditions of  $^{13}$ C-NMR data acquisition were as follows: pulse width 9.2 s; pulse repetition time 5.0 s; frequency range 5000 Hz; 16,000 data points; 20,000 scans. Chloroformd was used as a solvent. The concentration of the solution was about 5% (wt/vol). The chemical shift of the NMR spectrum was calibrated relative to tetramethylsilane (TMS) [(CH<sub>3</sub>)<sub>4</sub>Si]. A field desorption mass (FDMS) spectrum was obtained on a mass spectrometer (VG Analytical Co., Ltd. ZAB-SE) using field desorption ionization.

#### **RESULTS AND DISCUSSION**

Reaction of mesitylacetylene was carried out by annealing under high pressure (0.13 and 0.52 GPa). The products obtained were classified into soluble and insoluble products in chloroform. The



Figure 1 Infrared absorption spectrum of insoluble product reacted under 0.13 GPa.

fraction of the insoluble product was approximately independent of pressure [the fraction of the soluble product: 51 wt % (0.13 GPa), the fraction of the soluble product: 56 wt % (0.52 GPa)]. Elemental analysis showed that the [H]/[C] (number of hydrogen atom/number of carbon atom) values of the soluble and the insoluble products under the reaction pressure of 0.13 GPa were 1.08 and 1.10, respectively, corresponding to that of mesitylacetylene (1.09).

Figure 1 shows the infrared spectrum of the insoluble product reacted under 0.13 GPa. The  $-C \equiv C$ — stretching vibration of the original mesitylacetylene occurred at 2100 cm<sup>-1</sup>. This band is absent in the infrared spectrum of the insoluble product. For the insoluble product, the band at 840 cm<sup>-1</sup> indicates a monosubstituted benzene structure.<sup>13</sup> This means that the insoluble product is the mesitylacetylene polymer.

The infrared spectrum of the soluble product reacted under 0.13 GPa shows a band at 2100  $cm^{-1}$ , owing to the presence of the monomer. SEC was used to estimate the molecular weight of the soluble products in chloroform. Based on a polystyrene calibration, the molecular weight distribution was estimated. The molecular weight distribution of the soluble product reacted at 0.13 GPa is shown in Figure 2. The product is classified as the monomer and the oligomer [numberaverage molecular weight  $(M_n)$ : 390, weight-average molecular weight  $(M_w)$ : 453, Oligomer yield  $(O_{\nu})$ : 36%]. The oligomer yield is accelerated by pressure [pressure: 0.13-0.52 GPa,  $M_n$ : 390–315,  $\overline{M}_w$ : 453–968,  $O_v$ : 36–98%] as shown in Figure 2, but the [H]/[C] of the soluble product



Figure 2 Molecular weight distribution of soluble products.

under the reaction pressure of 0.52 GPa was 0.91 and lower than that of mesitylacetylene. It is suggested that the oligomer includes polycyclic aromatic compounds. The result of the elementary analysis revealed that the insoluble product reacted under 0.52 GPa was a polycyclic aromatic compound because of the [H]/[C] of 0.47. It is, thus, believed that pressure accelerates the carbonization of mesitylacetylene.<sup>14</sup> The characterization of the oligomer synthesized under 0.13 GPa was carried out after the separation of four components F1–F4 shown in Figure 2. The IR spectra of components F2–F4 were similar to that of the insoluble product reacted under 0.13 GPa.

Figure 3 shows the <sup>13</sup>C-NMR spectrum for the component F3. Two broad peaks appear at 128 and 136 ppm owing to the sp<sup>2</sup>-carbon.<sup>15,16</sup> The



**Figure 3** <sup>13</sup>C-NMR spectrum of mesitylacetylene oligomer (component: F3).



**Figure 4** Field desorption mass (FDMS) spectrum of mesitylacetylene oligomer (component: F2).

peak obtained at 21 ppm comes from the sp<sup>3</sup>carbon, but the <sup>13</sup>C-NMR spectrum due to the sp-carbon is absent. It is assumed that the NMR spectrum of component F3, appearing at 132-150 ppm, is assigned to the sp<sup>2</sup>-carbon bonded to the sp<sup>2</sup>-carbon and the sp<sup>2</sup>-carbon bonded to the methyl group of the C-CH<sub>3</sub> oligomer.<sup>15,16</sup> Furthermore, we assume that the NMR spectrum of the component F3 appearing at 125-132 ppm is assigned to the sp<sup>2</sup>-carbon bonded to hydrogen (=C-H) of the oligomer.<sup>15,16</sup> The ratio  $[sp^2$ -carbon bonded to hydrogen/ $(sp^2$ carbon bonded to the  $sp^2$ -carbon +  $sp^2$ -carbon bonded to the methyl group)] of the component F3 (0.58) was approximately in agreement with the calculated value for the polymer (0.6).

Figure 4 shows the FDMS spectrum of the component F2 {apparent molecular weight: 240-700 (polystyrene calibration)}. As the error of the FDMS spectrum is mass of  $\pm 1$ , we can accurately obtain the absolute molecular weight of the oligomer. The molecular weight of mesitylacetylene monomer composed of  ${}^{12}C$  and  ${}^{1}H$  is  $144.2^{15}$  and the FDMS spectrum showed peaks that are multiples of the molecular weight of the monomer. The FDMS spectrum of component F2 also shows the presence of oligomers from tetramer to heptamer below an absolute molecular weight of 1100. We found that the mesitylacetylene oligomer synthesized under high pressure had a cyclic structure. Figure 5 shows the structure model of the cyclic hexamer. The synthesis of the cyclic oligomer has not been previously reported.



Figure 5 Structure model of mesitylacetylene oligomer.

Thus, the mesitylacetylene oligomers are new compounds having cyclic structures.

In conclusion, mesitylacetylene oligomer was prepared by reacting mesitylacetylene under high pressure. The oligomer yield was accelerated by pressure. FDMS spectrum showed that the oligomer had cyclic structure.

The authors thank Professor T. Masuda of Kyoto University for the sample of mesitylacetylene.

## REFERENCES

- Natta, G.; Mazzanti, G.; Corradini, P. Rend Accad Naz Lincei 1958, 25, 3.
- 2. Ito, T.; Shirakawa, H.; Ikeda, S. J Polym Sci, Polym Chem Ed 1974, 12, 11.
- 3. Wegner, G. Angew Chem Int Ed Engl 1981, 20, 361.
- Masuda, T.; Higashimura, T. Adv Polym Sci 1986, 81, 121.
- Simonescu, C. I.; Percec, V.; Dumitrescu, S. J Polym Sci Polym Chem Ed 1977, 15, 2497.
- Masuda, T.; Hasegawa, K.; Higashimura, T. Macromolecules 1974, 7, 728.
- Naarmann, H.; Theophilou, N. Synth Met 1987, 22, 1.
- Kajzar, F.; Etemad, S.; Baker, G. L.; Messier, J. Synth Met 1987, 17, 563.
- Le Moigne, J.; Hilberer, A.; Strazielle, C. Macromolecules 1992, 25, 6705.
- Schildknecht, C. E.; Skeist, I., Eds.; Polymerization Processes; (High Polymers; vol. 29); John Wiley & Sons: New York, 1977.
- 11. Kojima, Y.; Tsuji, M.; Matsuoka, T.; Takahashi, H. Macromolecules 1994, 27, 3735.
- Kojima, Y.; Matsuoka, T.; Sato, N.; Takahashi, H. J Polym Sci, Polym Chem Ed 1995, 33, 2935.
- Bellamy, L. J. The Infra-red Spectra of Complex Molecules; Chapman and Hall: London, 1975.
- Kojima, Y.; Tsuji, M.; Matsuoka, T.; Takahashi, H. J Polym Sci, Polym Chem Ed 1994, 32, 1371.
- Silverstein, R. M.; Bassler, G. C. Spectrometric Identification of Organic Compound; John Wiley & Sons: New York, 1981.
- Levy, G. C.; Lichter, R. L.; Nelson, G. L. Carbon-13 Nuclear Magnetic Resonance Spectroscopy; John Wiley & Sons: New York, 1980.