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High-Pressure Synthesis of Polyacene-Based Oligomer

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ABSTRACT: A new conjugated oligomer was synthesized by reacting diphenyldiacetylene under high pressure of 0.03–0.13 GPa at 250 °C for 5 h. The oligomer was obtained from reacted diphenyldiacetylene in liquid state and of a number-average molecular weight of 1200–1270 in polystyrene calibration. The fraction of the oligomer increased with increasing pressure. The structure of the oligomer was investigated from its visible absorption and infrared spectra, field desorption mass (FDMS) spectrum, thin-layer chromatography, and ^{13}C NMR spectrum. We found that the oligomer had a cyclic structure by the FDMS spectrum. The ^{13}C NMR spectrum for the oligomer corresponded to the polyacene-based structure. It was proposed that high-pressure oligomerization of diacetylene is a powerful method to produce a cyclic oligomer.

Introduction

Poly(diacetylene)s are conjugated polymers and can be obtained by the solid-state topochemical polymerization of substituted diacetylenes,[1] by heating or high-energy radiation, and have 1,4 polymer repeat structure. Poly(diacetylene)s have attracted much attention as electrical and nonlinear optical materials.[2-4] On the other hand, diphenyldiacetylene having bulky phenyl groups on the acetylene carbons is difficult to polymerize in the solid owing to its steric hindrance.[5] Polymerization of diphenyldiacetylene was carried out in solution by using conventional Ziegler type catalysis.[6] In general, polymerization of an unsaturated compound starts from initiator or catalysis and the linear polymer is formed.[7] The application of pressure is well-known to influence the structure, property, and reaction of substances.[8-13] Polyacetylene, which has been synthesized by the catalytic polymerization of the monomer, was formed by the reaction-induced high pressure.[9] By high-pressure polymerization of diphenyldiacetylene in the absence of initiator or catalysis, it is expected that a new cyclic conjugated polymer composed of diphenyldiacetylene is synthesized.

In this study, reaction of diphenyldiacetylene under high pressure was carried out using a high hydrostatic pressure reactor. The structure of the product by reaction of diphenyldiacetylene under high pressure was evaluated by elementary analysis, gel permeation chromatography (GPC), visible absorption spectrum, FTIR, field desorption mass (FDMS) spectrum, thin-layer chromatography, and ^{13}C NMR experiments.

Experimental Section

Materials. Diphenyldiacetylene (molecular weight, 202.26; melting temperature, 86 °C) in the form $C_6H_5C{\equiv}CC{\equiv}CC_6H_5$ (Wako Pure Chemical Industries Ltd., Japan) was used for the reaction without further purification. Reaction of diphenyldiacetylene under high pressure was carried out using a high hydrostatic pressure reactor, as shown in Figure 1. The specimen (about 1.3 g) was packed into a poly(tetrafluoroethylene) cell (inside diameter, 8 mm; length, 40 mm). After closing the cell, it was introduced into the high-pressure vessel. The specimen was compressed at various pressures in the range of 0.03–0.13 GPa by a hand oil pump, substantially annealed at 250 °C for a constant time of 5 h, with a pressure-transmitting medium (silicone oil). The specimens were annealed at a heating ratio of 10 °C/min. After reaction under high pressure, the product was cooled to room temperature, decompressed, and removed from the cell.

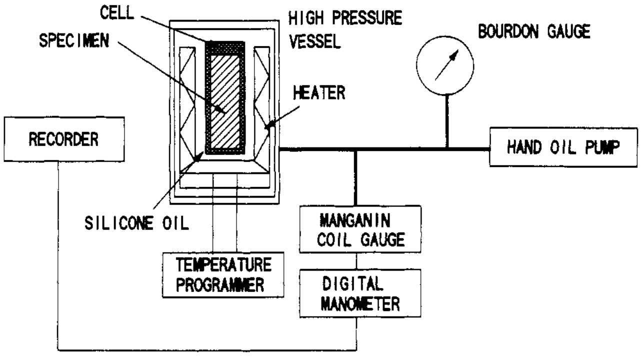

Figure 1. Schematic diagram of a high hydrostatic pressure reactor.

Characterization. Elementary analysis was made using an instrument of combustion analysis (Perkin-Elmer elemental analyzer 240C) for carbon and hydrogen. The product of 1.5 mg was used for the analysis. The molecular weight of the product was determined using a liquid chromatograph (Japan Analytical Industry Co., Ltd. LC-08) consisting of a refractive index detector and column. Chloroform was used as the mobile phase at a flow rate of 3 mL/min on the column. It was also used as the solvent, and the concentration of the product solution was 3% (w/v). The product was a mixture of diphenyldiacetylene oligomer and monomer, as shown later.

The characterization of the diphenylacetylene oligomer was performed by visible absorption and infrared spectra, FDMS spectrum, thin-layer chromatography, and ^{13}C NMR spectrum. Visible absorption spectra of the solution in chloroform (concentration, 0.1, 0.01 wt %) in a quartz cell (specimen path length, 10 mm) were recorded on a UV–visible recording spectrophotometer (Shimadzu UV-2100). The spectrum in 400–800 nm was measured. A Fourier transform infrared spectrophotometer (Japan Spectroscopic Co., Ltd. FT/IR-5M) was used for infrared studies in the wavenumber from 4000 to 600 cm^{-1}. Specimens in powder form were mixed with KBr (0.7–0.9 mg of the specimen with 200 mg of KBr), and tablets were formed by applying pressure. The field desorption mass (FDMS) spectrum was obtained on a mass spectrometer (VG Analytical Co. Ltd. ZAB-SE) using field desorption ionization. Thin-layer chromatography was carried out using methyl alcohol as eluent. A carbon-13 (^{13}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 μs; pulse repetition time, 5.0 s; frequency range, 5000 Hz; 16 000 data points; 20 000 scans.

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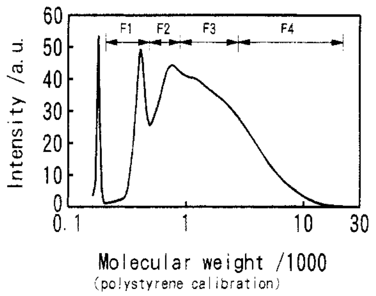


Figure 2. Molecular weight distribution of the product (0.03 GPa, 250 °C, 5 h).

Chloroform-*d* was used as a solvent. The concentration of the specimen solution was about 5% (w/v). The chemical shifts of the NMR spectra for the specimens in chloroform were calibrated relative to tetramethylsilane [TMS; $(CH_3)_4Si$].

Results and Discussion

Reaction of diphenyldiacetylene (1,4-diphenylbutadiyne) was carried out by annealing under high pressure (0.03–0.13 GPa). The melting temperature and the broad exothermic peak temperature of diphenyldiacetylene were obtained from results of the high-pressure DTA measurement.[14] The melting temperature of diphenyldiacetylene increased linearly with increasing pressure (pressure, 0.03–0.13 GPa; melting temperature, 98.8–131 °C).[14] It is revealed that diphenyldiacetylene is in the liquid phase at the reaction temperature of 250 °C under high pressure. The exothermic peak temperature was in the range of 234–252 °C independent of the pressure. This implies that exothermic peak temperature corresponds to the reaction of diphenyldiacetylene under high pressure.

The results of the elementary analysis showed that the H/C ratio of the product agreed with that of diphenyldiacetylene (H/C = 0.63). The products obtained are easily soluble in the usual organic solvents such as chloroform and toluene, giving a yellow or deep red solution. GPC was used to estimate the molecular weight of the products in chloroform. Based on the polystyrene calibration, the molecular weight distribution was obtained. The molecular weight distribution of the product reacted at 0.03 GPa is shown in Figure 2. The product is classified as monomer and oligomer. The number-average molecular weight (M_n) is 1200, weight-average molecular weight (M_w) is 2100, and M_w/M_n is 1.8. The oligomer yield was determined by the area ratio of chromatograms of the monomer and oligomer. Oligomerization was accelerated by pressure (pressure, 0.03–0.13 GPa; oligomer yield, 88–96%). Pressure accelerated the reaction rate of diphenyldiacetylene. M_n, M_w, and M_w/M_n of the diphenyldiacetylene oligomers at various pressures were 1200–1270, 2100–2430, and 1.75–1.91, respectively. It is considered that they are approximately independent of pressure.

The visible absorption spectra in chloroform for the oligomer synthesized under a high pressure of 0.13 GPa showed no absorption maxima. There was a continuous absorption of the oligomer in the visible region from 400 to 800 nm. As the concentration of the solution was increased, the absorbance also increased. The absorbance was weaker at longer wavelength. The solution of the diphenyldiacetylene was a colorless, transparent liquid and has no absorption in the visible region. This suggests that the oligomer has a number of chromophores which have different absorption maxima according to the length of the conjugated system. IR spectroscopy yields the structural information. Figure 3 shows the infrared spectra of the diphenyldiacetylene oligomer synthesized under a high pressure of 0.13 GPa together with the original diphenyldiacetylene. The $=\overset{|}{C}—H$ stretching vibration of the oligomer occurs at 3040 and 3060 cm^{-1}.[15] The IR band at 2150 cm^{-1} of the original diphenyldiacetylene is assigned to the stretching vibration of $-C{\equiv}C-$ triple bond.[15] This band shifts to 2200 cm^{-1} in the infrared spectrum of the diphenyldiacetylene oligomer. For the oligomer the bands at 760 and 700 cm^{-1} indicate the monosubstituted benzene structure.[15] The band at 690 cm^{-1} of the monomer shifts to 700 cm^{-1} by oligomerization. The presence of a conjugated double bond in the oligomer was confirmed by IR absorption. There is an increase in intensity of 1600-cm^{-1} absorption. The 1600-cm^{-1} absorption is assigned to the fully conjugated double bond, while the 1620–1680-cm^{-1} absorption is assigned to nonconjugated double bonds.[15] The characterization of the oligomer was carried out by separation of four components (F1–F4) shown in Figure 2. There are one peak and shoulder in the chromatogram of the component F1. The component F1 was separated with recycling chromatography. The chromatogram of component F1 (separation with recycling chromatography) showed a monodisperse oligomer. The molecular weight was 416 and corresponded with styrene tetramer. The FDMS spectrum from component F1 (separation with recycling chromatography) was obtained. As the error of the FDMS spectrum is a mass of ±1, we can accurately obtain the absolute molecular weight of the oligomer. The molecular weight of the diphenyldiacetylene monomer composed of ^{12}C and ^{1}H is 202.08,[16] and the FDMS spectrum showed peaks at 606 and 808 that were multiples of the molecular weight of the monomer. On the solid-state polymerization of diacetylene, it was reported that the polymer had a 1,4 polymer repeat unit structure, having an acetylenic structure.[17]

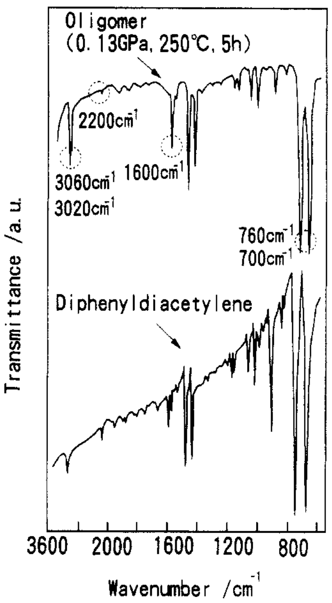
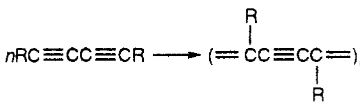


Figure 3. Infrared spectrum of the diphenyldiacetylene oligomer.



$$nRC{\equiv}CC{\equiv}CR \longrightarrow (=\overset{\overset{R}{|}}{C}C{\equiv}C\underset{\underset{R}{|}}{C}=)_n$$

For the oligomer having an acetylenic structure, the molecular weight should be above multiples of the monomer because of the existence of the end groups. However, the molecular weight of the oligomer is a multiple of the monomer by the FDMS spectrum. Therefore, oligomerization of diphenyldiacetylene under high pres-

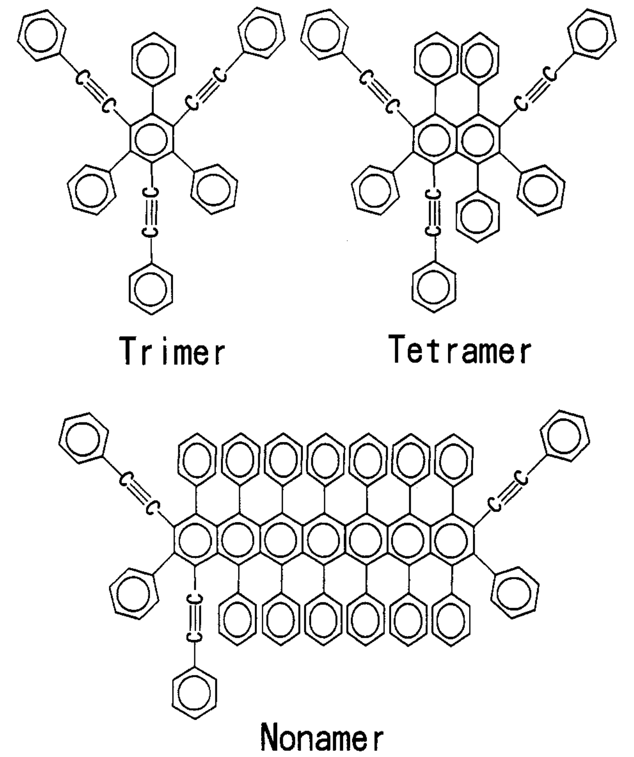


Figure 4. Structure models of the diphenyldiacetylene oligomer.

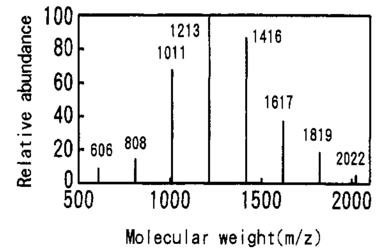


Figure 5. Field desorption mass (FDMS) spectrum of the diphenyldiacetylene oligomer (component, F2).

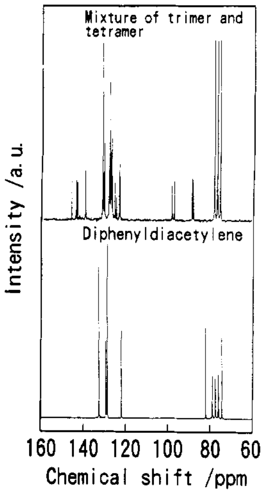


Figure 6. ^{13}C NMR spectrum of the mixture of diphenyldiacetylene trimer and tetramer [component, F1 (separation with recycling chromatography)].

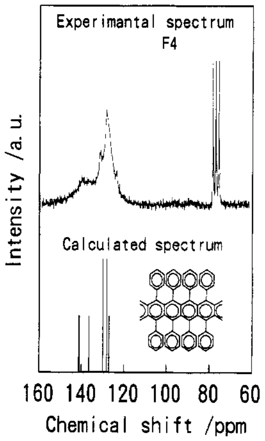


Figure 7. ^{13}C NMR spectrum of the diphenyldiacetylene oligomer (component, F4).

sure does not take place at the 1,4-position. It is revealed that the diphenyldiacetylene oligomer has a cyclic structure. Moreover, it is compact because of the large absolute molecular weights of 606 and 808 compared with the molecular weight of 416 (polystyrene calibration). Figure 4 shows the structure models of cyclic trimer and cyclic tetramer. Diphenyldiacetylene monomer produces a cyclic trimer and tetramer with benzene structure and unreacted terminal phenyl acetylenic groups and naphthalene structure and unreacted terminal phenyl acetylenic groups, respectively. According to the structure models in Figure 4, the cyclic trimer has two isomers and the cyclic tetramer has four isomers. Thin-layer chromatography of component F1 (separation with recycling chromatography) using a methyl alcohol as eluent developed five colorless bands. It is considered from this result that two isomers are in the same band. Figure 5 shows the FDMS spectrum of component F2. The spectrum shows the presence of oligomers from cyclic trimer to cyclic decamer. As an example, the structure shown in Figure 4 is proposed for the nonamer. The additional reaction takes place at the 1,2-position and 3,4-position and leads to an oligomer of the polyacene-based structure.[18] It is presumed that the phenyl substituent has little conjugation to the polyacene backbone owing to the steric hindrance.

^{13}C NMR measurements for the mixture of the trimer and tetramer [F1 (separation with recycling chromatography)] and components F1–F4 were performed to support the structure model of the oligomer of polyacene-based structure. Figure 6 shows the ^{13}C NMR spectra for the mixture of the cyclic trimer and tetramer and diphenyldiacetylene. Sharp peaks observed over 120–150 and 80–100 ppm in the ^{13}C NMR spectrum of the mixture come from the sp^2-carbon $(-\overset{|}{C}=)$ and sp-carbon $(-C\equiv)$, respectively.[19] The sp^3-carbon was absent in the region 0–60 ppm. In the spectrum of diphenyldiacetylene, peaks for sp^2-carbon and sp-carbon appear over 120–135 ppm (122, 128, 129, 132 ppm) and 70–90 ppm (74, 84 ppm), respectively. It has been known that ^{13}C chemical shifts of substituted benzene and naphthalene with a phenyl group appear at about 140 ppm.[19] For the spectrum of the mixture of the cyclic trimer and tetramer, the peaks that appear at 139–146 ppm are assigned to carbons of substituted benzene and naphthalene with a phenyl group. Fractional sp^2-carbon of the substituted benzene and naphthalene and sp-carbon for the mixture were calculated using a structure model of the trimer and tetramer shown in Figure 4 and the FDMS spectrum, in which the number of the trimer and tetramer was estimated. The calculated values of the sp^2-carbon and sp-carbon are 0.135 and 0.115, respectively. These values are in good agreement with the experimental values (fraction of sp^2-carbon in the region 139–146 ppm, 0.133; fraction of sp-carbon, 0.107. Figure 6 also shows that the peaks for the sp-carbon of the oligomer shift to lower field by oligomerization. Figure 7 shows the ^{13}C NMR spectrum for the component (F4). Two broad peaks appear at 128 and 141 ppm owing to the sp^2-carbon.[19] Two broad and small peaks that appear at

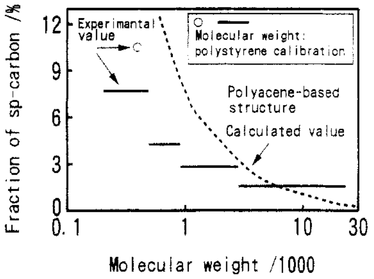


Figure 8. Fraction of sp-carbon obtained by the ^{13}C NMR spectrum versus molecular weight.

90 and 97 ppm were assigned to sp-carbon.[19] It is considered that the broad ^{13}C NMR spectrum of the component (F4) is due to the molecular weight distribution between 2800 and 24 000. The ^{13}C NMR spectrum from the diphenyldiacetylene macromolecule composed of polyacene-based structure was calculated using database (C13NMR) of INformation system KArlsruhe (INKA) developed by Fachinformationszentrum Energie, Physik, Mathematik GmbH (Germany). In the calculated spectrum, six peaks appear at 127, 128, 130, 137, 141, and 142 ppm. The peaks of sp^2-carbon are 127, 128, 130, and 137 ppm from the phenyl group and 141 and 142 ppm from the polyacene structure. The experimental NMR spectrum of component F4 obtained experimentally is similar to the calculated one of the macromolecule composed of polyacene-based structure.

It is expected that the fraction of the sp-carbon of the oligomer with polyacene-based structure decreases with the molecular weight. The fraction of the sp-carbon versus molecular weight obtained by the ^{13}C NMR spectrum is shown in Figure 8. A decrease of the fraction of the sp-carbon occurs with an increase in the molecular weight of the oligomer. The molecular weight dependence of the fraction is similar to that of the polyacene-based oligomer. The experimental value of the fraction is small compared with the calculated value. This is due to the fact that the molecular weight of the oligomer obtained by GPC is smaller than the absolute molecular weight. These results indicate that the oligomer has a polyacene-based structure. It has been reported that the reaction of complex dicarbonyl(n-cyclopentadienyl)cobalt with diphenyldiacetylene gives cyclic trimers of 1,2,4-tris(phenylethynyl)-3,5,6-triphenylbenzene and 1,3,5-tris(phenylethynyl)-2,4,6-triphenylbenzene.[20] Above the degree of polymerization of 4, the diphenyldiacetylene oligomers are new compounds having polyacene-based structure. We propose the idea that high-pressure oligomerization of diacetylenes is a powerful synthetic method to produce a cyclic oligomer.

Conclusion

Reaction of diphenyldiacetylene under high pressure was carried out to synthesize a new conjugated polymer. It was indicated that the product was a diphenyldiacetylene oligomer (number-average molecular weight, 1200–1270). Visible and infrared absorption spectra, field desorption mass (FDMS) spectrum, thin-layer chromatography, and ^{13}C NMR spectrum for the oligomer showed that the oligomer had the polyacene-based structure. Above the degree of oligomerization of 4, the diphenyldiacetylene oligomers are new compounds having polyacene-based structure.

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