Annealing of Polyacene-Based Oligomer Synthesized Under High Pressure

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ABSTRACT: A polyacene-based oligomer was synthesized by reaction of diphenyldiacetylene under high pressure (pressure: 0.1 GPa; temperature: 250° C; time: 5 h). Annealing of the polyacene-based oligomer was carried out (temperature: $300-800^{\circ}$ C; time: 5 h). Gas analysis, BET surface area measurement, Raman scattering, X-ray diffraction, elemental analysis, ¹³C-NMR, and conductivity measurements were performed to characterize the structure of the product. The oligomer was annealed with the appearance of mainly hydrogen. The H/C of the product decreased with increasing annealing temperature. The Raman band is observed at 1610 cm⁻¹ assigned to a doubly degenerate deformation vibration of the carbon hexagonal ring. The additional band observed at 1340 cm⁻¹ is attributed to the size effect. X-ray diffraction indicated that the product had no sharp peak because of the disordered carbon structure. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 289–292, 1999

Key words: diphenyldiacetylene; polyacene; high pressure; annealing; disordered carbon

INTRODUCTION

Graphite stores Li ions electrochemically, forming graphite intercalation compounds. The storage process is reversible, and the graphite is used as a negative electrode in Li secondary batteries. Recently, some disordered carbons were shown to have a specific capacity much higher than that expected from the first-stage graphite intercalation compounds (C₆Li : 372 mAh/g), where Li is most highly intercalated between each graphite sheet.^{1–3}

We have synthesized a polyacene-based oligomer by high-pressure oligomerization of diphenyldiacetylene.³ In this study, the annealing of poly-

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acene-based oligomer was carried out to synthesize a disordered carbon. Gas analysis, elemental analysis and measurements of conductivity, Raman scattering, ¹³C nuclear magnetic resonance, specific surface area, and X-ray diffraction were performed to characterize the structure of the product.

EXPERIMENTAL

Materials

Diphenyldiacetylene (molecular weight, 202.26; melting temperature, 86°C) in the form C_6H_5 — C=C-C=C-C₆H₅(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 to syn-

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thesize a polyacene-based oligomer.⁴ The specimen (1 g) was packed into a polytetrafluoroethylene 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 0.1 GPa by a hand oil pump, substantially annealed at 250°C for 5 h, with pressuretransmitting medium (silicone oil). The polyacene-based oligomer was annealed under Argon flow at various temperatures in the range of 300-800°C for 5 h. The heating ratio is 20°C/min during annealing.

Characterization

Gas analysis was performed with a gas chromatograph [Shimadzu, GC-R1A (hydrocarbon), HP5970A (hydrogen)] at a scanning rate of 20°C/min and a sampling time of 1 min. Elemental analysis was made using an instrument of combustion analysis (Perkin–Elmer Model 240) for carbon and hydrogen. Specimens in powdered form were mixed with adhesive (10 wt %), substantially compressed to form a tablet. The tablet (thickness, 0.8-1.2 mm; diameter, 10 mm) was placed between electrodes, and the conductivity was measured with a digital multimeter. Raman scattering measurement was carried out using a spectrometer (JEOL RPM-1000). The spectrum in $600-2300 \text{ cm}^{-1}$ was measured with the 488-nm excitation line of Ar-ion laser. ¹³C cross-polarization-magic angle spinning (CP-MAS) nuclear magnetic resonance (NMR) spectrum of the product was measured by means of an NMR spectrometer (Bluker MSL-



Figure 1 Influence of temperature on the ratio of the number of hydrogen atoms and the number of carbon atoms (H/C).



Figure 2 Raman spectrum of the product.

300) operating at 75.47 MHz (¹³C). Single-point Brunauer-Emmett-Teller (BET) surface area measurement was made using a surface analyzer (Ohkura Riken, AMS 8000). Samples were weighed, placed in a sample holder, and outgassed at 150°C under a mixture of nitrogen and helium for 15 min prior to measurement. The adsorption of nitrogen on the product proceeded for a time once when the sample holder was immersed in liquid nitrogen. Desorption was initiated by warming the sample quickly to room temperature. X-ray diffraction (XRD) measurement of the product was conducted with $CuK\alpha$ radiation (30 kV, 30 mA) from a Rigaku Denki Rad-B. A glass sample holder with a size of $35 \times 35 \times 2$ mm was used. Divergence, scatter, and receiving slits were fixed at 1, 1, and 0.3° , respectively.

RESULTS AND DISCUSSION

Polyacene-based oligomer was annealed with the appearance of mainly hydrogen. The gases released at around 400°C were H_2 , CH_4 , C_2H_4 , and C_6H_6 . C_2H_6 , C_3H_6 , C_3H_8 , and $C_6H_5CH_3$ began to evolve at 500°C. The weight loss occurred at an annealing temperature above 400°C. The relative weight of the product (weight of the product/ weight of the polyacene-based oligomer) decreased with increasing annealing temperature above 400°C. The results of the elemental analysis for the products annealed are shown in Figure 1. A dramatic 10-fold decrease of the [H]/[C] (number of hydrogen atom/ number of carbon atom) is seen. Annealing accelerates the dehydrogenation of polyacene-based

oligomer. The conductivity was varied in the range of 7.3×10^{-14} to $1.4\times10^{-3}\,\mathrm{S\,cm^{-1}}$ through the annealing temperature.

The Raman spectrum of the product of the polyacene-based oligomer annealed at 700°C is shown in Figure 2. The Raman band observed at 1610 cm⁻¹ in single crystal of graphite is assigned to a doubly degenerate deformation vibration of the hexagonal ring. The additional band at 1340 cm⁻¹ is attributed to the size effect in the direction of the polycondensed aromatic plane. Tuinstra and Koenig suggested a linear relationship between the intensity ratio of the Raman bands and the reciprocal of crystal diameter La, as measured by XRD line broadening.⁵ The crystallite diameter of the products in the direction of the polycondensed aromatic plane was obtained by the following equation⁵:

$$La = 4.4/(I_{1340}/I_{1610}) \tag{1}$$

The La of the products was 2.8-4.5 nm and independent of the annealing temperature. The size was about one-tenth of that of the synthetic graphite (MCMB-25-28, Osaka Gas Co., Ltd.; La, 43 nm). In the CP-MAS NMR spectrum of the product, 1 broad peak owing to sp²-carbon $\left(- \stackrel{|}{C} =\right)$ appeared at 122 ppm.^{6,7} Figure 3 shows the specific surface area as a

Figure 5 shows the specific surface area as a function of the annealing temperature. As the annealing temperature increases, the surface area increases and has a maximum value of 95 m²/g at an annealing temperature of 600°C. The products obtained at 500–800°C have large specific surface



Figure 3 Influence of temperature on the specific surface area.



Figure 4 X-ray diffraction intensity curves of products.

areas in comparison with the synthetic graphite $(1.7 \text{ m}^2/\text{g})$. The increase of the surface area could account for the increase of the nanopore.

X-ray diffraction intensity curves of the products and the graphite are shown in Figure 4. The products annealed in the range of 300-800°C, and the polyacene-based oligomer show broad XRD peaks. The broad peak position $(2\theta, 19.3^{\circ})$; d-spacing, 0.459 nm) of the product annealed at 300°C is different from that of the graphite $(2\theta,$ 26.4°; d-spacing, 0.337 nm), and 2θ decreases from 19.1 to 17.6° with annealing temperature (d-spacing, 0.464–0.505 nm). When the product is prepared above and including 500°C, a new diffraction peak appears at a slightly higher angle of 23.6-24.1° (d-spacing, 0.378-0.370 nm). The peak position is independent of the annealing temperature. The broad diffraction peaks of the products at a scattering angle 2θ of $19-25^{\circ}$ are 002 reflections of the graphite crystallite. It is indicated that the interlayer spacing of the crystallite is large compared with that of the synthetic graphite. In those products, minor broad peaks were also obtained at 2θ near 44° because of 100 or 101 reflection of the graphite crystallite. These broad peaks establish the disordered carbon structure of the product.

In conclusion, polyacene-based oligomer was annealed with appearance of gas. The conductivity of the product increased with the annealing temperature. Elemental analysis, Raman scattering, ¹³C-NMR, and XRD revealed that the product was a hydrogen containing disordered carbon. The carbon had large specific surface area in comparison with the synthetic graphite.

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