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Carbon Microbeads Produced through Synthesis and Pyrolysis of Poly(1,8-dibutyl-1,3,5,7-octatetrayne)

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A self-polymerizable liquid octatetrayne, 1,8-dibutyl-1,3,5,7-octatetrayne, was heated to 80 °C and produced cross-linked poly(1,8-dibutyl-1,3,5,7-octatetrayne) microbeads via suspension polymerization with diameters adjustable from hundreds of micrometers to a few micrometers. Carbon microbeads that may be useful for catalyst supports or in high-performance carbon materials were obtained by the pyrolysis of poly(1,8-dibutyl- 1,3,5,7-octatetrayne) microbeads at 800 °C under an inert atmosphere.

Introduction

Carbon microbeads are useful materials in many fields including lithium battery anodes,[1,2] column packing materials for separation science,[3,4] absorbents with high surface area,[5] catalyst supports,[5] and high-performance carbon components.[6] Carbon microbeads are commonly prepared from pitches.[7−9] Typically coal tar or petroleum pitch is heated at high temperature, usually 350−500 °C, to produce mesophase spheres in pitch. Before extensive growth and aggregation of the spheres, carbonization is quenched and the spheres are separated as solids from soluble pitch by extraction with a suitable solvent. The yield of carbon microbeads is typically 5−10%. The term meso-carbon microbeads (MCMB) was given to the carbon spheres prepared by this method.[1] Although high-temperature treatment of pitches is useful for the production of MCMB, the drawbacks of this method are also very evident, such as low bead yield, tedious extraction, and uncontrollable bead size. Carbon microbeads also have been synthesized by inverse emulsion polymerization of resorcinol with formaldehyde, followed by freeze-drying or supercritical drying and pyrolysis in an inert atmosphere.[10,11] However, both freeze-drying snd supercritical drying consume large amounts of energy and time.

Linear conjugated oligoynes, $-(C{\equiv}C)_x-$, are interesting compounds in carbon chemistry.[12] As a special form of carbon allotropes, all-carbon oligoyne molecules are thought to be the intermediates in the growth of carbon nanotubes and fullerenes.[13] Oligoynes higher than ethyne are very reactive (even explosive), and thus are not available under usual conditions. The high reactivity of oligoynes can be lowered by end-capping with suitable end-groups, like R_3-Si−, alkyl, and other stable groups. This strategy was first used by Walton et al.[14] who prepared oligoynes containing up to 32 carbon atoms end-capped with Me_3Si- group. By laser vaporization of graphite in the presence of $CN^{\bullet}$ or $CF_3^{\bullet}$ radicals, linear polyynes capped by CF_3 and CN groups also were synthesized.[15] Due to long-scale conjugated triple bonds, end-capped oligoynes are still reactive at relatively vigorous conditions such as moderate temperature or UV irradiation, and consequently intermolecular cross-linking and carbon-like structures can be formed. Pyrolysis of the cross-linked products at high temperature will leave the carbon structures formed by $-(C{\equiv}C)_x-$ units while volatizing the protected groups in the molecules. This behavior makes it possible to prepare various carbon structures using end-capped oligoynes as reactive precursors.

Herein the chemical synthesis of carbon microbeads via suspension polymerization of a self-polymerizable liquid octatetrayne, 1,8-dibutyl-1,3,5,7-octatetrayne, followed by pyrolysis of cross-linked poly(1,8-dibutyloctatetrayne) microbeads is reported.

Experimental Section

Materials. 1-Hexyne, 2-(trimethylsilyl) acetylene, *N*,*N*,*N*,*N*-tetramethylethylenediamine (TMEDA), iodine, *n*-butyllithium (2.0 M in pentane), bis(triphenylphosphine)palladium(II) dichloride,

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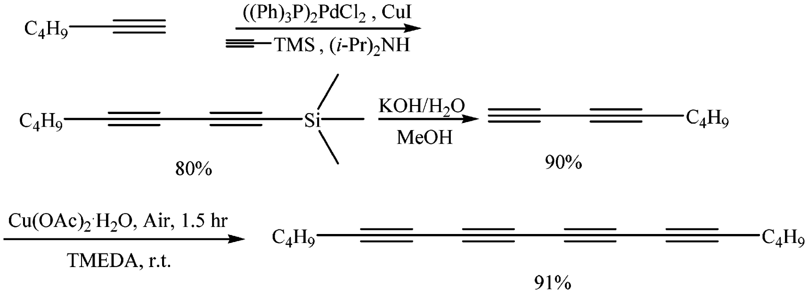
10.1021/cm048781g CCC: $30.25

Scheme 1. Synthetic Route for the Preparation of 1,8-Dibutyl-1,3,5,7-octatetrayne



copper(I) iodide, copper(II) acetate monohydrate, di-(*iso*-propyl)-amine, poly(vinyl alcohol) (87−89% hydrolyzed, average M_w = 31 000−50 000) were used as received from Aldrich. 1-Iodo-2-(trimethylsilyl) acetylene was prepared using a literature procedure.[16]

Preparation of 1-Butyl-4-(trimethylsilyl)-1,3-butadiyne. To 90 mL of diisopropyleneamine were added bis(triphenylphosphine)-palladium(II) dichloride (0.21 g, 0.31 mmol) and copper(I) iodide 0.058 g, 0.31 mmol). The mixture was stirred and degassed with a stream of argon, and a mixture of 1-hexyne (1.0 g, 12.2 mmol) and 1-iodo-2-(trimethylsilyl) acetylene (2.73 g, 12.2 mmol) was added. The solution was stirred at room temperature for 2.5 h; a heavy precipitate formed during this period of time. The reaction mixture was filtered to remove salts. The filtrate was concentrated with a rotary evaporator under vacuum and the oily residue was obtained. The crude product was purified by passing it through a silica gel column with hexane as the eluent. The pure product was obtained as a yellow liquid at the yield of 89% (1.94 g). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.16(9H), 0.88(3H), 1.39 (2H), 2.24(2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ −0.47, 13.40, 18.79, 21.83, 30.11, 65.49, 79.84, 82.58, 88.56. IR 2552, 2527, 2492, 2464, 1936, 1789, 1671, 1628, 1003, 962, 914, 857, 780, 709, 629 cm^{-1}.

Preparation of 1-Butyl-1,3-butadiyne. To a solution of 1-butyl-4-(trimethylsilyl)-1,3-butadiyne (4.0 g, 22.4 mmol) prepared above in methanol (65 mL), was added a 5% aqueous solution of potassium hydroxide (2.4 mL). The solution was stirred at room temperature for 2 h. The reaction mixture was diluted with an equal volume of water, and extracted with *n*-pentane (4 × 50 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure to yield a yellow liquid. The product was purified using a silica gel column with *n*-pentane as the eluent and yielded 1-butyl-1,3-butadiyne as a yellow liquid (2.10 g, 90%). ^{1}H NMR (250 MHz, $CDCl_3$): δ 0.87 (3H), 1.44(4H), 1.91(1H), 2.19(2H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 13.87, 19.25, 22.30, 30.80, 64.76, 65.69, 68.88, 78.80. IR 2959, 2934, 2224, 1466, 1427, 1252, 1054, 846, 620 cm^{-1}.

Preparation 1,8-Dibutyl-1,3,5,7-octatetrayne. A solution of acetone (50 mL), TMEDA (0.54 g, 4.5 mmol), and copper(II) acetate monohydrate (0.29 g, 1.50 mmol) was stirred at room temperature. Air was introduced into the solution with an inlet tube immersed in the solution. To the solution 1-butyl-1,3-butadiyne (2.0 g, 18.9 mmol) was added. The reaction mixture was stirred at room temperature for about 2 h until TLC indicated that the reaction was completed. The reaction mixture was poured into a beaker containing both a 5% HCl aqueous solution (45 mL) and hexane (45 mL). The organic layer was collected and the aqueous solution was extracted with hexane (3 × 40 mL). The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure leaving a yellow liquid as the crude product. The crude product was purified using a silica gel column with hexane as the eluent and yielded 1,8-dibutyl-1,3,5,7-octatetrayne as a yellow liquid (1.82 g, 91%). ^{1}HNMR (200 MHz, $CDCl_3$): δ 0.80(6H), 1.42(8H), 2.22-(4H). ^{13}C NMR (63 MHz, $CDCl_3$): δ 13.83, 19.22, 22.36, 30.84, 60.90, 61.76, 66.07, 80.75. IR 2960, 2935, 2874, 2226, 1466, 1425, 1380, 1322, 1249, 1105, 740, 618 cm^{-1}.

Suspension Polymerization of Dibutyloctatetrayne. Poly(1,8-dibutyloctatetrayne) microbeads were prepared by suspension polymerization using water as the continuous phase. Typically, deionized water (8.0 mL) and 2% (w/w) PVA/H_2O (3.0 g) were placed in a reactor equipped with a mechanical motor. 1,8-Dibutyloctatetrayne (2.0 g) was added to the mixture. The mixture was heated to 80 °C using an oil bath. The mechanical motor was turned on, and the stirring speed was gradually increased and fixed at the level at which the desired size of droplets was achieved. The heating and stirring were continued for 48 h. The beads formed in the aqueous solution were filtered and washed with deionized water. The beads were dried in oven at 95 °C and 1.52 g (76%) of black beads was obtained.

Preparation of Carbon Microspheres. The cross-linked polydibutyloctatetrayne beads (0.50 g) prepared above were placed in a quartz tube furnace and gradually heated to 800 °C (heating rate 1 °C/min) under nitrogen atmosphere and held at 800 °C for 24 h. After cooling to room temperature, 0.25 (50%) g of carbon microbeads was obtained from the quartz tube.

Analysis. All NMR spectra were recorded on a Bruker AC-200. FTIR spectra were obtained with a Perkin-Elmer 1600 FTIR spectrometer. KBr and polymer samples were thoroughly mixed, and the mixture was pressed to form a pellet, then the spectra were recorded. Raman spectra were recorded on a Spex 1403 double monochromator, a RCA 31034A photomultiplier, and a 514.5-nm laser with ca. 50 mW. Microscopic images of polydibutyloctatetrayne beads and carbon beads were obtained from a Sirion scanning electron microscope. Numeric average particle diameters (D_n), weight average particle diameters (D_w), and polydispersity index of particle size distribution (PSD, D_w/D_n) were determined based on the diameters of more than 100 particles in SEM images. TGA analyses were carried out on a TA Instruments TGA 2050 thermogravimetric analyzer. XPS was conducted on a Kratos AXIS ultra. The XPS data were processed using Kratos Vision Processing. Powder X-ray diffraction was conducted on a Rigaku Geigerflex X-ray Powder Diffractometer with Cu Kα line (0.154 nm) as the incident beam. A Micromeritics ASAP 2020 surface area and porosity analyzer was used to measure the surface areas and average pore sizes of the particles.

Results and Discussion

The synthetic pathway used to produce the monomer, 1,8-dibutyl-1,3,5,7-octatetrayne, is illustrated in Scheme 1. 1-Hexyne was reacted with 1-iodo-2-(trimethylsilyl)acetylene using palladium and copper catalysts in diisopropylamine to produce 1-butyl-4-(trimethylsilyl)-1,3-butadiyne.[17] The

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Table 1. Results of Qualitative and Quantitative XPS Analysis of Poly(dibutyloctatetrayne) Beads and the Correspondent Carbon Beads[25,26]

Poly(dibutyloctatetrayne)			Carbon Beads		
binding energy/eV	assignment	%	binding energy/eV	assignment	%
C_1 284.67	C═C	38.2	284.50	C═C	79.9
C_2 285.31	CH_2, CH_3	38.4	285.35	CH_2, CH_3	14.4
C_3 286.54	C−OH	16.7	286.36	C−OH	4.7
C_4 288.06	C═O	6.8	287.78	C═O	2.0
O_1 532.09	C═O	28.5	531.98	C═O	30.6
O_2 532.94	C−OH	71.5	532.90	C−OH	69.4

trimethylsilyl protecting groups were removed in quantitative yield by treatment with a catalytic quantity of potassium hydroxide in aqueous methanol to yield 1-butyl-1,3-butadiyne.[17] The oxidative coupling reaction of 1-butyl-1,3-butadiyne using oxygen and copper(II) acetate monohydrate in acetone provided the liquid product—1,8-dibutyl-1,3,5,7-octatetrayne.[14,18] Note that all the intermediates in Scheme 1, including the final product, 1,8-dibutyl- 1,3,5,7-octatetrayne, are stable at room temperature and can be separated in the pure state.

It is well-known that diacetylenes can be polymerized under UV irradiation in solid state, and this polymerization reaction has been used extensively in a wide range of chemical applications.[19] Solid-state polymerization of octatetraynes with aromatic end-groups also has been reported.[20] Perhaps due to the large size and inflexible aromatic end-groups, octatetraynes with directly linked aromatic end-groups, e.g., 1,8-bis(2-thienyl)-1,3,5,7-octatetrayne, only can be polymerized at temperatures above 150 °C.[20] In contrast, the 1,8-dibutyl-1,3,5,7-octatetrayne can be polymerized below 90 °C; accordingly, the liquid monomer is converted to the insoluble dark-brown solid polymer. To obtain FTIR spectra of the products, the polymerization reactions were conducted in sealed vials. The vials of the dibutyloctatetrayne monomer were placed in an oven at a specific temperature for 24 h. IR spectra of 1,8-dibutyl-1,3,5,7-octatetrayne and its corresponding polymerization products (see Supporting Information) at temperature ranging from 70 to 95 °C showed that the intensity of the peaks at 2226 cm^{-1}, which are attributed to the −C≡C− skeleton stretching vibrations, decreases and almost disappears as the reaction continues. Quantitative XPS data shown in Table 1 confirm this result by showing that no carbon atom from C≡C is observed and 38.2% carbon atoms in the form of C═C are detected on the surface of poly(1,8-dibutyl-1,3,5,7-octatetrayne) microbeads. Therefore, it can be surmised that the main reactions for the polymerization involve the conversion of sp^1-hybridized carbon atoms in the molecule of 1,8-dibutyl-1,3,5,7-octatetrayne into sp^2-hybridized carbon atoms by a variety of triple bond additions[21] (Scheme 2) including [4+2] cycloaddition[22] and any further cyclizations[20,23] to form graphite-like structures.

The unique properties of 1,8-dibutyl-1,3,5,7-octatetrayne, such as self-polymerizability at 70−90 °C of the liquid state, and stability in water, provided the possibility to perform suspension polymerization of 1,8-dibutyl-1,3,5,7-octatetrayne in aqueous solution similar to that for vinyl monomer suspension polymerization.

The suspension polymerizations of 1,8-dibutyl-1,3,5,7-octatetrayne were conducted under conditions similar to those of suspension polymerizations for vinyl monomers by using water as the continuous phase and poly(vinyl alcohol) as the stabilizer,[24] and accordingly cross-linked poly(1,8-dibutyl-1,3,5,7-octatetrayne) microbeads were obtained. The results of 1,8-dibutyl-1,3,5,7-octatetrayne suspension polymerization are illustrated in Figure 1 and Table 2. Cross-linked poly(1,8-dibutyl-1,3,5,7-octatetrayne) microbeads with various diameters ranging from hundreds of micrometers to a few micrometers were obtained by adjusting the concentration of the stabilizer, poly(vinyl alcohol), in the continuous phase and the stirring rate of the motor. As shown in Table 2, the average diameters of poly(1,8-dibutyl-1,3,5,7-octatetrayne) microbeads decrease by increasing the stabilizer's concentration in aqueous solution. Because some of the monomer was emulsified in aqueous solutions, and also some of poly(1,8-dibutyl-1,3,5,7-octatetrayne) adhered to the surface of the stirrer during the polymerization, the yields of poly(1,8-dibutyl-1,3,5,7-octatetrayne) microbeads were in the range of 71−76%. The same phenomenon also occurred in the suspension polymerizations of vinyl monomers.[24] The polydispersity index listed in Table 2 indicates that poly(1,8-dibutyl-1,3,5,7-octatetrayne) microbeads size distributions are broad, which is also similar to the results of vinyl monomer suspension polymerization.[24]

The cross-linked poly(1,8-dibutyl-1,3,5,7-octatetrayne) microbeads can further be converted to carbon microbeads by pyrolysis at high temperature under an inert atmosphere. The temperature was gradually increased at the rate of 10 °C/min from room temperature to above 800 °C in nitrogen. Weight loss of poly(1,8-dibutyl-1,3,5,7-octatetrayne) stopped when the temperature reached 800 °C and the total weight loss was approximately 50% in the whole process of carbonization (see Supporting Information, S2). This result may indicate that only the structures formed by octatetrayne units remained as carbon materials and most of the butyl groups were volatized in the course of the pyrolysis. The weight percentage lost does correspond to the weight proportion of the polymer due to the butyl groups. The carbon beads formed by pyrolysis are shown in Figure 2. The sizes and polydispersity indexes of carbon microbeads are listed in Table 2. The carbonized products shrank compared with the original microbeads of poly(1,8-dibutyl-1,3,5,7-octatetrayne). However, the polydispersity index of

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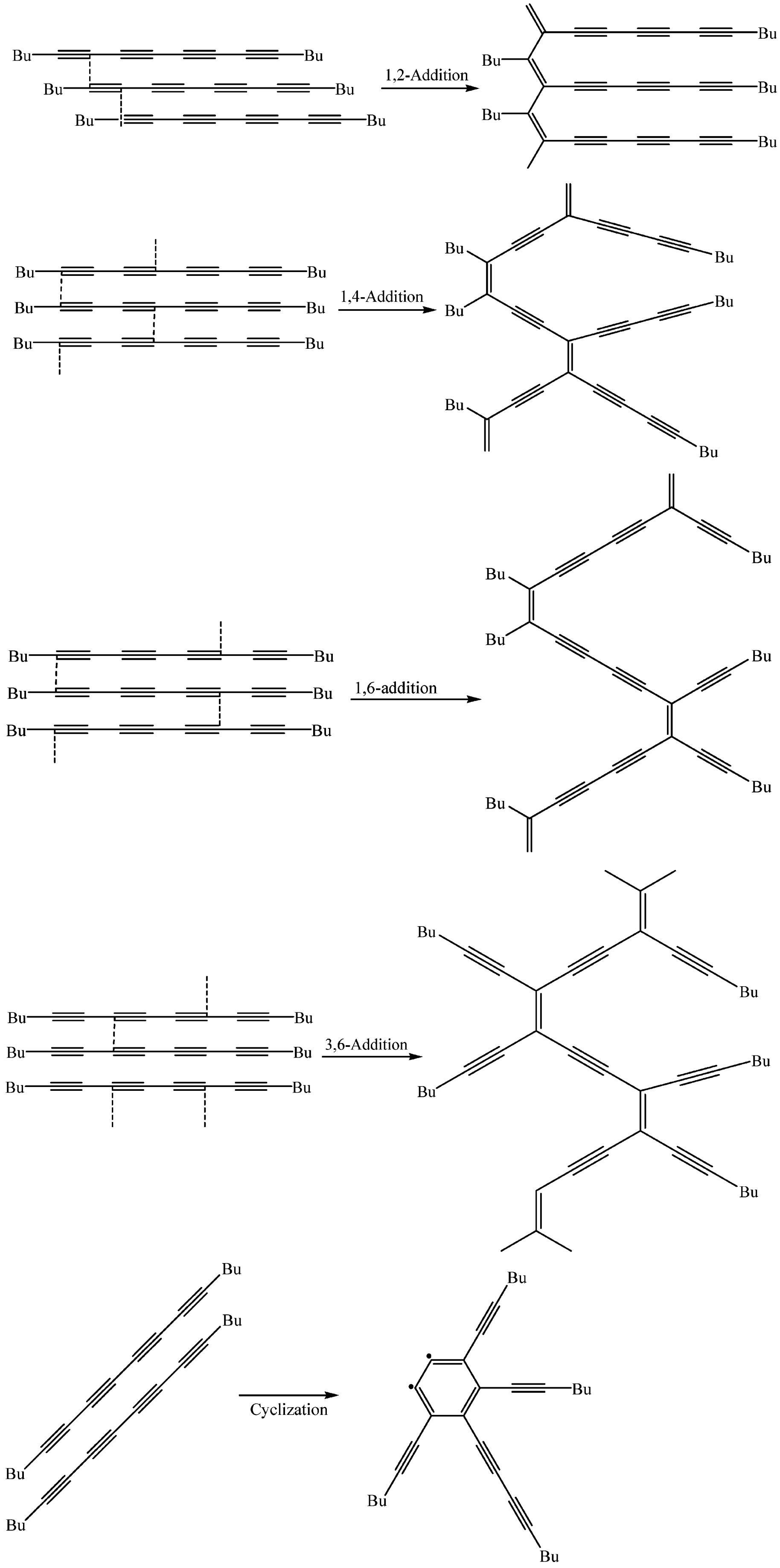
Scheme 2. Triple Bond Additions and Cyclization in the Polymerization of 1,8-Dibutyl-1,3,5,7-octatetrayne



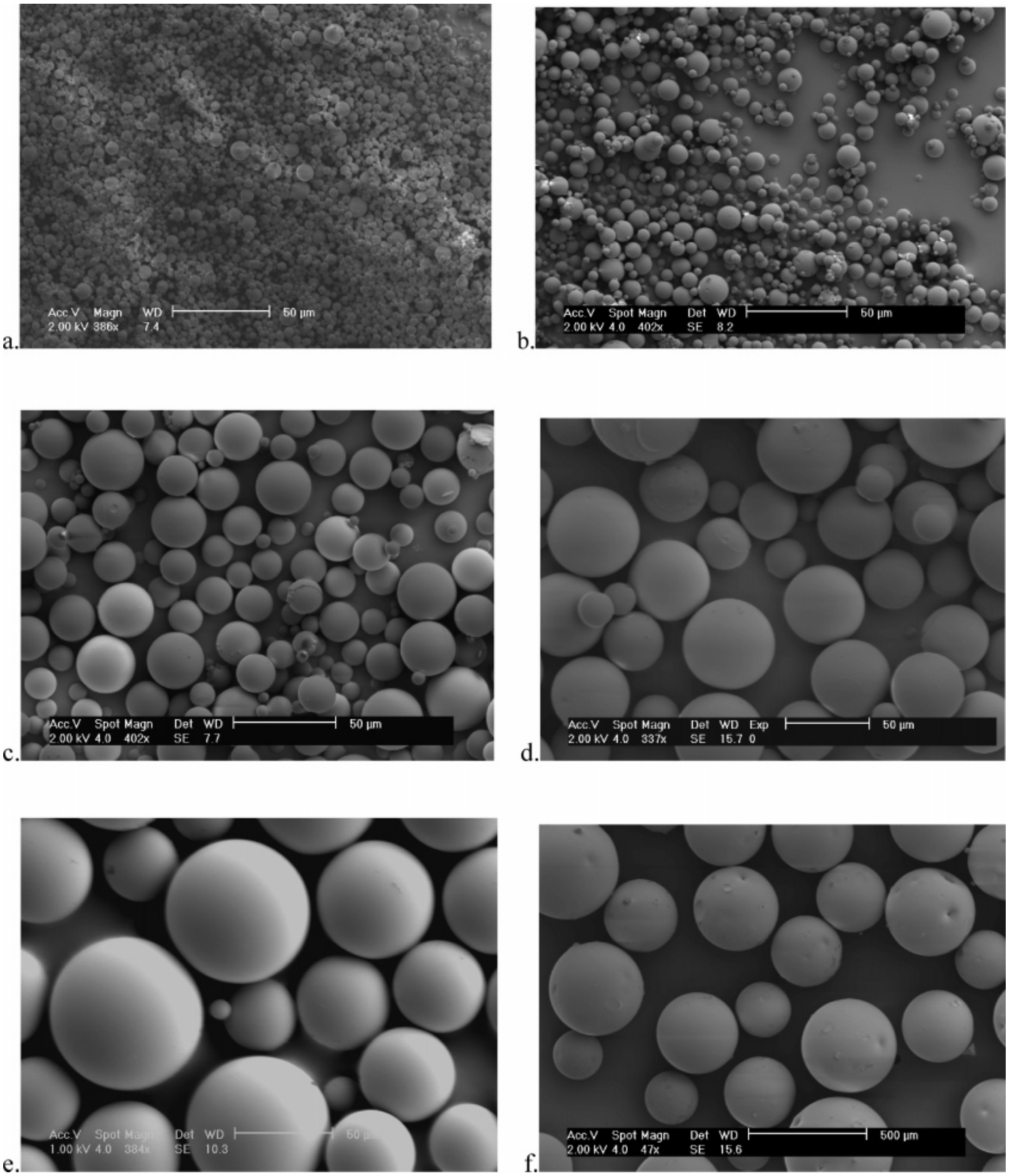


Figure 1. SEM micrographs of poly(dibutyloctatetrayne) beads prepared with suspension polymerizations. The detailed conditions are listed in Table 2.

Table 2. Conditions and Results of Suspension Polymerization of 1,8-Dibutyloctatetrayne

no.	polymerization conditions	yield (%)	PDBO d_n (mm)	PDBO PSD	Carbon Beads d_n (mm)	Carbon Beads PSD	Carbon Beads SA_{BET}[a] (m^2/g)	Carbon Beads PS_{BET}[a] (nm)	figures
1	1% PVA; 640 rpm	71	2.52	2.68	1.43	2.57	611	1.5	2a, 4a
2	0.8% PVA; 500 rpm	72	5.19	2.00	3.74	2.01			2b, 4b
3	0.5% PVA; 380 rpm	74	15.1	1.47	12.5	1.58			2c, 4c
4	0.4% PVA; 300 rpm	76	37.5	1.60	27.2	1.54			2d, 4d
5	0.2% PVA; 380 rpm	75	46.9	1.62	41.9	1.51	1.76	1.8	2e, 4e
6	0.1% PVA; 300 rpm	71	316	1.78	240	1.83			2f, 4f

[a] SA_{BET}, surface area by BET; PS_{BET}, pore size by BET.

carbon beads did not change and the beads still maintained their spherical shape despite the nearly 50% weight loss. The carbon microbeads are easily dispersible in various organic solvents, indicating that no aggregation occurred in the pyrolysis and most of the carbon microbeads kept the shape of a single bead. This behavior is different from the production of mesoporous micrbeads, MCMB, and can be ascribed to the cross-linked structures of poly(dibutyloctatetrayne) beads. It is known that MCMB, formed by stacking or aggregation of polyaromatic molecules, are fusible when the temperature is higher than the one at which MCMB were prepared which is typically 350−500 °C. The mechanical strength of the carbon beads was demonstrated by placing the beads in a sealed tank where 272 atm pressure was applied for 24 h. SEM images of the beads showed that no changes in the size or shape occurred.

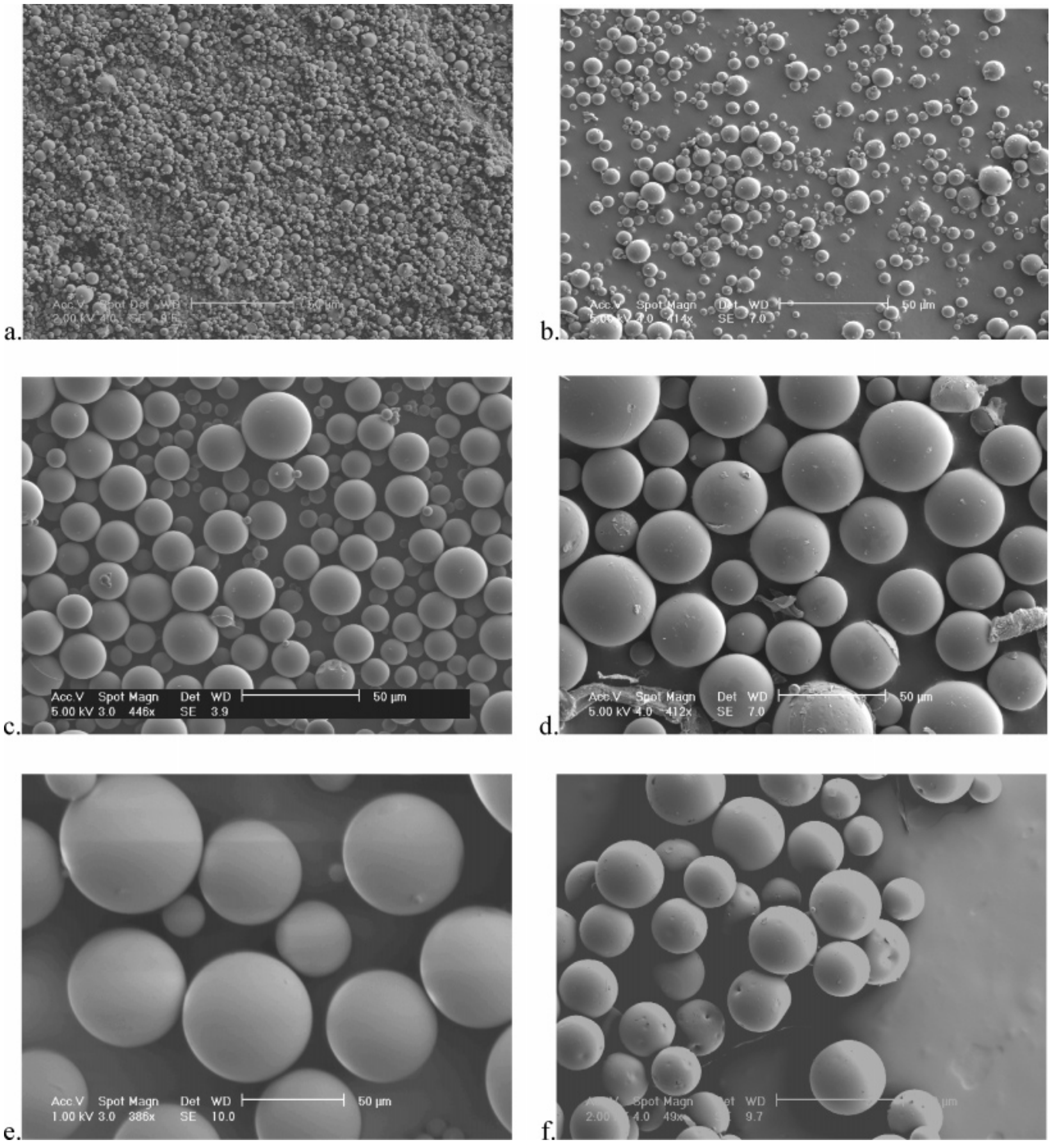


Figure 2. SEM micrographs of carbon microbeads prepared from poly(dibutlyoctatetrayne) microbeads at 800 °C. The detailed conditions are listed in Table 2.

The Brunauer−Emmett−Teller (BET) surface areas and average pore sizes for two samples of carbon beads were measured (Table 2). The small particles (diameter 2 μm) have very high surface areas. These surface areas are comparable to those obtained in carbon aerogels.[25] However, the largest carbon particles (diameter 316 μm) have very low surface areas but have average pore sizes similar to those found in the small particles. More studies are underway to attempt to control the surface area of the particles through the polymerization reaction conditions.

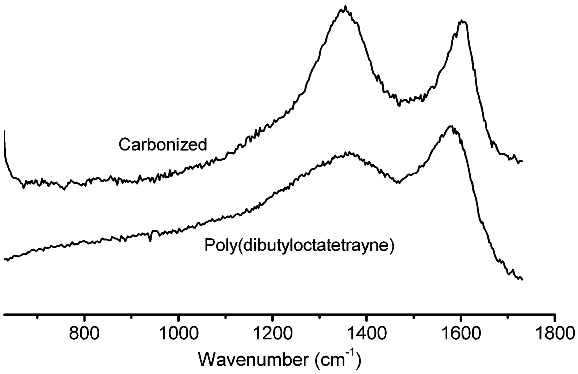


Figure 3. Raman spectra of poly(dibutyloctatetrayne) microbeads and its carbonized products.

Raman spectra of both poly(1,8-dibutyl-1,3,5,7-octatetrayne) and carbon microbeads are compared in Figure 3. The Raman spectra of poly(1,8-dibutyl-1,3,5,7-octatetrayne) and the carbon microbeads consist of two strong and broad peaks at 1363 and 1582 cm^{-1}. The band near 1582 cm^{-1} is the E_{2G} fundamental. This band is indicative of the creation of an sp^2-hybridized carbon structure.[26−28] The 1363 cm^{-1} only occurs in disordered carbons and is typically attributed to in-plane disorder. The in-plane microcrystallite size, L_{α}, can be estimated using Knight's empirical formula, $L_{\alpha} = 44(I_{1580}/I_{1360})$.[27] The order of magnitude of L_{α} is believed to

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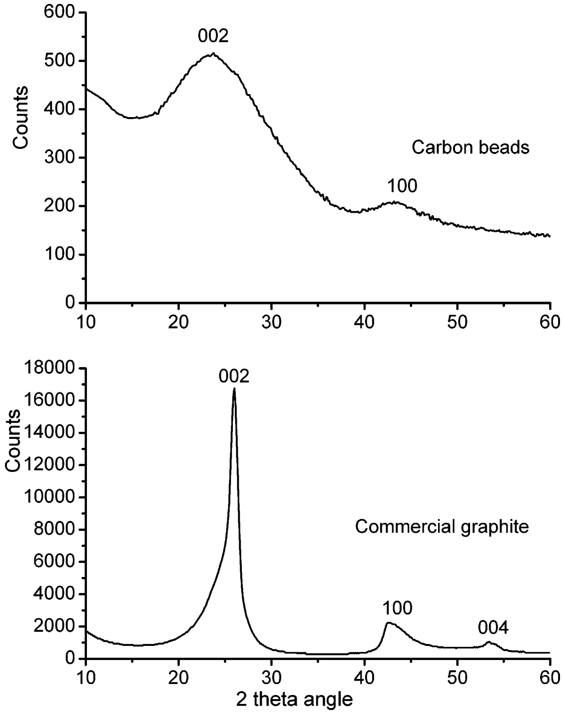

Figure 4. X-ray diffraction patterns of the carbon beads and commercial graphite.

probe the dimension of the sp^2 ribbons that make up the amorphous particles. The L_α value of the carbon beads is 4.7 nm which is comparable to values observed for other disordered carbons such as aerogels and glassy carbons.[29] The significant broadening of two Raman bands is also typical of carbon materials with small microcrystallite size. The bands tend to broaden as the microcrystallite size decreases.[27] These results conclusively confirm the structural similarity between poly(dibutyloctatetrayne) and the sp^2 carbon-bonded amorphous carbon, and also confirm the results of the XPS and IR experiments.

The X-ray diffraction patterns of commercial graphite and carbon beads are presented in Figure 4. The commercial graphite has three peaks in the range of $2\theta = 10-60°$ for the planes (002), (100), and (004) at 26.34°, 43.01°, and 53.86°, respectively.[30] Carbon beads have two broad peaks at 23.78° and 43.29° in this range, which further confirms the existence of graphitic crystallites in the structures. However, the position for plane (002) in the carbon beads shifts to a low value (23.78°) compared to that of the commercial graphite (26.34°). The interplanar distance *d* in carbon beads according to the Bragg's law is larger than that in the commercial graphite, which demonstrates that the amorphous structures disorder the crystal structures.

X-ray photoelectron spectra of poly(dibutyloctatetrayne) beads and carbon microbeads were also recorded. Wide scan XPS shows the presence of oxygen electron at 532.6 eV in both cases. Oxygen atoms in the spectra evidently are from poly(vinyl alcohol) which was used as the stabilizer for suspension polymerization. Although most of poly(vinyl alcohol) was removed by washing the beads with water, there may still be a small amount of poly(vinyl alcohol) absorbed on the surface of the beads which resulted in a strong peak in the XPS spectrum. In contrast, the intensity of oxygen peak in the spectrum of carbonized beads is much weaker due to the carbonization. High-resolution C1s and O1s spectra are shown in Figure 5. The components obtained from curve-fitting are also plotted.[31,32] Detailed results for each component are collected in Table 1. Four different carbon species, including $C{=}C$, CH_2/CH_3, $C{-}OH$, and $C{=}O$, were observed in both spectra, where $C{=}O$ is from partially hydrolyzed poly(vinyl alcohol). It can be seen that sp^2-hybridized carbon atoms become the main component in carbon beads and the amount of other carbon species in carbon beads decreases dramatically as the result of pyrolysis. O1s XPS spectra confirm the results from C1s XP spectra. As shown in Table 1, the binding energy and percentage ratios for O1s components are in agreement with the assignments made for carbon species.

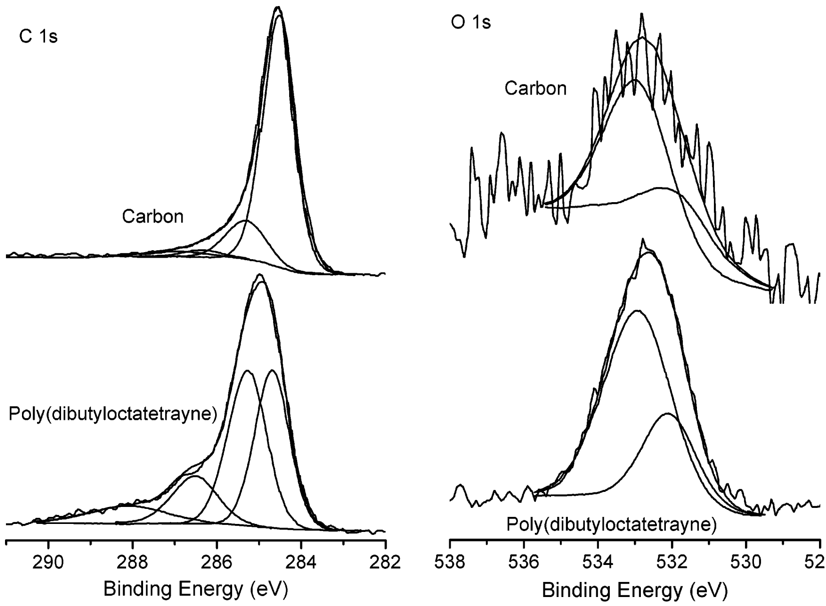

Figure 5. C1s and O1s high-resolution XPS spectra for poly(dibutyloctatetrayne) microbeads and carbon microbeads. Component peaks were determined through curve fitting analysis. The position and atomic ratios are reported in Table 1.

Conclusions

1,8-Dibutyl-1,3,5,7-octatetrayne was synthesized. It is quite stable at low temperatures and can be polymerized at temperature above 70 °C. Suspension polymerizations of 1,8-dibutyl-1,3,5,7-octatetrayne were conducted under conditions similar to those used for suspension polymerization of vinyl monomers and this gave cross-linked poly(1,8-dibutyl-1,3,5,7-octatetrayne) microbeads. Carbon microbeads were obtained by slow pyrolysis of poly(1,8-dibutyl-1,3,5,7-octatetrayne) microbeads up to 800 °C with a yield of nearly 50%.

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Supporting Information Available: IR spectra of dibutyloctatetrayne and its polymerization products as a function of temperature and weight loss curve of poly(dibutlyoctatetrayne) as a function of temperature (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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