Preparation of Carbon Nanospheres from Diblock Copolymer Micelles with Cores Containing Curable Acetylenic Groups

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ABSTRACT: We prepared carbon nanospheres by pyrolysis of core cross-linked diblock copolymer micelles. Poly(ethylene oxide)-*b*-poly(4-ethynylstyrene) (PEO−PES) with a hydrophobic block having curable acetylenic groups was synthesized by atom transfer radical polymerization. The number-average molecular weight (M_n) of the PES block was calculated to be 2200 from the peak area ratio of the PEO block to the PES block and the M_n of PEO (5000). A micelle with the size of about 28 nm was prepared by dissolving PEO−PES in water (0.05 mg/mL). A micelle core consisting of PES blocks was cross-linked by the photoreaction of acetylenic groups. In the subsequent pyrolysis, the cross-linked core was carbonized and the PEO block of the shell eliminated, resulting in a carbon nanosphere with a diameter of about 8 nm. The FT-IR spectrum showed that all of the characteristic bands for the diblock copolymers disappeared after pyrolysis. The Raman scattering spectrum of the carbon nanosphere exhibited typical partially graphitic carbon characteristics, with a strong and relatively narrow band at 1590 cm^{-1} and a broad band at 1350 cm^{-1}, corresponding to graphitic species (G-band) and disordered species (D-band), respectively.

Introduction

Carbon nanomaterials have unique electronic, mechanical, and chemical properties and can be used in advanced fillers,[1] electronic devices,[2] catalyst supports,[3] energy storage systems,[4] proximal probes,[5] and optical components.[6] There are two main methods of preparing carbon nanomaterials,[7] namely the physical/chemical vapor deposition technique and the pyrolysis of organic precursors. The latter method is applicable to large-scale production, and extensive research has been done on the development of organic precursors.

Block copolymers are of great interest as organic precursors since they can spontaneously self-assemble into a structure having a periodic morphology with a well-controlled size.[8] If their structural features are maintained during pyrolysis, nanostructured carbon materials are produced.[9] Recently, Kowalewski et al.[10] demonstrated that well-defined carbon nanoparticles can be obtained by the pyrolysis of shell cross-linked block copolymer micelles that contain polyacrylonitrile cores. The cross-linking of the micelle prior to pyrolysis is essential because otherwise its spherical shape will be completely destroyed. Nanostructured materials, including nanospheres,[11] nanochannels,[12] nanofibers,[13] and nanotubes,[14] obtained from block copolymers can be stabilized by the cross-linking reaction.

In this paper, we present a core cross-linked micelle approach to the preparation of carbon nanospheres. Compared with the shell cross-linked micelle method, the core cross-linked micelle approach has the advantage of controlling the size and shape of a carbon nanosphere since the core is the part which is intended to be carbonized, whereas the shell is supposed to be sacrificed. We synthesized an amphiphilic diblock copolymer with a hydrophobic block having curable groups, which constitutes a micelle core in an aqueous system. We chose to use an acetylenic group as a curable group since it is thermally curable under moderate conditions without the evolution of volatiles. The acetylenic group is widely used as a reactive end group for the synthesis of thermosetting heat-resistant polymers and high carbon materials.[15]

Experimental Section

Materials and Measurements. 4-Bromostyrene (98%), (trimethylsilyl)acetylene (98%), poly(ethylene glycol) methyl ether (average $M_n = 5000$), 2-bromoisobutyryl bromide (98%), dichlorobis(triphenylphosphine)palladium(II) (98%), copper(I) iodide (98%), copper(I) bromide (99.99%), and 4,4′-dinonyl-2,2′-bipyridine (97%) (dNbpy) were purchased from Aldrich Chemical Co. and used without further purification. Reagent grade solvents were dried and purified as follows. Triethylamine (TEA) was dried and distilled from calcium hydride. Methyl alcohol was dried over molecular sieves (4 Å) and distilled. Tetrahydrofuran (THF) was dried and distilled from sodium. The infrared spectra were recorded by using a Perkin-Elmer Spectrum GX I. The ^{1}H NMR (300 MHz) spectra were recorded by using a JEOL JNM-LA300 spectrometer. Gel permeation chromatography (GPC) was carried out with a Viscotek model 250 equipped with a M410 refractive index detector and PL Gel Mix-B (10 μm) and Mix-D (5 μm) columns at flow rate of 1 mL/min at 30 °C by using THF as eluent. Polystyrene standards were used for calibration. Thermogravimetric analysis (TGA) was performed on a TA modulated TGA2050 with a heating rate of 10 °C/min under nitrogen. Differential scanning calorimetry (DSC) measurement was performed by a TA modulated DSC 2920 with a scanning rate of 10 °C/min under nitrogen. Elemental analyses were carried out on an EAGER 200 elemental analyzer. A transmission electron microscopy (TEM) image was obtained by a JEM-200CX instrument operating at 120 kV. TEM samples were prepared by aspirating a fine spray of a dilute nanosphere solution onto a carbon-coated copper grid. After drying, the sample was stained by RuO$_4$ vapor for 5 min. Dynamic light scattering studies (DLS) were carried out with a Photal electrophoretic light scattering and zeta-potential analyzer (ELS8000) equipped with a He−Ne laser operated at 632.8 nm (laser power = 10 mW). A solution of a micelle in water (0.12 mg/mL) was prepared and clarified by passing it through a 0.2 μm filter. The Raman spectrum was obtained from a Jobin Yvon T64000 Raman system. The excitation was at 514 nm. The laser power was set to 35 mW. Fluorescence measurements were performed using an RF-5301PC (Shimadzu)

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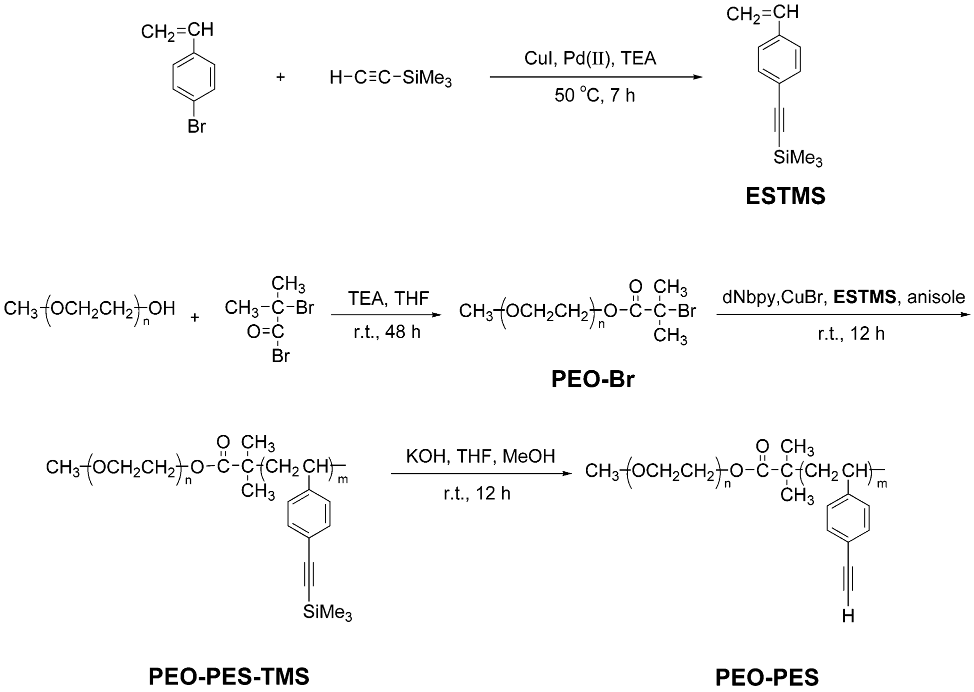
Scheme 1. Synthesis of Poly(ethylene oxide)-*b*-poly(4-ethynylstyrene)[a]



[a] dNbpy = 4,4′-dinonyl-2,2′-bipyridine, Pd(II) = dichlorobis(triphenylphosphine)palladium(II).

spectrofluorometer. Ultraviolet−visible spectra were obtained with a Hewlett-Packard HP8452A UV−vis spectrometer.

Synthesis of 4-(Trimethylsilylethynyl)styrene (ESTMS). 4-Bromostyrene (5.0 g, 27 mmol) was dissolved in 250 mL of TEA. Small amounts of hydroquinone were added to prevent polymerization. (Trimethylsilyl)acetylene (3.2 g, 33 mmol), dichlorobis-(triphenylphosphine)palladium(II) (0.38 g, 0.55 mmol), and copper(I) iodide (52 mg, 0.027 mmol) were added to the solution, and then the reaction mixture was stirred for 7 h at 50 °C. After filtration and evaporation, the product was isolated as a pale yellow liquid by column chromatography on silica gel (*n*-hexane); yield: 2.6 g (48%).

Anal. Calcd (in wt %) for $C_{13}H_{16}Si$: C; 77.93, H; 8.05. Found: C; 77.59, H; 7.97. ^1H NMR ($CDCl_3$): δ 7.46−7.34 (dd, aromatic proton), 6.70 (q, vinylic proton), 5.80 (d, vinylic proton), 5.30 (d, vinylic proton), 0.23 (s, $-Si(CH_3)_3$). IR (KBr pellet, cm^{-1}): 2158 (m, C≡C), 1628 (w, C=C), 1506 (s, aromatic C=C), 865 (vs, Si−C).

Synthesis of Macroinitiator (PEO-Br). Poly(ethylene glycol) methyl ether (average $M_n = 5000$) (6.0 g) was dissolved in THF (100 mL). TEA (0.60 g, 5.9 mmol) and 2-bromoisobutyryl bromide (0.44 g, 1.9 mmol) were added dropwise at room temperature. After stirring for 48 h at room temperature, the amine salt was removed by filtration. After concentration by evaporation of the solvent, the product was isolated by precipitation in a large excess of diethyl ether and purified by reprecipitation of the polymer solution from THF into diethyl ether; yield: 5.2 g (84%).

^1H NMR ($CDCl_3$): δ 3.66 (s, $-CH_2CH_2O-$), 1.96 (s, $-C(CH_3)_2-$Br). IR (KBr pellet, cm^{-1}): 1100 (s, C−O−C).

Synthesis of Diblock Copolymer (PEO−PES). A solution of PEO-Br (0.55 g, 0.10 mmol) and ESTMS (0.55 g, 2.7 mmol) in anisole (1 mL) was added to a solution of copper bromide (15 mg, 0.10 mmol) and 4,4′-dinonyl-2,2′-bipyridine (82 mg, 0.20 mmol) in anisole (1 mL) in a polymerization tube (5 mL). After three freeze−thaw cycles under N_2, the tube was sealed and placed in an oil bath at 110 °C for 6 h with stirring. The reaction mixture was passed through a column of neutral alumina to remove metal salts. The filtrate was poured into diethyl ether. The precipitated polymer (PEO−PES−TMS) was isolated by filtration and purified by reprecipitation of the polymer solution from THF into diethyl ether; yield: 0.94 g (72%).

Figure 1. The core cross-linked micelle approach to the preparation of carbon nanospheres.

^1H NMR ($CDCl_3$): δ 7.28−6.54 (mm, aromatic proton), 3.66 (s, CH_2CH_2O-), 1.65−0.90 (m, PES backbone), 0.23 (s, $-Si(CH_3)_3$). IR (KBr pellet, cm^{-1}): 1100 (s, C−O−C), 2158 (s, C≡C), 865 (vs, Si−C).

Trimethylsilyl groups of the diblock copolymer (PEO−PES−TMS) were removed under basic conditions. PEO−PES−TMS (0.20 g, 0.023 mmol) and potassium hydroxide (0.010 g, 0.17 mmol) were dissolved in THF/methyl alcohol (50 mL/50 mL). The mixture was stirred for 12 h at room temperature and then transferred into a cellulose tubing membrane (Cellu Sep, molecular weight cutoff, 3500) for dialysis against water. The dialysate was exchanged every 2 h over 3 days. The polymer solution in the dialysis bag was concentrated to dryness to give PEO−PES; 0.18 g (89%).

^1H NMR ($CDCl_3$): δ 7.28−6.54 (mm, aromatic proton), 3.66 (s, CH_2CH_2O-), 3.08 (s, ethynyl proton), 1.65−0.90 (m, PES backbone). IR (KBr pellet, cm^{-1}): 1100 (s, C−O−C), 2107 (w, C≡C), 2870 (s, C−H), 3280 (m, ≡C−H). GPC: $M_n = 12\,000$, $M_w = 14\,100$.

Micellization. The micelle formation of diblock copolymer PEO−PES was achieved by adding 1 mL of the diblock copolymer solution in THF (1 mg/mL) dropwise into 20 mL of deionized water at room temperature. Then the trace amount of THF was removed by a low-pressure distillation.

Photo-Cross-Linking and Pyrolysis. The micellar solution in an irradiation cell was irradiated with light from a high-pressure mercury arc lamp (100 w) for 2 h at room temperature under air. A fine spray of the solution was aspirated onto a carbon-coated copper grid and pyrolysized. The sample was put into a TGA chamber and heated for 5 min at 600 °C under nitrogen.

Results and Discussion

Synthesis. Figure 1 illustrates the core cross-linked micelle approach to the preparation of carbon nanospheres. Poly(ethylene oxide)-*b*-poly(4-ethynylstyrene), an amphiphilic diblock

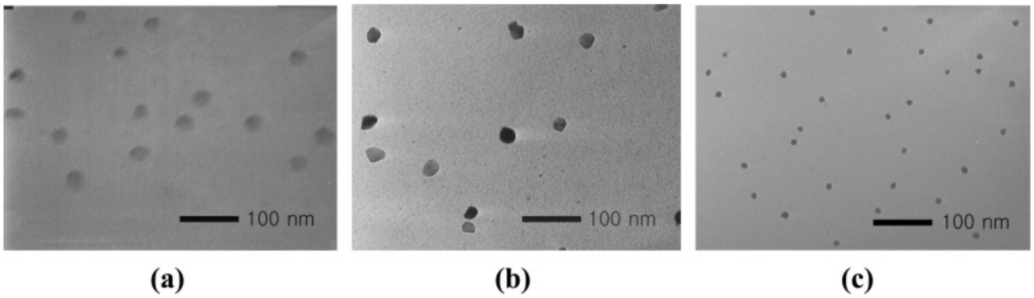


Figure 2. Transmission electron microscopy images of poly(ethylene oxide)-*b*-poly(4-ethynylstyrene) diblock copolymer micelles: (a) before UV irradiation (stained with RuO_4), (b) after UV irradiation (stained with RuO_4), and (c) after pyrolysis at 600 °C (without staining).

Table 1. Molecular Weights of Poly(ethylene oxide)-*b*-poly(4-ethynylstyrene)

M_n[a]	M_w[a]	M_w/M_n[a]	n/m[b]	M_n[b]	n[c]	m[c]
12000	14100	1.17	6	7200	113	18

[a] Determined by gel permeation chromatography calibrated with polystyrene standards in tetrahydrofuran. [b] Calculated by integration of ^1H NMR resonances of a PEO and a PES block. [c] Number of repeating unit of a PEO block (*n*) and a PES block (*m*) in Scheme 1.

copolymer, forms a micelle in water with a core consisting of PES blocks. The core is cross-linked by the photoreaction of the acetylenic groups. In the subsequent pyrolysis, the cross-linked core is carbonized and the PEO block of the shell eliminated, resulting in the production of carbon nanospheres.

PEO−PES was synthesized by atom transfer radical polymerization (ATRP) as shown in Scheme 1. The monomer, ESTMS, containing a trimethylsilyl-protected acetylenic group was prepared by the reaction of 4-bromostyrene with (trimethylsilyl)acetylene over a Pd(II)/CuI catalyst.[16] The macroinitiator, PEO-Br, was prepared by the reaction of poly(ethylene glycol) methyl ether ($M_n = 5000$) with 2-bromoisobutyryl bromide under basic conditions.[17,18] ATRP of ESTMS was carried out by using PEO-Br as the initiator and copper bromide/dinonylbipyridine as the catalyst. The trimethylsilyl groups were removed under basic conditions to yield PEO−PES.[19] The removal of the trimethylsilyl groups was confirmed by ^1H NMR spectroscopy. The resonance at 0.23 ppm disappeared, and a new resonance appeared at 3.08 ppm corresponding to an acetylenic proton in the spectrum measured in $CDCl_3$. The benzene ring proton peaks of the PES blocks appeared at 6.54−7.28 ppm, and the methylene proton peaks of the PEO blocks were observed at 3.66 ppm. The number-average molecular weight of the PES block was calculated to be 2200 from the integral ratio of the PEO block to the PES block and the M_n of PEO (5000). The number-average molecular weight measured by GPC in THF with polystyrene standards was 12 000, which was higher than that obtained by ^1H NMR spectroscopy. The polydispersity index (M_w/M_n) was 1.17, showing the relatively narrow molecular weight distribution. The ^1H NMR spectroscopy and GPC analysis results are summarized in Table 1.

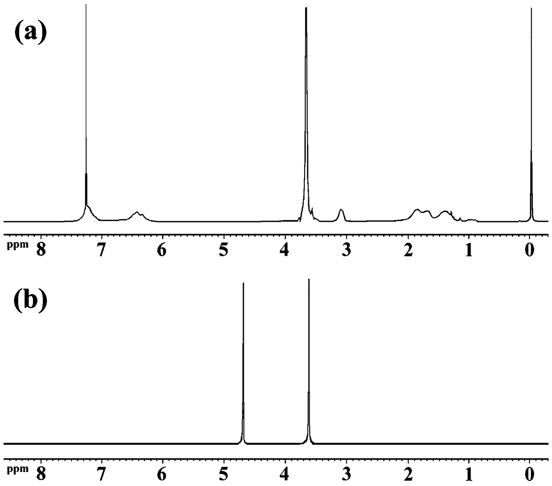


Figure 3. ^1H NMR spectra recorded for poly(ethylene oxide)-*b*-poly(4-ethynylstyrene) diblock copolymer in $CDCl_3$ containing tetramethylsilane (a) and in D_2O (b) at room temperature.

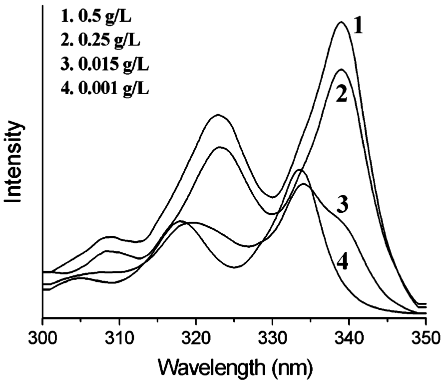


Figure 4. Excitation spectra ($\lambda_{em} = 392$ nm) of pyrene in water as a function of poly(ethylene oxide)-*b*-poly(4-ethynylstyrene) concentration from 0.001 to 0.5 g/L.

Micellization. Micelles were prepared by dissolving PEO−PES in water (0.05 mg/mL). A visual image of the micelles was obtained by using TEM. TEM samples were prepared by aspirating a fine spray of a solution of PEO−PES in water (0.05 mg/mL) onto a carbon-coated copper grid. The TEM micrograph in Figure 2a shows spherical type micelles with sizes of 28 ± 3 nm by averaging over 40 particles. The micelle sizes were also measured by the dynamic light scattering technique. In water, the average hydrodynamic diameter (d_h) of the micelle was about 32 nm, which was larger than that obtained from the TEM measurement, probably because the micelle shrunk due to the loss of water during the TEM measurement. The core−shell structure of the micelle was investigated by ^1H NMR spectroscopy. As discussed above, the ^1H NMR spectrum measured in $CDCl_3$ showed all the proton resonances of PEO−PES. However, the spectrum obtained in D_2O showed only the methylene proton resonances of the PEO block at 3.66 ppm, suggesting that the micelle core was composed of PES blocks and surrounded by a PEO shell (Figure 3).

Figure 4 shows the fluorescence spectra of pyrene in water in the presence of the diblock copolymer. The fluorescence of pyrene is sensitive to changes in the microenvironment. Pyrene concentration was 6×10^{-7} M. Above the critical micelle concentration (cmc), the fluorescence intensity values changed substantially, indicating pyrene transferring into the hydrophobic micelle domain. In the excitation spectra monitored at the wavelength of 392 nm, the pyrene spectra gradually shifted from

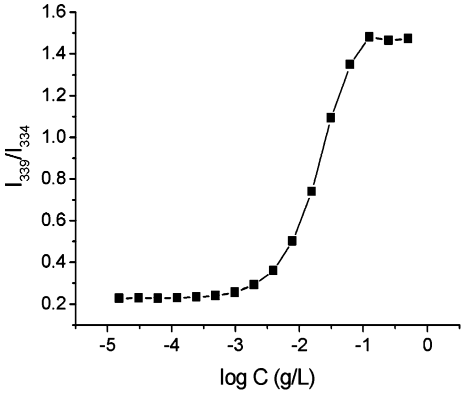


Figure 5. Plot of intensity ratio (I_{339}/I_{334}) from pyrene excitation spectra vs logarithmic concentration for poly(ethylene oxide)-*b*-poly(4-ethynylstyrene) in water.

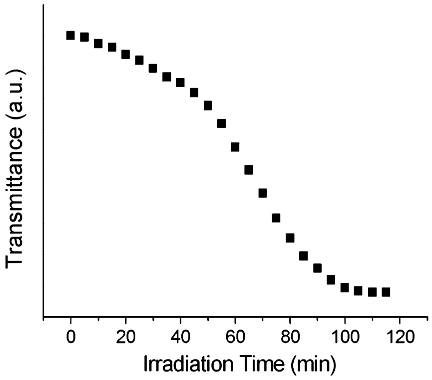


Figure 6. Plot of optical transmittance vs time for an aqueous poly(ethylene oxide)-*b*-poly(4-ethynylstyrene) micellar solution (0.15 mg/mL) measured at 500 nm under UV irradiation with a high-pressure mercury arc lamp (100 W).

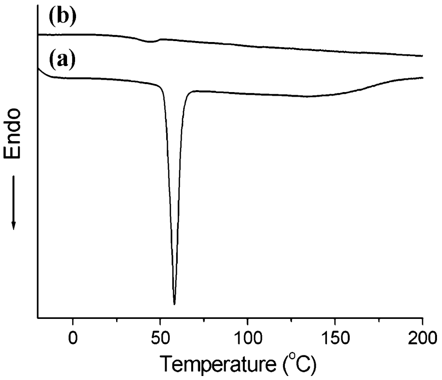


Figure 7. DSC thermograms of the poly(ethylene oxide)-*b*-poly(4-ethynylstyrene) micelle (a) and after UV irradiation for 2 h (b) obtained with a scanning rate of 10 °C/min under nitrogen.

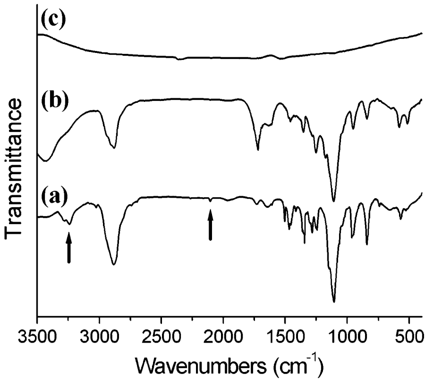


Figure 8. IR spectra of the poly(ethylene oxide)-*b*-poly(4-ethynylstyrene) micelle (a), after UV irradiation for 2 h (b), and after pyrolysis at 600 °C for 5 min under nitrogen (c). Arrows in (a) indicate the peaks from acetylenic groups.

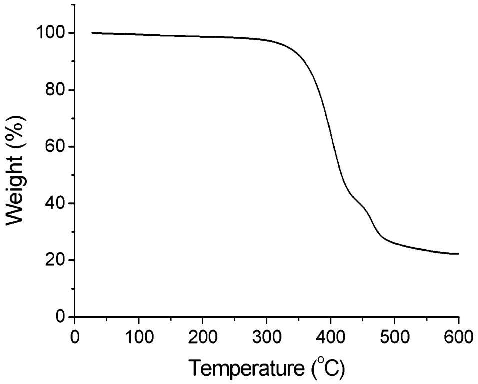


Figure 9. TGA thermogram of the poly(ethylene oxide)-*b*-poly(4-ethynylstyrene) micelle obtained with a heating rate of 10 °C/min under nitrogen.

334 to 339 nm as pyrene was transferred into the less polar micelle domain. The spectral shift in pyrene excitation spectra was utilized to determine the cmc of diblock copolymer. Figure 5 shows the intensity ratio (I_{339}/I_{334}) of pyrene excitation spectra depending on the concentration of diblock copolymer. The cmc was determined from the crossover point at the low concentration range. The cmc of diblock copolymer was 4 mg/L.

Core Cross-Linking and Pyrolysis. The micelles in water were exposed to UV light to fix their spherical structures. The UV cross-linking process was monitored in situ by recording the optical transmittance of a probe light (500 nm) through the diblock copolymer micellar solution (0.15 mg/mL) under UV irradiation with a high-pressure mercury arc lamp (100 W) at room temperature. The polymer was not precipitated by UV irradiation, but as the irradiation time increased, the transmittance decreased (Figure 6). The DSC study also showed that the UV irradiation caused cross-linking. In the DSC thermogram of the diblock copolymer micelle, a strong endothermic peak due to the melt transition of the PEO block and a broad exothermic peak originating from the thermal reaction of acetylenic groups appeared at 58 and 180 °C, respectively. After UV irradiation for 2 h at room temperature, however, the melt transition peak was no longer observed in the DSC thermogram, and no peaks appeared before the exothermic thermal reaction peak at 180 °C (Figure 7). It is not clear how the photoreaction proceeded during the UV irradiation, but we presume that oxidative coupling between the acetylenic groups was likely involved in the process.[20] In fact, FT-IR spectroscopy study showed that the acetylenic groups were consumed during the UV irradiation. When a thin film of the diblock copolymer micelles deposited on a KBr pellet was exposed to UV light for 2 h at room temperature, the acetylenic absorptions at 2107 and 3280 cm^{-1}, corresponding to the C−C triple bond and C−H stretchings, respectively, decreased significantly (Figure 8b).

Figure 2b shows the TEM image of the diblock copolymer micelles obtained after the UV irradiation. The diameters of the micelles are almost the same as those of the un-cross-linked micelles. Some particles were not completely spherical, indicating that the core part is distorted by the UV cross-linking reaction. The micelles were pyrolyzed at 600 °C for 5 min under nitrogen. In the process of pyrolysis, the PES blocks of the core were carbonized and the PEO chains constituting the shell degraded and volatilized. The FT-IR spectrum showed that all of the characteristic bands for the diblock copolymers disappeared after pyrolysis (Figure 8c). Spherical carbon nanospheres

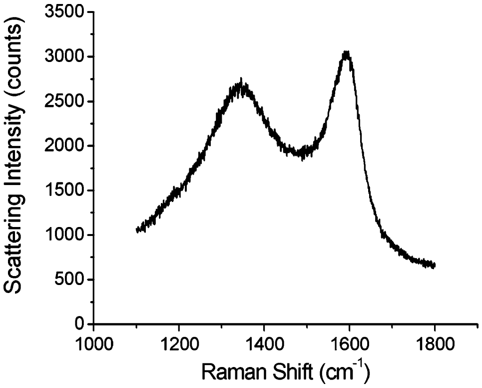


Figure 10. Raman scattering spectrum of the poly(ethylene oxide)-*b*-poly(4-ethynylstyrene) micelle after pyrolysis at 600 °C for 5 min under nitrogen.

with diameters of 8 ± 2 nm were observed in the TEM image (Figure 2c). TGA analysis of the diblock copolymer micelle under a nitrogen flow showed that the amount of residue was 22 wt % at 600 °C (Figure 9). Elemental analysis of the carbon nanosphere revealed the following composition: 90% C and 1.1% H. Raman scattering spectrum of the carbon material prepared by pyrolysis of diblock copolymer micelle exhibited typical partially graphitic carbon characteristics (Figure 10). There appeared a strong and relatively narrow band at 1590 cm^{-1} and a broad band at 1350 cm^{-1}, corresponding to graphitic species (G-band) and disordered species (D-band), respectively.[10]

Conclusion

In this work, we prepared carbon nanospheres by pyrolysis of the core cross-linked diblock copolymer micelles. Curable amphiphilic diblock copolymers (PEO−PES) were prepared by ATRP, wherein reactive acetylenic groups were introduced into a hydrophobic block. After micellization in an aqueous system, the core structure was fixed by UV irradiation, and subsequent pyrolysis resulted in the production of carbon nanospheres with a diameter of ∼8 nm. Various amphiphilic diblock copolymers having a curable PES block and different comonomer compositions can be prepared by the living radical polymerization technique. Future studies will focus on their use as an organic precursor to synthesize carbon nanomaterials with structures controlled by the block copolymer compositions.

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