

Synthesis of a Triblock Copolymer Containing a Diacetylene Group and Its Use for Preparation of Carbon Nanodots

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Abstract: Carbon nanodots were prepared by the pyrolysis of a triblock copolymer. The triblock copolymer, poly(methyl methacrylate)-*b*-polystyrene-*b*-poly(methyl methacrylate) was synthesized by atom transfer radical polymerization using an initiator containing a diacetylene group. A polymer thin film on a mica substrate was prepared by spin-casting at 2,000 rpm from a 0.5 wt% toluene solution of the triblock copolymer. After drying, the cast film was vacuum-annealed for 48 h at 160 °C. The annealed film formed a spherical morphology of polystyrene domains with a diameter of approximately 30 nm. The film was exposed to UV irradiation to induce a cross-linking reaction between diacetylene groups. In the subsequent pyrolysis at 800 °C, the cross-linked polystyrene spheres were carbonized and the poly(methyl methacrylate) matrix was eliminated, resulting in carbon nanodots deposited on a substrate with a diameter of approximately 5 nm.

Keywords: carbon nanodot, atom transfer radical polymerization, diacetylene, pyrolysis, triblock copolymer.

Introduction

Block copolymers are of great interest as organic precursors of carbon nanomaterials since they can spontaneously self-assemble into a structure having a periodic morphology with a well-controlled size.¹⁻⁵ Block copolymers with a curable block have gained much attention since their self-assembled structures can be further stabilized by cross-linking reaction to produce nanospheres,^{6,7} nanochannels,⁸⁻¹⁰ nanofibers,¹¹ and nanotubes.^{12,13} If their structural features are maintained during pyrolysis, nanostructured carbon materials are produced.¹⁴⁻¹⁶ Recently, Kowalewski *et al.*¹⁷ reported the preparation of carbon nanoparticles by the pyrolysis of block copolymer micelles of a poly(acrylic acid)-*b*-polyacrylonitrile (PAA-PAN) copolymer. The shells of the micelles were cross-linked prior to pyrolysis and thereby their spherical shapes could be maintained. More recently, Jérôme and coworkers demonstrated that carbon nanocapsules could be prepared by pyrolysis of PAA-PAN micelles, whose PAN cores were cross-linked by gold nanoparticles.¹⁸ In our previous report, we presented a core cross-linked micelle approach to the preparation of carbon nanospheres.¹⁹ We used an amphiphilic diblock copolymer with a hydrophobic block having curable groups for micellization. The hydrophobic block constituted a micelle core in

an aqueous system. Since the core is the part which is intended to be carbonized, whereas the shell is supposed to be sacrificed, the core cross-linked micelle approach offers better control of the size and shape of a carbon nanosphere compared with the shell cross-linked micelle method.

In this paper, we report the preparation of carbon nanodots deposited on a substrate from a triblock copolymer, poly(methyl methacrylate)-*b*-polystyrene-*b*-poly(methyl methacrylate). We synthesized the triblock copolymer by atom transfer radical polymerization (ATRP) using an initiator containing a diacetylene group and thereby a middle PS block had a photocurable functionality. A polymer thin film was prepared by casting a polymer solution on a substrate. The copolymer exhibited a spherical PS microdomain morphology after microphase separation by annealing, which was fixed by UV irradiation. In the subsequent pyrolysis, the cross-linked polystyrene spheres were carbonized and the poly(methyl methacrylate) matrix was eliminated, resulting in carbon nanodots deposited on the substrate. Our approach to the preparation of carbon nanodots is schematically shown in Figure 1.

Experimental

Materials and Measurements. 4-Iodobenzyl alcohol, (trimethylsilyl)acetylene, dichlorobis(triphenylphosphine)palladium(II), copper(I) iodide, copper(I) bromide, 4,4'-

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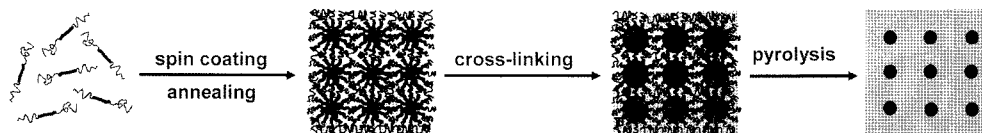


Figure 1. The preparation of carbon nanodots from a curable triblock copolymer.

dinonyl-2,2'-bipyridine (dNbpy), *N,N,N',N',N''*-pentamethyldiethylenetriamine (PMDETA), copper(II) acetate, and phosphorus tribromide 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. Methanol was dried over molecular sieves 4 Å and distilled. Tetrahydrofuran (THF), toluene, and pyridine were dried and distilled from sodium. The $^1\text{H-NMR}$ (300 MHz) spectra were recorded by using a Jeol JNM-LA300 spectrometer. FT-IR spectra were obtained with the use of a PERKIN ELMER Spectrum 2000 FT-IR 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 a 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. Elemental analyses were performed by an EA1110 (CE instrument). Transmission electron microscopy (TEM) image was obtained by a JEM-200CX instrument operating at 120 kV. 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.

Synthesis of (4-Trimethylsilylethynylphenyl)methanol (1). 4-Iodobenzyl alcohol (4.0 g, 17 mmol) and (trimethylsilyl)acetylene (2.9 mL, 21 mmol) were dissolved in 250 mL of triethylamine and then dichlorobis(triphenylphosphine)-palladium(II) (0.24 g, 0.34 mmol) and copper iodide (0.032 g, 0.68 mmol) were added to the solution. The reaction mixture was stirred for 6 h at room temperature. After filtration and evaporation, the product was isolated by column chromatography on silica gel (40% ethyl acetate in *n*-hexane); yield: 2.7 g (77%).

Anal. Calcd for $\text{C}_{12}\text{H}_{16}\text{OSi}$: C, 70.53, H, 7.89. Found: C, 70.60, H, 7.91. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$): δ 7.49–7.28 (dd, aromatic proton, 4H), 4.69 (d, CH, 2H), 1.8 (t, OH, 1H), 0.27 (s, SiMe_3 , 9H).

Synthesis of (4-Ethynylphenyl)methanol (2). (4-Trimethylsilylethynylphenyl)methanol (3.2 g, 16 mmol) was dissolved in 100 mL of methanol and then KOH (1.3 g, 24 mmol) was added to the solution. The reaction mixture was stirred for 2 h at room temperature. After evaporation of the solvent, the product was isolated by column chromatography on silica gel (40% ethyl acetate in *n*-hexane); yield: 2.0 g (93%).

Anal. Calcd for $\text{C}_9\text{H}_8\text{O}$: C, 81.79, H, 6.10. Found: C, 81.60, H, 6.23. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$): δ 7.45–7.31 (dd, aromatic proton, 4H), 5.28 (t, OH, 1H), 4.5 (d, CH_2 , 2H), 4.1 (s, $\text{C}\equiv\text{CH}$, 1H). IR (KBr pellet, cm^{-1}): 3286 (s, OH), 3266 (s, $\equiv\text{C-H}$), 2904 (s, C-H), 2107 (w, $\text{C}\equiv\text{C}$).

Synthesis of 1,4-[Bis(4-hydroxymethylphenyl)]butadiyne (3). To a solution of compound 2 in 100 mL of a mixture of pyridine and methanol (1:1, v/v) was added copper acetate (1.4 g, 7.6 mmol). The reaction mixture was stirred for 12 h with reflux. After filtration and evaporation, the product was isolated by column chromatography on silica gel (50% ethyl acetate in *n*-hexane); yield: 0.6 g (30%).

Anal. Calcd for $\text{C}_{18}\text{H}_{14}\text{O}_2$: C, 82.42, H, 5.38. Found: C, 82.33, H, 5.49. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$): δ 7.64–7.42 (dd, aromatic proton, 8H), 5.39 (t, OH, 2H), 4.6 (d, CH_2 , 4H). IR (KBr pellet, cm^{-1}): 3259 (s, OH), 2924 (s, C-H), 2220 (w, $\text{C}\equiv\text{C}$ asymmetric stretching vibration), 2141 (w, $\text{C}\equiv\text{C}$ symmetric stretching vibration).

Synthesis of 1,4-[Bis(4-bromomethylphenyl)]butadiyne (4). To a solution of compound 3 (0.44 g, 1.7 mmol) in 150 mL of THF was added PBr_3 (0.38 mL, 4.1 mmol). The reaction mixture was stirred for 12 h at room temperature. After evaporation of the solvent, the product was isolated by column chromatography on silica gel (25% tetrahydrofuran in *n*-hexane); yield: 0.46 g (72 %).

Anal. Calcd for $\text{C}_{18}\text{H}_{12}\text{Br}_2$: C, 55.71, H, 3.12. Found: C, 55.85, H, 3.09. $^1\text{H-NMR}$ ($\text{DMSO-}d_6$): δ 7.60–7.48 (dd, aromatic proton, 4H), 4.7 (s, CH_2 , 2H). IR (KBr pellet, cm^{-1}): 2954 (s, C-H), 2220 (w, $\text{C}\equiv\text{C}$ asymmetric stretching vibration), 2141 (w, $\text{C}\equiv\text{C}$ symmetric stretching vibration).

Synthesis of PS (5). A solution of compound 4 (0.30 g, 0.77 mmol) and styrene (4.4 mL, 39 mmol) in toluene (3.0 mL) was added to a solution of CuBr (0.22 g, 1.6 mmol) and PMDETA (0.32 g, 1.6 mmol) in toluene (2.0 mL) in a polymerization tube (10 mL). After three freeze-thaw cycles under argon, the tube was sealed and placed in an oil bath at 90 °C for 6 h with stirring. The reaction mixture was passed through a column of neutral alumina to remove metal salts. After concentration of the filtrate under reduced pressure, the residue was poured into methanol. The precipitated polymer was isolated by filtration and purified by reprecipitation of the polymer solution from toluene into methanol; yield: 1.9 g (39%).

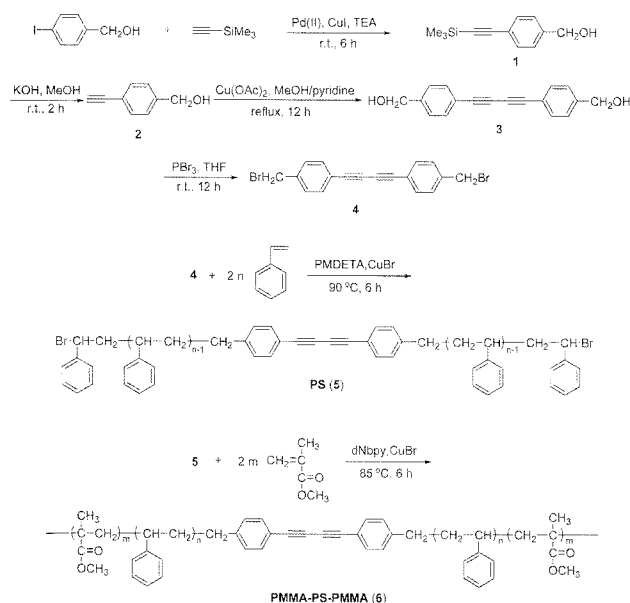
Synthesis of PMMA-PS-PMMA (6). A solution of polymer 5 (0.10 g) in toluene (1.0 mL) was transferred to a solution of CuBr (1 mg, 0.0080 mmol), dNbpy (6.1 mg, 0.015 mmol), and methyl methacrylate (0.50 mL, 4.7 mmol) in tol-

uene (1.0 mL) in a polymerization tube (5.0 mL). After three freeze-thaw cycles under argon, the tube was sealed and placed in an oil bath at 85 °C for 6 h with stirring. The reaction mixture was passed through a column of neutral alumina to remove metal salts. After concentration of the filtrate under reduced pressure, the residue was poured into methanol. The precipitated polymer was isolated by filtration and purified by reprecipitation of the polymer solution from THF into methanol; yield: 0.33 g (49%).

Film Preparation and Pyrolysis. A polymer film was prepared by spin-casting at 2,000 rpm from a 0.5 wt% toluene solution of PMMA-PS-PMMA on a mica substrate. After drying for 6 h, the cast film was vacuum-annealed for 48 h at 160 °C. The annealed sample was exposed to UV irradiation with a high pressure mercury arc lamp (100 w) for 10 min in order to induce cross-linking reaction between diacetylene groups. Then UV irradiated sample was carbonized in a TGA chamber. The temperature was increased to 800 °C at a rate of 10 °C/min and kept isothermally for 5 min under a nitrogen gas flow. For TEM measurement, the annealed film was separated from the mica substrate by floating on water and transferred to a Si-coated copper grid. The PS phase was stained with RuO₄ vapor.

Results and Discussion

Syntheses of Triblock Copolymer. The ATRP initiator having a photocurable diacetylene group was synthesized according to Scheme I. (4-Ethynylphenyl)methanol (**2**) was obtained by the reaction of 4-iodobenzyl alcohol and (trime-



Scheme I. Syntheses of the triblock copolymer (PMMA-PS-PMMA); PMDETA = *N,N,N',N',N''*-pentamethyldiethylenetriamine, dNbpy = 4,4'-dinonyl-2,2'-bipyridine, and Pd(II) = dichlorobis(triphenylphosphine)palladium(II).

Table I. Molecular Weights of the Triblock Copolymer (PMMA-PS-PMMA)

Polymer	M_n^a	M_w^a	M_w/M_n^a	m/n^b
PS 5	19,400	23,900	1.23	-
PMMA-PS-PMMA 6	37,500	51,000	1.36	3

^aDetermined by GPC measurements with PS standards in THF.

^bCalculated by integration of characteristic ¹H-NMR peaks for a PS and a PMMA block.

thylsilyl)acetylene using Pd(II)/CuI catalysts and the subsequent deprotection reaction of a trimethylsilyl group under a basic condition. The oxidative coupling reaction of (4-ethynylphenyl)methanol using copper(II) acetate and the bromination reaction using phosphorous tribromide yielded bifunctional initiator **4**. PMMA-PS-PMMA triblock copolymer **6** was prepared by ATRP. First, a telechelic PS block having benzyl bromide groups at both ends was synthesized by the ATRP of styrene using initiator **4** and PMDETA/Cu(I)Br catalysts. The ¹H-NMR spectrum of the polymer in CDCl₃ showed broad peaks from aromatic protons of benzene rings at 7.2-6.8 ppm, methylene and methine protons in the main chain at 2.2-1.7 and 1.7-1.2 ppm, respectively. The number average molecular weight (M_n) and the weight average molecular weight (M_w), measured by GPC in THF, were 19,400 and 23,900, respectively. The ATRP of methyl methacrylate was carried out using polystyrene **5** as a macroinitiator and dNbpy/Cu(I)Br as catalysts to produce triblock copolymer **6**. In the ¹H-NMR spectrum of the resulting triblock copolymer in CDCl₃, the peaks from pendent methyl protons appeared at 3.6 ppm, methylene and methyl protons in the main chain at 1.8-1.7 and 0.9-0.8 ppm, respectively, and benzene ring protons of a PS block at 7.2-6.8 ppm. The ratio of the repeat unit number of styrene to that of MMA was determined to be 1:3 by comparing the intensities of the benzene ring proton peaks at 7.2-6.8 ppm and a methyl proton peak at 3.6 ppm. The M_n and M_w , measured by GPC in THF, were 37,500 and 51,000, respectively (Figure 2). The polymerization results are summarized in Table I.

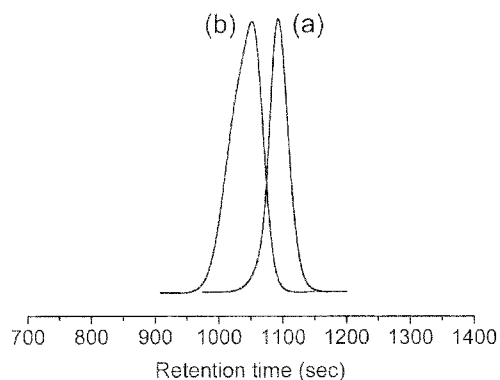


Figure 2. Gel permeation chromatograms of (a) PS **5** and (b) PMMA-PS-PMMA **6**.

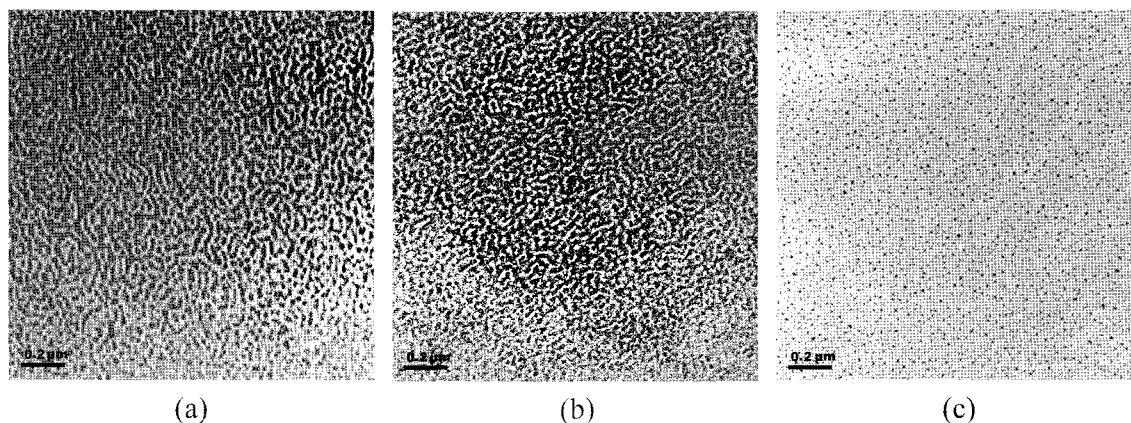


Figure 3. TEM images of the triblock copolymer (PMMA-PS-PMMA) (scale bar = 0.2 μm): (a) before UV irradiation (stained with RuO_4), (b) after UV irradiation (stained with RuO_4), and (c) after carbonization at 800 $^\circ\text{C}$ (without staining).

Film Preparation and Pyrolysis. A polymer thin film was prepared by spin-casting from a 0.5 wt% toluene solution of the triblock copolymer (PMMA-PS-PMMA) on a mica substrate. After drying, the cast film was vacuum-annealed for 48 h at 160 $^\circ\text{C}$. The image in Figure 3(a) is obtained from the annealed film stained with RuO_4 . It shows that the triblock copolymer formed a spherical PS domain morphology having a diameter of about 30 nm.²⁰

The annealed film was exposed to UV irradiation to fix the spherical morphology. The cross-linking reaction between diacetylene groups of the PS block was confirmed by FT-IR spectroscopy. In the FT-IR spectrum of the triblock copolymer, two absorption bands at 2141 and 2220 cm^{-1} corresponding to symmetric and asymmetric stretching vibrations of C-C triple bonds, respectively, appeared. After UV irradiation, they became disappeared and a new absorption band

at 2194 cm^{-1} for C-C triple bonds emerged as the reaction proceeded. The bands around 1600 cm^{-1} became broader and stronger because of newly formed C-C double bonds (Figure 4).^{21,22} Figure 3(b) shows the TEM image of the triblock copolymer obtained after the UV irradiation. The diameters and morphology of PS blocks are almost the same as those of the uncross-linked annealed film.

Thermal behaviors of the diacetylene initiator and the triblock copolymer were examined by TGA under a nitrogen flow (Figure 5). The amounts of residues of the initiator and the triblock copolymer at 800 $^\circ\text{C}$ were 42.1 and 8.3 wt%, respectively. The cross-linked polymer film was carbonized under a nitrogen gas flow. The temperature was increased to 800 $^\circ\text{C}$ at a rate of 10 $^\circ\text{C}/\text{min}$ and kept isothermally for 5 min. The TEM image in Figure 3(c) shows carbon dots with a diameter of ca. 5 nm.²⁰ Based on the TGA results and the spherical shape of the carbon particles formed on the

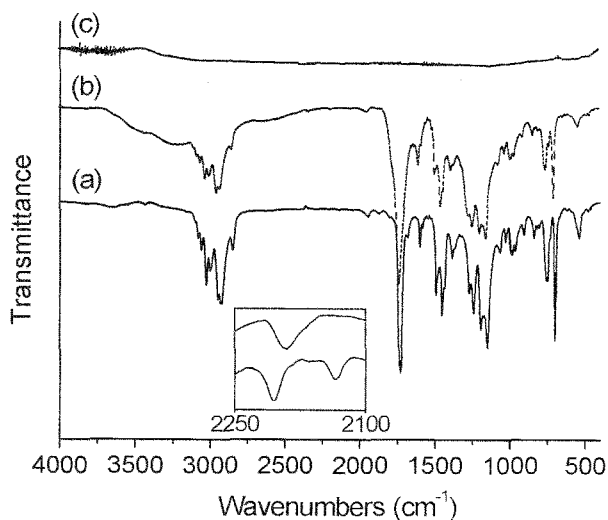


Figure 4. FT-IR spectra of PMMA-PS-PMMA **6**: (a) before UV irradiation, (b) after UV irradiation, and (c) after pyrolysis at 800 $^\circ\text{C}$ for 5 min under nitrogen.

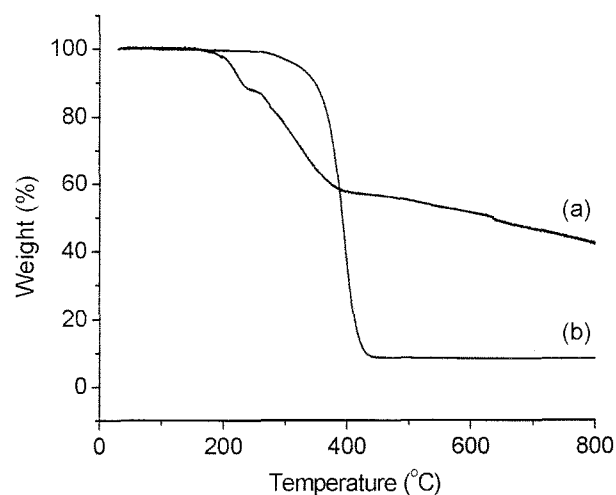


Figure 5. TGA thermograms of (a) initiator **4** and (b) the triblock copolymer (PMMA-PS-PMMA) in flowing nitrogen at a heating rate of 10 $^\circ\text{C}/\text{min}$.

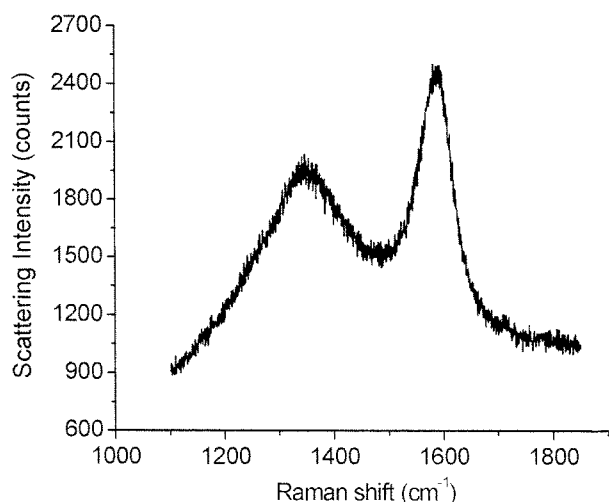


Figure 6. Raman scattering spectrum of the triblock copolymer (PMMA-PS-PMMA) after pyrolysis at 800 °C for 5 min under nitrogen.

substrate, we presume that the carbon nanodots formed mainly by carbonization of the cross-linked PS domains. The PMMA blocks were likely degraded and volatilized in the process of pyrolysis.

Carbon structures of the nanodots were characterized by FT-IR and Raman spectroscopy. In the FT-IR spectrum, all of the characteristic bands for the triblock copolymers disappeared after pyrolysis (Figure 4(c)). Raman scattering spectrum of carbon nanodots exhibited partially graphitic carbon characteristics, with D-band corresponding to disordered structures at 1350 cm^{-1} and graphitic G-band at 1595 cm^{-1} (Figure 6).¹⁷

Conclusions

In this work, we prepared carbon nanodots by pyrolysis of a self-assembled triblock copolymer. The triblock copolymer, PMMA-PS-PMMA was prepared by ATRP using an initiator containing a photocurable diacetylene group. The polymer thin film was prepared by spin-casting on a mica substrate and annealed to exhibit a spherical morphology of PS domain. The spherical structure of PS domain was stabilized by photocross-linking reaction between diacetylene groups and thereby maintained during pyrolysis, resulting in carbon nanodots with a diameter of about 5 nm. These results showed the possibility that carbon nanomaterials with tailored shapes and patterns could be fabricated by using self-

assembled block copolymers as an organic precursor for the pyrolysis.

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