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Carbon Nanotubes with Small and Tunable Diameters from Poly(ferroacenylsilane)-block-polysiloxane Diblock Copolymers

Jennifer Q. Lu,*† David A. Rider,‡ Emanuel Onyegam,† Hai Wang,† Mitchell A. Winnik,‡ Ian Manners,‡§ Qian Cheng,⊥ Qiang Fu,⊥ and Jie Liu⊥

Agilent Technologies, 3500 Deer Creek Road, Palo Alto, California, 94304, Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario, Canada, M5S 3H6, School of Chemistry, University of Bristol, Bristol, England, BS8 1TS, Department of Chemistry, Duke University, Durham, North Carolina, 27708, and Electrical Engineering Department, University of Texas at Austin, Austin, Texas 78712

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Iron-containing nanostructures produced from various self-assembled poly(ferroacenylsilane)-block-polysiloxane thin films are catalytically active for the initiation and growth of high density, small diameter carbon nanotubes (CNTs). Moreover, the tube diameter and density can be tuned by adjusting the chain lengths of the block copolymer. Iron-containing nanostructures from poly(ferrocenylmethyllethylsilane)-b-poly(methylvinylsiloxane) polymer with 25 repeat units of an iron-containing segment and 265 repeat units of a non-iron-containing segment are able to produce CNTs with diameters around or less than 1 nm. Lithographically selective growth of CNTs across a large surface area has been demonstrated using this polymer system. Under the same growth condition, it has been found that the yield of defect-free CNTs varies with the size of the catalytically active nanostructures, which are dictated by the chain lengths of the two blocks. This result indicates that, for a specific-sized catalyst nanocluster, a unique set of growth conditions is required for synthesizing high yield, defect-free CNTs. This finding further addresses the importance of using uniform-sized catalyst-containing nanostructures for consistently achieving high yield and high-quality CNTs with a minimum number of defects and amount of amorphous carbon.

Introduction

Carbon nanotubes (CNTs), have attracted a great deal of attention in numerous disciplines because of their unique electronic properties, excellent chemical and thermal stabilities, and superior mechanical resilience. Single-walled CNTs can be semiconducting or metallic, depending on their geometric arrangement of carbon atoms. Additionally, for semiconducting nanotubes, the band gap also varies with their diameters. The versatile electronic properties offered by this one-dimensional system make it interesting for both fundamental studies and electronic applications. Such sensitivity to size and geometry imposes the demand for controllable synthesis of CNTs since consistent electronic properties are required for many device applications. In an effort to surmount this barrier, the site-specific arrangement of carbon atoms. Additionally, for semiconducting or metallic, depending on their geometric

1. R = Me, R’ = Et
2. R = Me, R’ = Ph
3. R” = R”’ = vinyl
4. R” = R”’ = Me

PFEMS-block-PMVS : R = R” = Me, R’ = Et, R”’ = vinyl
PFMPS-block-PDMS : R = R” = R”’ = Me, R’ = Ph

Figure 1. Sila[1]ferrocenophane monomers (1 and 2), tricyclosiloxane monomers (3 and 4), and the subsequent diblock copolymers obtained via the sequential anionic ring-opening polymerization of 1 with 3 and 2 with 4.

the size and placement of catalyst nanoclusters still gives rise to CNTs with a broad diameter distribution. Such broad diameter distribution prevents utilization of their highly touted properties for most device applications.

Using self-assembled block copolymer morphologies to produce periodically ordered catalytically active nanostructures with controlled size has been developed recently. In this

approach, a catalyst-containing block copolymer is used to generate well-defined catalyst-containing domains on the nanometer scale. Catalytically active nanostructures can thus be formed by the removal of all the organic components followed by annealing at elevated temperature and subsequent H2 reduction. For example, we have demonstrated that nanostructures produced from self-assembled polystyrene-b-poly(ferrocenylethylmethylsilane) (PS-b-PFEMS) polymers, which generate iron-rich nanodomains, are capable of producing very small diameter CNTs with a very small number of defects. The presence of silica ceramic material in iron-containing nanostructures is believed to reduce the aggregation of iron species at the growth temperature. The typical growth temperature for high-quality single-walled CNTs is around 700–900 °C. To further reduce the aggregation of iron-containing nanostructures at elevated temperatures, one can consider replacing the polystyrene block in the block copolymer with silicon-containing polysiloxane. After self-assembly and removal of all the organic components, silica derived from the polysiloxane segment should encase the catalytically active iron-containing nanostructures, thus further alleviating the concern over the agglomeration of iron-rich nanostructures before and during the growth of CNTs.

We therefore investigated two systems, poly(ferrocenylethylmethylsilane)-block-poly(methylvinylsiloxane) (PFEMS-b-PDMS) and poly(ferrocenylnethylphenylsilane)-block-poly(dimethylsiloxane) (PFMPS-b-PDMS). Both diblock copolymers were synthesized via the sequential anionic ring-opening polymerization of ring strained siala[1]ferrocenophane monomers 1 or 2, followed by polymerization of cyclooctasiloxane monomers 3 or 4. The molecular structures of the monomers and block copolymers are depicted in Figure 1. Through this study, we found that the density of CNTs increased dramatically with increasing the density of catalytically active nanostructures, which was attained by reducing the molecular weight of the block copolymer. The average diameter of the resulting CNTs can be tailored by adjusting the chain lengths of the iron-containing and non-iron-containing segments. For PFEMS-b-PMVS system, the average diameter of CNTs decreased with the size of catalytically active nanostructures, resulting from shortening the iron-containing polymer chain length. CNTs with diameters around or less than 1 nm were synthesized using smaller sized catalytically active nanostructures produced from the block copolymer with a shorter iron-bearing block. Using top-down photolithography, we were able to obtain locationally controlled CNT growth from a lithographically defined pattern comprised of an array of the iron-containing nanostructures. We also discovered that, using the same CNT growth condition, the total number of dangling bonds on the surfaces after growth varied with the polymer system or the size of the catalytically active nanostructures.

**Experimental Section**

**Materials Preparation, Equipment and Materials.** Hexanes were purified using a Grubbs-type solvent system. Methanol was deoxygenated by passing a stream of dry N2 gas through the liquid under an inert atmosphere. Tetrahydrofuran (THF) was distilled under reduced pressure from Na/benzophenone. BuLi (1.6 M) in hexanes, anhydrous toluene, and triethylamine were used as received from Aldrich. Ethylmethyldisila[1]ferrocenophane (1) and methylphenylsila[1]ferrocenophane (2) were synthesized and purified according to literature procedures. Prior to use, 1,3,5-tri-methyl-1,3,5-trivinylcyclotrisiloxane (3) and hexamethyleneclotrisiloxane (4) were purchased from Gelest and distilled and repeatedly sublimed under reduced vacuum (10−3 mm Hg), respectively. Trimethylchlorosilane (Alrich) was distilled under reduced pressure (10−3 mm Hg) immediately prior to use. All polymerizations were
conducted in an MBrain inert atmosphere glovebox purged with prepurified N₂. The ¹H NMR, ¹³C NMR, and ²⁹Si NMR spectra were obtained from Varian Gemini 300, Varian XL 400, or Varian Unity 500 spectrometers. Molecular weight determinations were using a Viscotek GPC MAX liquid chromatograph equipped with a Viscotek Triple Detector Array. A flow rate of 1.0 mL/min was used with THF as the eluent.

Synthesis of PFEMS₅₂₅-b-PMVS₂₆₅. In an inert atmosphere glovebox, BuLi (1.6 M in hexanes, 7.5 μL, 1.2 × 10⁻² mmol) was rapidly delivered to a reaction vessel charged with a solution of I (77 mg, 0.30 mmol) in THF (3 mL). After approximately 50 min, monomer 3 (207 mg, 0.80 mmol) was introduced. The polymerization was allowed to proceed for an additional 70 min. Deliberate termination was executed by the addition of a few drops of trimethylchlorosilane. The diblock copolymer was precipitated into methanol (≈100 mL) containing triethylamine (≈1 mL) to quench any unreacted trimethylchlorosilane and dried under vacuum (10⁻³ mmHg) for 24 h. Gel permeation chromatography (GPC) and ¹H NMR analysis indicated that the number of repeat units of PFEMS was 25 and the number of repeat units of PMVS was 265. Using a PFEMS density of 1.29 g/mL,¹⁴a and a PMVS density of 0.96 g/mL,¹⁴b the q⁰PFEMS (volume fraction of PFEMS) was determined to be 0.17. GPC analysis of the diblock copolymer pointed out that the number average molecular weight was 39 000, with a polydispersity of 1.06.

Synthesis of PFEMS₅₂₅-b-PMVS₂₆₅. The synthetic procedures for PFEMS₅₂₅-b-PMVS₂₆₅ are analogous to the above procedures. BuLi (1.6 M in hexanes, 4.2 μL, 6.7 × 10⁻³ mmol) was rapidly delivered to a solution of 77 mg, 0.30 mmol) in THF (4 mL). After approximately 50 min, 3 (387 mg, 1.5 mmol) was added. The polymerization was allowed to proceed for an additional 70 min. Deliberate termination was executed by the addition of a few drops of trimethylchlorosilane. According to the analysis from the combination of ¹H NMR and GPC, the number of repeat units of PFEMS and PMVS were 45 and 765, respectively, and the q⁰PFEMS (volume fraction of PFEMS) was 0.11.¹⁴ GPC analysis of the diblock copolymer indicated that the number average molecular weight was 83 500, with a polydispersity of 1.10.

Synthesis of PFPMPS₅₈-b-PDMS₃₈. The synthetic procedure for PFPMPS₅₈-b-PDMS₃₈ has been published elsewhere¹⁴ and is analogous to the above procedures. The number of repeat units of PFPMPS was 58, and the number of repeat units of PDMS was 353, based on a combination of ¹H NMR and GPC. Using a PFPMPS density of 1.33 g/mL,¹⁴a and a PDMS density of 0.97 g/mL,¹⁴b the q⁰PFPMPS (volume fraction of PFPMPS) was determined to be 0.33. GPC analysis of the diblock copolymer indicated that the number average molecular weight was 43 000, with a polydispersity of 1.02.

Catalytically Active Nanostructure Formation and CNT Growth. The aforementioned ferrocenylsilane-based block copolymers were dissolved in toluene to afford 0.2 wt % solutions. The aforementioned ferrocenylsilane-based block copolymers were introduced in a glovebox, and dried under vacuum (10⁻³ mmHg) for 24 h. Gel permeation chromatography (GPC) and ¹H NMR analysis indicated that the number average molecular weight was 39 000, with a polydispersity of 1.06.

Results and Discussion

Self-Assembly. Figure 2a–c contains AFM height images of as-coated films of PFEMS₅₂₅-b-PMVS₂₆₅ (q⁰PFEMS = 0.17), PFEMS₅₂₅-b-PMVS₇₆₅ (q⁰PFEMS = 0.11), and PFPMPS₅₈-b-PDMS₃₈ (q⁰PFPMPS = 0.33). (Subscripts denote the degree of polymerization of each block, and q⁰PF refers to the volume fraction of PFEMS or PFPMPS in the block copolymer.) According to the well-developed solid-state diblock copolymer phase diagram,¹⁵,¹⁶ and literature for poly(ferrocenylsilane) diblock copolymers in the solid state,¹⁷ the two PFEMS-b-PMVS diblock copolymers with low q⁰PF values should provide periodically arranged spherical PFEMS domains, whereas PFPMPS₅₈-b-PDMS₃₈ should yield cylindrical morphology. AFM height images indicated that highly ordered films were obtained from the two PFEMS-b-PMVS diblock copolymers. On the basis of the image analysis using in-house software, there are around 700 nanoclusters for PFEMS₅₂₅-b-PMVS₂₆₅ and 380 nanoclusters per square micron for PFEMS₅₂₅-b-PMVS₇₆₅. We cannot estimate the nanocluster density for PFPMPS₅₈-b-PDMS₃₈ since it failed to form an ordered and discrete morphology. The lack of order for the PFPMPS cylinders in the PDMS matrix, as shown in Figure 2c, is likely due to the presence of impurities. Annealing of PFEMS₅₂₅-b-PMVS₂₆₅ gave rise to a complicated morphology, as indicated in Figure 2d, whereas PFEMS₅₂₅-b-PMVS₇₆₅ films dewetted from the substrate, as observed in Figure 2e. This phenomenon can be explained by the liquid-like property of this polymer system at room temperature due to the very low glass transition temperatures of both segments: Tg for polysiloxane-based polymers less than −100 °C,¹⁹ and that of PFEMS is about 16 °C.¹³ Since a phenyl group is incorporated in the repeat unit of PFPMPS, Tg for PFPMPS is 90 °C.¹³ Even though the film was not well-ordered, no further change in morphology was observed upon annealing.

CNT Density and Quality. CNT growth results are displayed in Figure 2f–h. The density of CNTs synthesized from PFEMS₅₂₅-b-PMVS₂₆₅ is much higher than that from PFEMS₅₂₅-b-PMVS₇₆₅. Comparing PFEMS₅₂₅-b-PMVS₂₆₅ with PFEMS₅₂₅-b-PMVS₇₆₅, the former has much shorter PMVS and PFEMS chain lengths. As a result, small and dense catalytically active iron-containing nanostructures were produced, as seen in Figure 2a. Raman analysis was performed to examine the CNT density and quality. Figure 3 presents a set of representative Raman spectra at high frequency. The G band around 1590 cm⁻¹ corresponds to the in-plane oscillation of carbon atoms in the graphene sheet. The
Figure 4. (a) A set of representative Raman spectra at the RBM. (b) AFM height analysis results.
Table 1. Diameter Analysis Results of CNTs Prepared from PFEMS25-b-PMVS265

<table>
<thead>
<tr>
<th></th>
<th>Raman</th>
<th>AFM</th>
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<tr>
<td>number of measure</td>
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<td>47</td>
</tr>
<tr>
<td>mean diameter (nm)</td>
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<td>1.1</td>
</tr>
<tr>
<td>standard deviation (nm)</td>
<td>0.3</td>
<td>0.6</td>
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integrated area under G normalized by the Si signal can then be used to estimate tube density. It is clear that the tube density increases from PFEMS45-b-PMVS265 to PFMPSS8-b-PDMS335 to PFEMS25-b-PMVS265. This result indicates that the tube density is directly controlled by the concentration of the catalytically active nanostructures on a surface. We conclude that rational control of tube density can be achieved by tuning polymer chain lengths. Raman spectrum in the 1300–1600 cm<sup>-1</sup> region is very sensitive to sample quality. The G band is the tangential vibration of carbon atoms in the sp<sup>2</sup> arrangement in CNTs, while the D band near 1350 cm<sup>-1</sup> is activated by defects. Thus, the amount of amorphous carbon and the defect level in CNTs determine the integrated area under the D band. The ratio of G to D can therefore be used to monitor the purity of CNTs. The table inserted in Figure 3 lists the average values based on 30 CNT spectra obtained from each polymer system. The purity of CNTs increases from PFEMS25-b-PMVS265 to PFEMS45-b-PMVS265 to PFMPSS8-b-PDMS335. We were able to verify by Raman and AFM analyses described in the following section that larger catalytically active nanostructures produced by PFMPSS8-b-PDMS335 generated less amorphous carbon and dangling bonds. It is apparent that the growth condition used in this set of experiments is favorable to grow high-purity CNTs on relatively bigger catalytically active nanostructures. It is possible that the small-sized catalyst-containing nanostructures are very reactive. Under this growth condition, amorphous carbon might be more readily formed on very small catalyst nanoclusters, preventing the growth of CNTs. Apparently, under the growth condition for this set of experiments, the smaller catalyst nanoclusters produced from PFEMS25-b-PMVS265 result in smaller diameter CNTs with a relatively higher number of dangling bonds.

**CNT Diameter.** Intensive Raman and AFM height analyses of tube diameter were conducted to obtain statistically meaningful data. Figure 4a shows representative Raman spectra at lower frequencies produced by the CNTs radial oscillations, and 4b presents a summary of CNT diameters estimated from AFM height measurements. For PFMPSS8-b-PDMS335, even though CNTs were present based on the high intensity of the G band, more than 50% of the spectra have no Raman signal between 100 and 450 cm<sup>-1</sup>. This phenomenon suggests that at least some of the tubes under examination (1 μm<sup>2</sup>) have diameters greater than 2.0 nm, which is the detection limit of the Raman spectrometer. This conclusion is also supported by the AFM results. The average tube diameter based on the AFM height estimation is 2.6 nm. In the case of PFEMS45-b-PMVS765, the average tube diameter is reduced to 1.6 nm based on the AFM analysis. The majority of Raman spectra have more than one peak in the region between 100 and 450 cm<sup>-1</sup>. From AFM height image analysis, the average tube diameter is 1.1 nm for CNTs produced from iron-containing nanostructures derived from PFEMS25-b-PMVS265, which has the lowest number of repeat units of the iron-containing block. Raman analysis also confirms that there are an adequate number of CNTs with mechanical oscillation at 200–300 cm<sup>-1</sup>, which corresponds to CNT diameters around or less than 1 nm. These results indicate that the diameter of CNTs can be rationally tailored by adjusting the block lengths. It is believed that the activation energy required to grow CNTs varies with the size of catalytically active nanostructures. Therefore, quantitative comparison between iron-bearing polymer chain length, corresponding iron-containing nanostructure size, and resulting CNT diameter cannot be performed. Nevertheless, this set of data clearly shows that the average CNT diameter was reduced with decreasing the size of the catalyst-containing nanostructures, resulting from shortening the iron-bearing polymer chain length. Table 1 shows the average size and distribution of CNTs based on Raman analysis of the lattice vibrations of CNTs and AFM height estimation. The average tube diameters from AFM and Raman analysis agree with each other very well, but there is a big discrepancy in the standard deviation value. The size of the tube is very small, the surface roughness becomes consequential, therefore AFM analysis may artificially broaden the size distribution. In addition, we assume that all the CNTs are individual tubes. It is possible that ropes of CNTs were measured and treated as individual tubes in the AFM analysis. This would further widen the distribution.

**Patterned Growth.** A bilayer lift-off system, which has been previously reported, was used to generate patterned self-assembled iron-containing block copolymer film for lithographically selective CNT growth from PFEMS45-b-PMVS765. The SEM image in Figure 5a depicts the resulting CNTs grown from lithographically defined 1.5 μm islands consisting of arrays of the iron-containing nanostructure formed by the lift-off process. Using a conventional image transfer process, patterned arrays of
iron-containing nanostructures can also be formed on a periodically raised surface (step height = 0.5 μm, plateau width = 2.5 μm). We present in Figure 5b that selective growth of CNTs at predefined locations can also be achieved using this subtractive patterning etching approach.

Conclusions

We have demonstrated that by tuning the molecular weight of the ferrocenylsilane-based diblock copolymers, the density of CNTs can be varied accordingly. In addition, we have found that the block length provides control over the CNT diameter. CNTs with diameters around or less than 1 nm have been synthesized using smaller catalytically active nanostructures derived from PFEMS$_{25}$-b-PMVS$_{265}$. Using conventional semiconductor processes, spatially selective growth of CNTs has been attained by defining patterns consisting of iron-containing nanostructures using either a bilayer lift-off process or a subtractive etching process. It has also been observed that the G/D ratio decreases with reducing the size of the catalyst-containing nanostructure. This result indicates that the yield of defect-free CNTs is sensitive to catalyst size. In other words, a specific-sized catalyst has its own unique set of growth conditions for synthesizing defect-free CNTs with a minimum amount of amorphous carbon. This finding further points out the necessity of producing uniform-sized catalyst-containing nanostructures for achieving consistent and high-quality CNTs.

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