Research Article

Iron Oxide Arrays Prepared from Ferrocene- and Silsesquioxane-Containing Block Copolymers

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Received 13 August 2012; Accepted 11 October 2012

Academic Editor: Maki Itoh

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Arrays of iron oxides as precursors of iron clusters were prepared by oxygen plasma treatment of block copolymer microphase-separated nanostructures in thin films. Block copolymers composed of ferrocene-containing and silsesquioxane-containing polymethacrylate (PMAPOSS-*b*-PMAHFC) were successfully prepared, with different molecular weights and compositions and narrow molecular weight distributions, by living anionic polymerization. The formed microphase-separated nanostructures in the bulk were characterized by wide- and small-angle X-ray scattering (WAXS and SAXS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Thin films were prepared from a solution of PMAPOSS-*b*-PMAHFC in tetrahydrofuran by spin coating onto silicon wafers. Fingerprint-type line nanostructures were formed in the PMAPOSS-*b*-PMAHFCs thin films after solvent annealing with carbon disulfide. Oxygen plasma treatment provided the final line arrays of iron oxides based on the formed nanostructural patterns.

1. Introduction

Microphase-separated nanostructures of block copolymer thin films have been studied widely because they offer simple and low-cost pattern formation on the nanometer scale. In particular, they can be used as membranes, lithography masks, and as a variety of templates for the fabrication of a variety of devices [1–7]. For the creation of unique self-assembled nanostructures and the advancement of novel functions in these applications, various block segments consisting not only of conventional organic polymers, but also of organometallic and organic-inorganic polymers have been synthesized by recently developed controlled and living polymerization methods [8–14]. The size and spacing of the microdomains can be tailored on the scale of several tens of nanometers by varying the relative molar masses of the polymer segments within the blocks and the total molar masses of the copolymers.

Carbon nanotubes (CNTs) have attracted a great deal of attention in many areas of electronics because of their exceptional electrical properties, chemical stability, and mechanical strength [15, 16]. Among the numerous

potential applications, CNTs in the form of thin films are particularly interesting for use in flexible integrated circuits [17]. CNTs properties strongly depend on the geometric arrangement of carbon atoms and the diameters of the individual tubes [18–21]. Therefore, gaining adequate control of tube diameter and geometry is essential in the protocols used for synthesizing CNTs [22–26]. One promising route to controlling the size and geometry of CNTs is a growth method using a catalytic template with iron oxides based on block copolymer thin films. Lu and coworkers have shown that iron clusters generated by reduction of iron oxides prepared from polystyrene-*block*-poly(ferrocenylsilane) (PS-*b*-PFS) [22] and poly(dimethyl siloxane)-*block*-poly(ferrocenylsilane) (PDMS-*b*-PFS) [27] diblock copolymers act as an effective catalyst for the growth of CNTs. They first attempted to prepare arrays of iron oxides as precursors of iron clusters from PS-*b*-PFS thin films, but a mixture of single- and multiwalled CNTs was obtained. This was attributed to the different sizes of iron oxides generated during the high-temperature CNT growth procedure (700°C). The arrays of iron oxide generated by PS-*b*-PFS thin films have low thermal stability

because of occurring aggregation of iron oxides at the high temperature. They subsequently, improved the block copolymers in order to provide thermally and structurally stable arrays of iron oxides by using PDMS-*b*-PFS. The PDMS was able to convert to thermally stable silica that surrounded the iron structures and prevented their aggregation during CNT growth. The resulting catalytic arrays of irons provided uniform single-walled CNTs. In general, silicone-containing block copolymers can form well-ordered microphase-separated nanostructures; however, dewetting often occurs during film preparation in the PDMS-based diblock copolymer system because of its low glass transition temperatures (T_g), below -100°C . This induces difficulty in forming the desired uniform thin films for producing ordered arrays of iron oxides. Therefore, a challenge remains in the preparation of silicone-containing block copolymer thin films with well-defined and stable microphase-separated nanostructures containing iron and silicon species.

We recently developed a novel series of block copolymers containing a polyhedral oligomeric silsesquioxane (POSS)-containing block copolymers such as PS-*block*-POSS containing poly(methyl methacrylate) (PMAPOSS), PMMA-*block*-PMAPOSS, and poly(ethylene oxide)-*block*-PMAPOSS [28–32]. The PMAPOSS polymers have much higher T_g values than that of PDMS and depend on the organic substituents of the POSS silicon atoms. They are able to stay stable and can be converted to silica using an oxidation process without dewetting. The POSS-containing block copolymers have also demonstrated good segregation during microphase separation and form much smaller periodic nanofeatures compared with many conventional block copolymers [33]. Furthermore, the etch resistance of PMAPOSS to oxygen plasma is much higher than that of polymers consisting purely of hydrocarbons, such as PEO, PMMA, and PS. Therefore, they can act not only as block copolymer lithographic materials, but also as silica thin film templates.

Herein, we report the creation of arrays of iron oxides within a silica matrix in thin films based on microphase-separated nanostructures of a series of PMAPOSS-containing block copolymers. In this study, we designed and synthesized a new PMAPOSS-containing block copolymer where one block contained a ferrocene moiety in the side chain, namely, PMAPOSS-*b*-PMAHFC. Typical examples of ferrocene-containing side chain polymers include poly(ferrocenyl methacrylate) (PFMMA) and poly(vinyl ferrocene) (PVFc), which have relatively high T_g values (PFMMA T_g : 185°C) [34–39]. In order to obtain well-ordered nanostructures in block copolymer thin films, thermal and/or solvent annealing is often necessary. However, this is not easy for polymers with high T_g values because of the crucial annealing conditions required for reassembly of the polymer chains. Therefore, in this study, we also attempted to improve the design of the ferrocene-containing polymer to reduce its T_g to a level suitable for forming well-ordered microphase-separated nanostructures under mild annealing conditions. A new ferrocene-containing methacrylate monomer with an alkyl spacer (MAHFC) was synthesized and used for living anionic polymerization to create a new series

of diblock copolymers, PMAPOSS-*b*-PMAHFCs. We also describe the characterization of the resulting microphase-separated nanostructures in the bulk and thin films by small- and wide-angle X-ray scattering (SAXS and WAXS), transmission electron microscopy (TEM), and scanning electron microscopy (SEM). The oxygen plasma-treated PMAPOSS-*b*-PMAHFC thin films were then characterized by SEM and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Materials. *sec*-Butyllithium (*sec*-BuLi) was purchased from Kanto Chemical Co. (Tokyo, Japan). 3-(3,5,7,9,11,13,15-heptaisobutylpentacyclo-[9.5.1.^{3,9}1.^{5,15}1^{7,13}]octasiloxane-1-yl)propyl methacrylate (MAPOSS) was purchased from Hybrid Plastics Inc. (USA). The other reagents were purchased from TCI Co. (Tokyo, Japan). Prior to use, tetrahydrofuran (THF) was distilled over sodium/benzophenone in a nitrogen atmosphere until a deep purple color was achieved. MAPOSS was purified by recrystallization from methanol. 1,1-diphenylethylene (DPE) was distilled over *n*-butyllithium under reduced pressure, and lithium chloride (LiCl) was baked under vacuum at 180°C for 24 h. The other reagents were used as received.

2.2. Instrumentation and Characterization. For TEM analysis, bulk samples were embedded in epoxy resin and cured at 70°C for 24 h. The embedded samples were then microtomed using a DIATOME diamond knife at room temperature to a preset thickness of 70 nm using Microtome. The sections were placed on TEM grids and viewed directly using a JEOL JEM-200CX at 100 kV. WAXS and SAXS measurements on the bulk samples were performed on the BL17B3 beamline at the National Synchrotron Radiation Research Center (NSRRC). Monochromatic X-ray beams of 10.5 keV ($\lambda = 1.1809 \text{ \AA}$) were used. IR spectra were recorded on a JASCO FT/IR-460 Plus spectrometer. ^1H , ^{13}C , and ^{29}Si NMR spectra were recorded on a JEOL JNM-AL 300 spectrometer at 300 MHz, 75 MHz, and 59.4 MHz, respectively. Thermal analyses of the compounds, thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC) were carried out using a Seiko SSC/6000 (TG/DTA 6200 and DSC6200) thermal analyzer with ca. 5 mg of samples at a heating rate of $10^\circ\text{C min}^{-1}$. Nitrogen was used as the purge gas at a flow rate of 50 mL min^{-1} for both the TGA and DSC measurements. Size-exclusion chromatography (SEC) measurements were carried out using a Shodex GPC-101, two columns (Shodex KF-802 and Shodex KF-806 M), and a Shodex RI-71 detector. THF was used as the eluent with a 1 mL min^{-1} flow rate at 40°C . SEM imaging was carried out using a Hitachi S-4800 SEM with a field-emission source at 1.0 kV. XPS was carried out using $\text{AlK}\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$) as the photo source and was used to investigate the surface properties of the sample.

2.3. Synthesis. Hydroxymethylferrocene was synthesized according to the literature [40]. Iodomethane (21.9 g, 0.155 mol) in methanol (25 mL) was treated dropwise with dimethylamino (dimethylferrocene) (25 g, 0.103 mol) in

FIGURE 1: Synthesis of MAHFC monomer.

FIGURE 2: Synthesis of PMAHFC homopolymer by living anion polymerization.

methanol (20 mL) and stirred for 4 h at room temperature. Diethyl ether was then added to the mixture and the resulting precipitate was filtered and dried *in vacuo* at 30°C for 3 h (37.2 g, 94%).

N,N,N-trimethylaminomethyl-ferrocene iodine (20.0 g, 0.052 mol) was added to a 2N sodium hydroxide solution (200 mL) and the mixture was refluxed overnight. The reaction mixture was then diluted with diethyl ether and washed with brine. The organic layer was dried over magnesium sulfate (MgSO_4), filtered, and evaporated. The yellow residue was purified by recrystallization from *n*-hexane. The yellow needles were dried *in vacuo* at 30°C for 4 hours (8.1 g, 72%); m.p.; 77–78°C; ^1H NMR (CDCl_3 , r.t): δ 1.53 (1H, –OH), 4.24 (7H, H), 4.26 (2H, H), 4.32 (2H, –CH₂).

2.4. 1-Bromo-6-ferrocenylmethoxy-hexane. A round-bottomed flask was charged with sodium hydride (0.79 g, 0.033 mol) and THF (10 mL) in a nitrogen atmosphere. A solution of 1,6-dibromohexane (8.08 g, 0.033 mmol) and hydroxymethylferrocene (7.25 g, 0.033 mmol) in *N,N*-dimethylformamide (DMF)/THF (20 mL each) was added to the mixture and the mixture was kept at 0°C using an ice bath. After 24 h, the reaction mixture was diluted with *n*-hexane and washed with brine several times to remove the DMF and excess sodium hydride. The organic layer was dried over MgSO_4 , filtered, and evaporated. The dark red residue was purified by column chromatography on silica using *n*-hexane. The solvent was removed and the dark red liquid was dried *in vacuo* at room temperature for 3 h (7.20 g,

18.9 mmol, 57%). IR (KBr): 3094, 2954, 2867, 1100, 1000, 654 cm^{-1} ; ^1H NMR (CDCl_3 , rt): δ 4.89 and 4.26–4.09 (9H, cyclopentadienyl), 3.40 (m, 4H, –CH₂–O–CH₂–ferrocene), 1.84 (m, 2H, Br–CH₂–CH₂–), 1.58 (m, 4H, alkyl chain), 1.38 (m, 4H, alkyl chain); ^{13}C NMR (CDCl_3 , rt): δ 83.6, 77.2, 69.7, 69.4, 69.0, 68.3, 33.9, 32.7, 29.5, 27.9, 25.3 ppm.

2.5. Synthesis of MAHFC. A round-bottomed flask was charged with 1-bromo-6-ferrocenylmethoxy-hexane (1.50 g, 3.95 mmol) in DMF (24 mL). The methacrylic acid salt was prepared by mixing methacrylic acid (0.68 g, 7.90 mmol) and sodium hydrogen carbonate (0.79 g, 7.90 mmol) and was added to the flask along with a small amount of hydroquinone as an inhibitor. The resulting solution was heated to 100°C over the course of 6 h in a nitrogen atmosphere. The reaction mixture was then diluted with *n*-hexane and washed with brine. The organic layer was dried over MgSO_4 , filtered, and evaporated. The dark red residue was purified by column chromatography on silica using *n*-hexane. The solvent was removed and a dark red liquid was obtained (1.31 g, 3.42 mmol, 86%). IR (KBr): 3093, 2951, 2869, 1730, 1640, 1100, 1000 cm^{-1} . ^1H NMR (CDCl_3 , rt): δ 6.10 (s, 1H, C=CH₂), 5.56 (s, 1H, C=CH₂), 4.26–4.13 (br, 11H, cyclopentadienyl and –COO–CH₂–), 3.39 (br, 2H, –O–CH₂–ferrocene), 1.95 (s, 3H, –CH₃), 1.54 (m, 4H, alkyl chain), 1.34 (s, 4H, alkyl chain); ^{13}C NMR (CDCl_3 , rt): δ 1637.3, 136.3, 127.2, 125.0, 83.5, 79.7, 77.4, 69.6, 69.2, 68.9, 68.2, 64.5, 29.4, 28.4, 25.7, 18.2 ppm.

FIGURE 3: Synthesis of PMAPOSS-*b*-PMAHFC by living anion polymerization. FIGURE 4: ¹H NMR spectra of (a) MAHFC, (b) PMAHFC, and (c) PMAPOSS-*b*-PMAHFC.

FIGURE 5: SEC curves of (a) PMAHFC homopolymer and (b) PMAPOSS-*b*-PMAHFC (solid line) and PMAPOSS (dashed line).

FIGURE 6: DSC trace of PMAPOSS-*b*-PMAHFC 2 (from -50°C to 190°C).

2.6. Synthesis of PMAHFC Homopolymer by Living Anionic Polymerization. THF (40 mL) was transferred to a glass reactor equipped with stir bar containing dry LiCl (15 mg, 0.36 mmol) and cooled to -78°C . After 5 min, *sec*-BuLi was added until the color changed to slightly yellow. The reactor was removed from the cooling bath and allowed to reach room temperature, upon which the solution became colorless. The reactor was cooled back to -78°C , and 1.07 M *sec*-BuLi solution in hexane/cyclohexane (0.025 mL, 0.027 mmol) was added. After 5 min, DPE (0.025 mL, 0.14 mmol) was added to the reactor, resulting in the formation of a deep red color. After 30 min, MAHFC that had been dried under reduced pressure for several hours (0.30 g, 0.78 mmol) was dissolved in THF (4.0 mL) and transferred from the monomer reservoir to the polymerization flask via cannula with vigorous stirring. The solution changed from deep red to orange. After 8 h at -78°C , excess of methanol was added to the reactor to obtain the proton-terminated polymer. This was then precipitated into a large excess amount of methanol, filtered, and dried *in vacuo* at 80°C for 6 h, yielding 0.28 g of polymer. IR (KBr): 3093, 2951, 2869, 1730, 1640, 1100, 1000 cm^{-1} . ^1H NMR (CDCl_3 , rt): δ 4.26–4.13 (br, cyclopentadienyl), 3.89 (br, $-\text{O}-\text{CH}_2$ -ferrocene), 3.40 (br, $-\text{O}-\text{CH}_2-\text{CH}_2-$), 1.85–1.78 (m, main chain), 1.56–1.34 (br, alkyl side chain), 0.85 (m, αCH_3); ^{13}C NMR (CDCl_3 , rt): δ 177.7, 83.7, 69.8, 69.4, 69.0, 68.44, 68.40, 54.1, 51.8, 44.8, 44.5, 29.6, 28.1, 25.8 ppm.

2.7. Synthesis of PMAPOSS-*b*-PMAHFC by Living Anionic Polymerization. THF (40 mL) was transferred to a glass reactor equipped with a stirrer bar containing dry LiCl (15 mg, 0.36 mmol), and then cooled to -78°C . After 5 min, *sec*-BuLi was added until the color changed to slightly yellow. The reactor was removed from the cooling bath and allowed to reach room temperature upon which the solution became colorless. The reactor was cooled back to -78°C and 1.07 M *sec*-BuLi solution in hexane/cyclohexane (0.025 mL, 0.027 mmol) was added. After 5 additional minutes, DPE (0.025 mL, 0.14 mmol) was added to the reactor resulting in the formation of a deep red color. After 30 min, MAPOSS (0.5 g, 0.5 mmol) was dissolved in THF (4.0 mL) and transferred from the monomer reservoir to the polymerization flask via cannula with vigorous stirring. The deep red color changed to colorless. In a second sample, MAHFC (0.4 g, 0.78 mmol) was dissolved in THF (4.0 mL). After 8 h, the MAHFC solution was transferred to the polymerization flask via cannula. After additional 8 h at -78°C , excess methanol was added to the reactor yielding the proton terminated diblock copolymer. This was then precipitated into methanol, filtered, and dried *in vacuo* at 60°C for 8 h. IR (KBr): 3094, 2953, 2868, 1730, 1643, 1260, 1100, 1000 cm^{-1} . ^1H NMR (CDCl_3 , rt): δ 4.25–4.10 (br, ferrocene, PMAHFC), 3.86 (br, $-\text{O}-\text{CH}_2$ -ferrocene), 3.37 (br, $-\text{O}-\text{CH}_2-\text{CH}_2-$, PMAHFC), 1.84–1.78 (br, main chain $-\text{CH}_2-$, $-\text{CH}$, PMAPOSS, PMAHFC), 1.53–1.31 (br, alkyl side chain, PMAHFC), 0.98 (br, isobutyl $-\text{C}(\text{CH}_3)_2$, PMAPOSS), 0.81 (m, αCH_3 , PMAPOSS and PMAHFC), 0.55 (br, $-\text{SiCH}_2$, PMAPOSS); ^{13}C NMR (CDCl_3 , rt): δ 177.7, 176.9, 83.7, 69.8, 69.4, 69.0, 68.44, 68.40, 67.2, 54.1, 51.8, 45.2, 44.8, 44.5, 29.6, 28.1, 26.0, 25.8, 25.7, 25.5, 24.0, 23.8, 22.5, 22.4, 21.8, 8.4 ppm.; ^{29}Si NMR (CDCl_3 , rt): δ -67.6 , -67.9 ppm.

3. Results and Discussion

3.1. Synthesis and Polymerization of Ferrocene-Containing Monomer. The procedure for synthesizing MAHFC, with a hexyl chain between the ferrocene moiety and methacrylate group, is illustrated in Figure 1. The role of the hexyl chain is to prevent strong interactions between ferrocene groups. The hydroxymethylferrocene was first prepared according

FIGURE 7: SAXS profiles (a, b, c) and TEM images (d, e, f) of PMAPOSS-*b*-PMAHFC 1–3; (a) and (d) PMAPOSS-*b*-PMAHFC 1; (b) and (e) PMAPOSS-*b*-PMAHFC 2; (c) and (f) PMAPOSS-*b*-PMAHFC 3. Brighter region corresponds to PMAPOSS domain and darker region corresponds to PMAHFC domain.

to the literature. It then underwent etherification with 1,6-dibromohexane to obtain 1-bromo-6-ferrocenylmethoxyhexane. Finally, the MAHFC monomer was yielded as a dark red liquid after esterification of methacrylic acid. The monomer was characterized by ^1H and ^{13}C NMR and IR spectroscopy. Figure 4(a) shows ^1H NMR spectrum of MAHFC, which exhibits the resonance signals of the double bond (peaks a and b) and the ferrocene moiety. The characteristic peaks of the two carbons of the double bond appear at 136.3 and 125.0 ppm in the ^{13}C NMR spectrum. There is also a series of peaks between 68.4 and 69.8 ppm from the ten carbons of the ferrocene group. These observations indicate that the desired MAHFC was successfully obtained.

Living anionic polymerization of MAHFC was employed in order to control both the molecular weights and molecular weight distributions of the resulting block copolymers. The polymerization was carried out using 1,1-diphenyl-3-methyl-pentyllithium as the initiator, prepared by the reaction of *sec*-BuLi and DPE in the presence of a 5-fold excess of LiCl in THF at -78°C for 8 h to ensure complete

conversion was achieved (Figure 2). Finally, the active chains were terminated at -78°C using degassed methanol, and the products were precipitated in a large volume of methanol at room temperature. After precipitation, the methanol solution remained colorless, thereby verifying the absence of unreacted monomers and oligomers. The purification was carried out by reprecipitation into a large volume of methanol, twice, and PMAHFC was obtained as a yellowish-orange powder. All the signals and peaks of PMAHFC were accurately assigned in the ^1H and ^{13}C NMR and IR spectra. SEC was performed on PMAHFC to determine its number average molecular weight (M_n) and polydispersity index (PDI). The chromatogram demonstrates a sharp unimodal peak (Figure 5(a)). The M_n and PDI were found to be $11\,000\text{ g mol}^{-1}$ and 1.09, respectively, indicating that the living anionic polymerization of MAHFC successfully afforded the polymer with a controlled M_n and narrow PDI.

Based on the success of the homopolymerization of MAHFC, the synthesis of the block copolymer PMAPOSS-*b*-PMAHFC was carried out (Figure 3). The MAHFC was added as a second monomer to the living PMAPOSS reaction

FIGURE 8: WAXS profiles of (a) PMAPOSS-*b*-PMAHFC 1, (b) PMAPOSS-*b*-PMAHFC 2, and (c) PMAPOSS-*b*-PMAHFC 3.

mixture and the polymerization proceeded homogeneously, with no precipitation observed until the reaction was terminated. In this study, three PMAPOSS-*b*-PMAHFCs, 1, 2, and 3, with different molecular weights and compositions were prepared (Table 1). The chemical compositions of the block copolymers were characterized by ^1H , ^{13}C , and ^{29}Si NMR and IR spectroscopies, and the M_n values were measured using SEC. Figure 4 shows the ^1H NMR spectra of the MAHFC monomer, PMAHFC homopolymer, and PMAPOSS-*b*-PMAHFC. The ^1H NMR spectrum of PMAPOSS-*b*-PMAHFCs clearly shows that the incorporation of each block was successful, which is indicated by the appearance of methylene ($-\text{OSiCH}_2$) protons corresponding to PMAPOSS at 0.59 ppm and cyclopentadienyl protons corresponding to ferrocene groups in PMAHFC at 4.1–4.3 ppm. The SEC chromatograms of the polymers show that the M_n increased in a controlled manner, which is reflected by the shift to the higher molecular weight region (Figure 5(b)). The SEC analysis showed that the PDI for all polymers was below 1.08. The compositions of PMAPOSS-*b*-PMAHFCs were ascertained by using the ^1H NMR spectra integration ratios of methylene protons for PMAPOSS and ferrocene protons from PMAHFC, along with the M_n values. The thermal properties of PMAHFC and the PMAPOSS-*b*-PMAHFCs were investigated using TGA and DSC. To eliminate the effect of thermal histories of the samples, the samples were heated to 200°C and held for 10 min at this temperature before cooling to -50°C at a rate of $10^\circ\text{C min}^{-1}$. The DSC trace of PMAPOSS-*b*-PMAHFC

2 on the second heating showed baseline shifts at 13°C corresponding to the T_g of the PMAHFC block segment (Figure 6). The T_g of PMAHFC is significantly lower than that of poly(ferrocenyl methacrylate) (185°C). The alkyl chain in the ferrocene-tethered side chains might decrease the interactions between the ferrocene moieties increasing the conformational flexibility of the side chains.

3.2. Bulk Morphological Characterization. The morphologies of the PMAPOSS-*b*-PMAHFCs in their bulk state were studied using WAXS, SAXS, and TEM. The samples were prepared by slow evaporation from chloroform at room temperature. For TEM measurement, all samples were imaged without staining as the contrast between the ferrocene-containing block (dark regions) and the POSS-containing block (bright regions) was sufficient for achieving high-quality images.

Figure 7 shows SAXS and TEM results for PMAPOSS-*b*-PMAHFCs 1–3. The SAXS profile of the PMAPOSS-*b*-PMAHFC 1 exhibits first-order and second-order diffraction peaks, with ratios of 1 and $3^{1/2}$, respectively. The TEM image of PMAPOSS-*b*-PMAHFC 1 shows PMAHFC cylindrical nanostructures, which is strongly supported by the SAXS results. On increasing the PMAHFC wt% to 0.33, clear microphase-separated nanostructures were observed. The scattering profiles show up to five peaks with a characteristic ratio of 1:2:3:4:5, indicating a lamellar morphology. The lamellar d -spacing was found to be 49 nm, which is in good agreement with values obtained from the TEM image. Although the molecular weight and the composition of PMAPOSS-*b*-PMAHFC 3 are theoretically sufficient to enable microphase separation, the TEM image shows no well-defined microphase-separated nanostructures. In order to investigate this sample further, WAXS measurements were performed. The WAXS patterns of PMAPOSS-*b*-PMAHFC 1 and 2 (Figure 8) show some peaks in the high q region corresponding to a d spacing of 2.5–2.7 nm, but no diffraction peaks are evident for PMAPOSS-*b*-PMAHFC 3. As previously reported, these diffraction peaks correspond to the distance between the PMAPOSS chains in the self-assembled structures [30]. These results indicate that the microphase separation and the aggregation of PMAPOSS chains can only occur when the content of PMAHFC in the PMAPOSS-*b*-PMAHFC copolymer is low.

3.3. Thin Film Nanostructures and Oxygen Plasma Treatment.

In order to investigate the nanostructures of the thin films, solutions of the PMAPOSS-*b*-PMAHFCs in THF (1.0%–2.0%, w/w) were spin coated onto silicon wafers. Prior to coating, the substrates were cleaned with piranha solution (30% H_2O_2 /70% H_2SO_4 , v/v) at 110°C for 2 h, rinsed thoroughly with distilled water, and dried under a stream of nitrogen. The morphology of the thin films of the PMAPOSS-*b*-PMAHFCs was characterized by SEM, and the thickness of the films was estimated using ellipsometry. The as-cast thin film prepared from a THF solution of PMAPOSS-*b*-PMAHFC 2 had a thickness of 47 nm and did not show any ordered nanostructures caused by microphase

FIGURE 9: SEM images of thin films (a) PMAPOSS-*b*-PMAHFC 1, (b) PMAPOSS-*b*-PMAHFC 2, (c) oxygen plasma treated PMAPOSS-*b*-PMAHFC 1, and (d) oxygen plasma treated PMAPOSS-*b*-PMAHFC 2, the inset (e) is the cross-sectional SEM image of (d).

TABLE 1: Characteristics of block copolymers based on SEC and ^1H NMR analyses.

PMAPOSS- <i>b</i> -PMAHFC	M_n^a	M_w^a	PDI ^a	wt% PMAPOSS ^b	wt% PMAHFC ^b
1	16,300	17,300	1.06	75	25
2	49,000	52,600	1.07	67	33
3	56,100	60,400	1.08	42	58

^a Measured by SEC, relative to PS linear standard. ^b The numbers refer to the final composition determined by SEC calibrated against PS linear standard and integrations from ^1H NMR spectrum.

separation. Solvent and thermal annealing were carried out in order to initiate reassembly of the polymer chains to induce microphase separation. However, the thermal annealing did not affect the results with a wide range of temperatures and annealing times tested. Solvent annealing was therefore subsequently investigated. Solvent annealing of PMAPOSS-*b*-PMAHFC was performed using carbon disulfide (CS_2) because it was found that it could swell both PMAHFC and PMAPOSS. Thin films of PMAPOSS-*b*-PMAHFC 1 and 2 were annealed in saturated CS_2 vapor at room temperature for 5 min and 10 min, respectively. SEM images of the resulting films showed line nanostructures on the surface with d spacings of 19 nm (Figure 9(a)) and 46 nm (Figure 9(b)), respectively. Under these specific solvent annealing conditions, no dewetting was seen to

occur. In Figure 9, the brighter region corresponds to the PMAPOSS blocks. Because the PMAPOSS blocks tend to discharge more secondary electrons than the PMAHFC blocks.

Finally, in order to create the arrays of iron oxides, oxygen plasma treatment was carried out for 30 s on the series of PMAPOSS-*b*-PMAHFC thin films. The SEM images of the exposed films clearly show the remaining microphase-separated nanostructures. As shown in Figure 9(e), the cross-sectional SEM image of the PMAPOSS-*b*-PMAHFC 2 thin film treated with oxygen plasma indicates that perpendicular lamella formed through the entire 47 nm thick film. The XPS spectrum of PMAPOSS-*b*-PMAHFC 1 shown in Figure 10 exhibits a peak corresponding to $\text{Fe}_{2p_{3/2}}$ at 711 eV (Figure 10). This indicates that iron oxides

FIGURE 10: XPS spectrum in the range 730–700 eV for oxygen plasma-treated PMAPOSS-*b*-PMAHFC 1 thin film.

were generated by oxidation of the ferrocene moiety on the PMAPOSS-*b*-PMAHFCs at the thin film surface. These characterizations show that a well-defined line array of iron oxides was obtained, without any collapse, by simple oxygen plasma treatment of PMAPOSS-*b*-PMAHFC thin films. The catalytic ability for CNT growth is still under investigation, and will be described in a subsequent report.

4. Conclusion

In conclusion, a new series of POSS-containing block copolymers with a ferrocene-containing side-chain polymer of PMAHFC was prepared using living anionic polymerization. The use of this method enabled control of the molecular weights and the achievement of a narrow PDI below 1.08. PMAHFC demonstrated a T_g at 13°C, which is much lower than that of conventional ferrocene-containing side-chain polymers such as PFMA. Microphase separation occurred only when the content of PMAHFC in the PMAPOSS-*b*-PMAHFC copolymer was below 33 wt%. The line nanostructures in the thin films were formed using solvent annealing, and subsequent oxygen plasma treatment provided line arrays of iron oxides based on the microphase-separated nanostructures. This array is expected to be a promising catalytic material for the creation of CNT thin films.

Acknowledgments

The authors thank Ryohei Kikuchi, National University Corporation Tokyo Institute of Technology Center for Ascended Materials Analysis, for the TEM. The authors acknowledge NSRRC, Taiwan, for facilitating the SAXS and WAXS experiments performed as part of this work and Dr. U-Ser Jeng of NSRRC for assistance with these experiments. R. Goseki and T. Hayakawa gratefully thank Professor Sang-Ouk Kim (Korea Advanced Institute of Science and Technology) for his useful discussions.

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