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Phenylethynylstyrene−Cobalt Carbonyl Block Copolymer Composites

Liliana A. Mîinea, Laura B. Sessions, Kjell D. Ericson, David S. Glueck, and Robert B. Grubbs*

Department of Chemistry and Center for Nanomaterials Research, Dartmouth College, Hanover, New Hampshire 03755

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ABSTRACT: Treatment of a diblock copolymer containing an alkyne-functional block (polystyrene-*block*-poly(4-(phenylethynyl)styrene)) with dicobalt octacarbonyl ($Co_2(CO)_8$) leads to selective incorporation of $Co_2(CO)_6$ groups in the alkyne block. Examination of these composites in bulk and thin films by transmission electron microscopy reveals the formation of ordered phase-separated morphologies typical of block copolymers. Heating the polymer−cobalt carbonyl adducts at moderate temperatures (110 °C) leads to loss of CO and formation of insoluble polymer cobalt composites. High-temperature thermolysis of these materials leads to formation of carbonaceous materials containing cobalt nanoparticles.

Introduction

Metal-containing polymers are appealing synthetic targets because of their potential utility as electronic or magnetic materials or as precursors to ceramics and metallic nanoparticles.[1] Of special interest for the preparation of these advanced materials is the localization of metallic properties to well-defined nanometer-scale domains by, for example, incorporation of metal-containing polymer blocks into ordered microphase-separated block copolymer systems.[2,3]

One potential application of such composite systems arises from the increasing storage density requirements in microelectronic devices and the resulting drive for development of magnetic nanomaterials with addressable elements on the nanometer scale. Discrete nanometer-scale magnetic regions, such as those found in materials containing magnetic metallic nanoparticles, appear to be one promising choice in information storage, where magnetic and optical storage components as small as tens of nanometers will be needed in the future.[4,5] In such applications, where magnetic or redox properties are important, cobalt-containing systems represent a major class of useful materials.[6] Cobalt nanomaterials are typically prepared by reduction of Co(II) salts or thermolysis of $Co_2(CO)_8$ in the presence of a range of stabilizing molecules, which prevent aggregation into larger agglomerates.[7,8]

While small molecules such as phosphines and carboxylic acids are often used as stabilizers, functional polymers and block copolymers can also stabilize cobalt nanomaterials formed from inorganic or organocobalt precursors.[9−11] Furthermore, the ability of block copolymers to self-assemble into chemically distinct domains on the nanometer scale makes them good candidates for directing the ordered assembly and formation of nanoscale metallic objects while averting aggregation.[3,12−15]

Block copolymers, including poly(styrene)-*block*-poly(2-vinylpyridine)[14] and poly(styrene)-*block*-hydroxylated polyisoprene[13] in bulk and poly(styrene)-*block*-poly(4-vinylpyridine),[16] poly(styrene)-*block*-poly(2-vinylpyridine),[14,17] poly(styrene)-*block*-poly(methyl methacrylate),[18] and poly(dimethylsiloxane)-*block*-poly(3-cyanopropylmethylsiloxane)-*block*-poly(dimethylsiloxane)[19] in micellar assemblies in solution have previously been used to coordinate cobalt for the templated preparation of polymer-stabilized cobalt nanoparticles. The functional groups (i.e., pyridine, ester, alcohol, or nitriles) which coordinate the metals in each of these copolymers are relatively nonspecific for metal incorporation and will form complexes with many different metal species.

To enable incorporation of multiple types of metallic nanoparticles within the same copolymeric matrix, we are examining the incorporation of cobalt into alkyne-functional polymer blocks.[20] As the alkyne moiety can react in a highly specific fashion with dicobalt octacarbonyl and related cobalt compounds,[21,22] these blocks should exhibit orthogonal reactivity toward cobalt relative to those functional polymers previously examined and will facilitate the preparation of multicomponent polymer nanoparticle systems.

Several reports documenting the preparation of homopolymers with alkyne-functional backbones through condensation or ring-opening polymerization and their subsequent reaction with cobalt[6,23,24] or platinum[25] have appeared. Here we report the incorporation of cobalt carbonyl groups within the alkyne functional blocks of polystyrene-*block*-poly(4-(phenylethynyl)styrene) copolymers and the resulting phase separation. Preliminary investigations into the thermal properties of these composites and their suitability as precursors to cobalt-containing nanomaterials are reported.

Experimental Section

Materials. Styrene, phenylacetylene (both from Aldrich), and triethylamine (Fisher) were purified by passage through basic alumina (0.05−0.15 mm, Fluka). 4-Bromostyrene, benzoyl peroxide (BPO), 2,2,6,6-tetramethylpiperidin-1-yloxyl (TEMPO) (all from Aldrich), triphenylphosphine (Fluka), copper(I) iodide (Alfa Aesar), bis(triphenylphosphine)palladium(II) chloride (Strem), and $Co_2(CO)_8$ (Strem) were used without further purification. Solvents were dried by passage over activated alumina under dry N_2.[26] TEMPO-terminal polystyrene (PS-TEMPO) was prepared via nitroxide-mediated free-radical polymerization with BPO and TEMPO.[27,28] 4-(Phenylethynyl)styrene was prepared by Pd-catalyzed Sonogashira coupling of 4-bromostyrene and phenylacetylene.[29,30]

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* To whom correspondence should be addressed. Phone: (603)-646-9096. Fax: (603)-646-3946. E-mail: robert.b.grubbs@dartmouth.edu.

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Instrumentation. Molecular weights and molecular weight distributions, M_w/M_n, were estimated by size exclusion chromatography (SEC) at ambient temperature with THF as eluent at a flow rate of 1.0 mL/min on a system consisting of a K-501 pump (Knauer), a K-3800 Basic autosampler (Marathon), a set of two PLgel 5 μm Mixed-D columns (300 × 7.5 mm, rated for linear separations at polymer molecular weights from 0.2 to 400 kg/mol, Polymer Laboratories), and a PL-ELS 1000 Evaporative Light Scattering Detector (Polymer Laboratories). Data were acquired through a PL Datastream unit (Polymer Laboratories) and analyzed with Cirrus GPC software (Polymer Laboratories) based upon a calibration curve built upon polystyrene standards with peak molecular weights ranging from 0.58 to 400 kg/mol (EasiCal PS-2, Polymer Laboratories). Block copolymer composition was estimated by means of NMR (Varian Unityplus-500; $CDCl_3$) spectroscopy. IR (Perkin-Elmer 1600 FT-IR instrument) spectroscopy was carried out on thin films of polymer prepared from toluene solutions on NaCl IR windows. Thermogravimetric analysis (TGA) was carried out on a TA 50Q (TA Instruments) from 20 to 800 °C at a rate of 10 or 20 °C/min with a N_2 purge (40 mL/min) and air or N_2 as the sample gas (60 mL/min). TEM images were obtained using a JEOL 2000FX analytical electron microscope operating at 80 or 100 kV. AFM images (topography and phase) in tapping mode were obtained with a Veeco/Digital Instrument Scanning Probe Microscope (Dimension 3100 SPM) with a Nanoscope IV controller and Veeco Nanoprobe tips (RTESP, 125 μm, 300 kHz). Elemental analyses for C, H, N, and Co were performed at Schwarzkopf Microanalytical Laboratory, Woodside, NY.

Preparation of PS-PPES.[20] In a typical polymerization an air-free tube was loaded with PS-TEMPO (1.20 g, 62.4 μmol, $M_n \approx 19.2$ kg/mol, $M_w/M_n \approx 1.08$), 4-(phenylethynyl)styrene (2.29 g, 11.2 mmol), and toluene (11.6 mL). The reaction mixture was degassed by three freeze−pump−thaw cycles, sealed under N_2, and heated at 125 °C for 16.5 h (30% conversion by ^{1}H NMR) to afford a pale yellow, slightly opaque viscous liquid. CH_2Cl_2 (1 mL) was added, and the resulting solution was precipitated into hexanes (800 mL), filtered, washed with hexanes, and dried under vacuum to give PS_{181}-$PPES_{56}$ (1.46 g, 77% based upon conversion). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.45 (br); 1.85 (br); 2.12 (br); 6.53 (br); 7.08 (br); 7.25 (br); 7.48 (br). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 40−44 (br, $\boldsymbol{C}H_2\boldsymbol{C}H$); 89.1 (Ph−$\boldsymbol{C}$≡C); 89.8 (Ph−C≡$\boldsymbol{C}$); 120.9, 123.6, 125.7, 125.8, 127.5−128.5, 131.8, and 145.3. M_n(^{1}H NMR): 30.5 kg/mol; 37 wt % PPES. SEC: $M_w/M_n = 1.16$. IR (NaCl): 3080, 3062, 3025, 2926, 2855, 2225, 1601, 1513, 1492, 1454, 1030, 832, 755, 700 cm^{-1}. Anal. Calcd for $(C_7H_5O_2)PS_{181}PPES_{56}(C_9H_{18}NO)$: C, 92.71; H, 7.08; N, 0.05. Found: C, 92.77; H, 7.21; N, 0.17.

Preparation of PS-PPES[$Co_2(CO)_6$]. In a representative procedure a solution of PS_{173}-$PPES_{67}$ (0.298 g, 9.27 μmol, M_n (NMR) = 31.9 kg/mol; $M_w/M_n = 1.17$) in dry toluene (12 mL) was treated with $Co_2(CO)_8$ (0.212 g, 0.621 mmol) in toluene (5.0 mL) in a N_2-filled glovebox. The dark brown reaction mixture was heated at reflux under N_2 for 1 h followed by removal of the volatiles under vacuum. The dark brown solid residue was dissolved in CH_2Cl_2 (~2 mL) and precipitated in dry hexanes (200 mL). The supernatant was decanted, and the polymer was washed with hexanes and dried under vacuum to give $PS_{173}PPES_{67}[Co_2(CO)_6]_{61}$ (composition estimated by elemental analysis by fitting found %Co) as a dark brown powder (0.379 g, 85%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.43 (br); 1.87 (br); 2.05 (br); 6.47 (br), 7.06 (br); 7.1 (br), 7.27 (br); 7.47 (br). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ 40−41 ($\boldsymbol{C}H_2\boldsymbol{C}H$); 92.1 (Ph−$\boldsymbol{C}$≡C, Ph−C≡$\boldsymbol{C}$); 125.6, 125.9, 127.4−128.4, 129, 129.3, and145.6 (Ar); 199.4 (Co−$\boldsymbol{C}$≡O).

Anal. Calcd for complete reaction with $Co_2(CO)_8$, $(C_7H_5O_2)$-$PS_{173}PPES_{67}(Co_2(CO)_6)_{67}(C_9H_{18}NO)$: C, 67.47; H, 4.37; N, 0.03; Co, 15.45. Anal. Calcd for $(C_7H_5O_2)PS_{173}PPES_{67}(Co_2(CO)_6)_{61}$-$(C_9H_{18}NO)$: C, 68.96; H, 4.52; N, 0.03; Co, 14.55. Found: C, 68.61; H, 4.68; N, <0.10; Co, 14.50. IR (NaCl): 3047, 3015, 2916, 2839, 2083, 2048 (s), 2015 (vs), 1871, 1600, 1493, 1449, 751, 695 cm^{-1}.

FT-IR Studies. In a N_2-filled glovebox a thin film of PS-PPES or PS-PPES[$Co_2(CO)_6$] was cast from a toluene solution (5−10 mg/mL) on a NaCl IR window. Samples were taken outside the glovebox and heated under dynamic vacuum at 110 °C for ~24 h, during which period they were removed periodically for acquisition of IR spectra.

TEM Sample Preparation. Copolymer TEM samples were prepared by the following methods.

1. Drop-Casting. In a N_2-filled glovebox, one drop of a PS-PPES[$Co_2(CO)_6$] solution in toluene (5−10 mg/mL) was placed onto a carbon-coated Cu grid (400 mesh) atop a piece of filter paper. Residual solvent was allowed to evaporate at room temperature.

2. Spin-Coating. Films of PS-PPES[$Co_2(CO)_6$] were prepared in air by spin coating (4000 rpm, 30 s) from toluene solutions (5−10 mg/mL) on freshly cleaved mica. Following spin coating, the films were scored and peeled off of the substrate onto a deionized water surface. The films were then transferred onto a carbon-coated copper grid (400 mesh).

3. Ultramicrotomy. Bulk samples embedded in epoxy (Embed-It, Polysciences, Inc.) were cut with either a diamond knife on a RMC MT-6000 Ultramicrotome or a glass knife on a Sorvall MT-1 Ultramicrotome at room temperature. Approximately 70−120 nm thick cross-sections (estimated by section color) of the samples were floated onto a trough of deionized water and immediately picked up with a copper grid (300 mesh) or a carbon-coated copper grid (400 mesh) and dried by putting them in contact with filter paper.

For preparation of TEM samples from TGA samples, the TGA residue was first sonicated in toluene and the resulting suspension was allowed to settle before the supernatant was decanted. The resulting black powder was resuspended in toluene, and TEM samples were prepared by Method 1 above. Cobalt−alkyne domains appear darker due to the higher electron density afforded by the metal atoms.

AFM Sample Preparation. PS-PPES[$Co_2(CO)_6$] samples for AFM imaging were prepared by dip coating or spin coating (4000 rpm, 30−45 s) from toluene solutions (5−10 mg/mL) on freshly cleaved mica.

Results and Discussion

Diblock copolymers of styrene and 4-(phenylethynyl)styrene (PES) were prepared through nitroxide-mediated radical polymerization of the alkyne-functional monomers from TEMPO-capped poly(styrene) (PS-TEMPO).[20] Difficulties with side reactions in the radical polymerization of these alkyne-functional monomers limited the range of diblock copolymer compositions examined.[31] This work specifically focuses upon two polymers of roughly 40 wt % PPES (subscripts represent number-average degree of polymerization in each block): $PS_{181}PPES_{56}$ (M_n = 30.5 kg/mol; 37 wt % PPES) and $PS_{173}PPES_{67}$ (M_n = 31.9 kg/mol; 43 wt % PPES).

The selective formation of cobalt−alkyne adducts through treatment of alkynes with dicobalt octacarbonyl ($Co_2(CO)_8$) is well known for both small molecules and polymers.[22,32] Cobalt-containing diblock copolymer composites (PS-PPES[$Co_2(CO)_6$]) were prepared by the addition of $Co_2(CO)_8$ (1 equiv per PES repeat unit) to toluene solutions of polystyrene-*block*-poly((4-phenyl-

Scheme 1

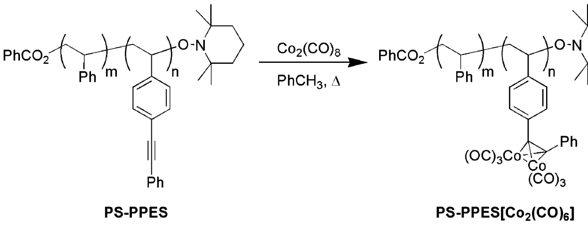

Table 1. Characterization of PS-PPES Diblock Copolymer Adducts with $Co_2(CO)_8$[a]

					elemental analysis				
	parent copolymer[b]	M_n (kg/mol)[c]	wt % PPES[d]	t (h)	%C	%H	%Co	CO/Co (calcd)[e]	f (calcd)[f]
1[g]	$PS_{181}PPES_{56}$	30.5	37	1	71.25	5.40	12.78	3.0	0.86
2	$PS_{181}PPES_{56}$	30.5	37	2	70.09	5.45	13.01	3.2	0.88
3	$PS_{173}PPES_{67}$	31.9	43	1	68.61	4.68	14.50	3.1	0.91
4	$PS_{173}PPES_{67}$	31.9	43	17	69.92	5.08	13.98	3.0	0.86

[a] All polymer−cobalt carbonyl adducts were prepared by heating a solution of the polymer and $Co_2(CO)_8$ in toluene at reflux for the given length of time. See Experimental Section for details. [b] Copolymer composition calculated from ^1H NMR. 1 equiv of $Co_2(CO)_8$ added per PES repeat unit. [c] Molecular weight calculated from SEC and ^1H NMR. [d] Diblock copolymer composition based upon SEC and ^1H NMR and confirmed by elemental analysis. [e] Calculation based upon EA data and the assumption that all oxygen is present in initiating and terminating residues or as Co-ligated CO. %O approximated as 100 − (%C + %H + %N + %Co). (Values ± 0.2, based upon ±0.3% absolute error in EA.). [f] Fraction of alkyne groups converted to dicobalt adducts. Calculated by fitting EA values to molecular weight data (values ± 0.03, based only upon error in EA measurements). [g] Values averaged from three different modification reactions.

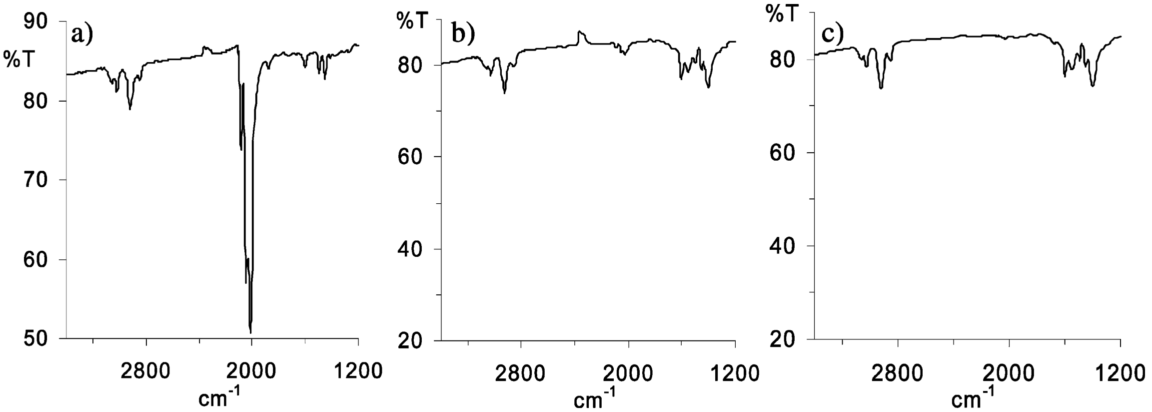

Figure 1. IR spectra of a film of $PS_{173}PPES_{67}[Co_2(CO)_6]_{61}$ heated at 110 °C under vacuum for (a) 0, (b) 9, and (c) 23 h.

ethynyl)styrene) (PS-PPES) at room temperature under N_2 (Scheme 1). The resulting solutions were heated at reflux for 1−17 h to promote complete reaction and then purified by precipitation into hexanes. Addition of a substoichiometric amount of $Co_2(CO)_8$ (2:1 alkyne group/$Co_2(CO)_8$) led to materials with little or no solubility in CH_2Cl_2 or toluene after 1 h at reflux, suggesting the occurrence of cross-linking.

Elemental analysis of cobalt-treated copolymers PS_{181}-$PPES_{56}$ and PS_{173}-$PPES_{67}$ indicated the formation of PS-PPES[$Co_2(CO)_6$] adducts in which 80−90% of alkyne groups have reacted with $Co_2(CO)_8$, regardless of the reaction time (Table 1). For example, reaction of $PS_{173}PPES_{67}$ with $Co_2(CO)_8$ in refluxing toluene for 1 h gives a cobalt-modified polymer with 14.5 wt % Co by elemental analysis (Table 1, entry 3). On the basis of the nominal composition of the block copolymer, this value is less than that predicted for complete conversion of alkyne groups by about 10% and suggests an average composition of $PS_{173}PPES_{67}[Co_2(CO)_6]_{61}$. The compositions of cobalt-modified copolymers $PS_{181}PPES_{56}[Co_2(CO)_6]_{50}$ (Table 1, entry 2) and $PS_{173}PPES_{67}[Co_2(CO)_6]_{58}$ (Table 1, entry 4) were calculated on a similar basis.

Additional calculations based upon elemental analysis can be used to approximate the extent of decomposition of cobalt carbonyl complexes during the initial reaction. If it is assumed that oxygen makes up the non-C/H/N/Co mass of the polymer and that all O present is from the initiator or in Co-ligated CO, CO/Co ratios for each sample can be estimated. This ratio is very close to 3 for each of the samples examined, suggesting that insignificant loss of CO and negligible Co nanoparticle formation occurs under these conditions (Table 1).

Complexation of $Co_2(CO)_6$ groups to the alkyne-functional polymer was further confirmed by IR spectroscopy, thermogravimetric analysis (TGA), and transmission electron microscopy (TEM). Comparison of IR spectra of PS-PPES to spectra of PS-PPES[$Co_2(CO)_6$] shows disappearance of the PS-PPES $\nu_{C\equiv C}$ band (2225 cm^{-1}) after treatment with $Co_2(CO)_8$ and appearance of strong bands at 2015, 2048, and 2083 cm^{-1}, which correspond to terminal CO groups in small molecule diarylacetylene−$Co_2(CO)_6$ adducts, and a band at 1600 cm^{-1}, due to the Co-coordinated alkyne (Figure 1a).[6,33,34] These PS-PPES[$Co_2(CO)_6$] adducts appear to be quite stable to thermolysis in solution. For example, even after 17 h in refluxing toluene at a concentration of 30 mg/mL, the intensity of the CO bands in the IR spectrum of $PS_{173}PPES_{67}[Co_2(CO)_6]_{61}$ does not appear to be diminished (see Supporting Information), and elemental analysis suggests the presence of three CO ligands per Co atom (Table 1, entry 4).

Thermolysis of these materials in bulk proceeds much more readily. TGA of Co-treated PS_{181}-$PPES_{56}$ and PS_{173}-$PPES_{67}$ samples was performed at a heating rate of 10 °C/min under an atmosphere of either nitrogen or air. While the parent PS-PPES diblock copolymers show no weight loss below 350 °C, weight loss in Co-treated samples is observed to begin at ~70 °C, irrespective of atmosphere. In the Co-containing samples analyzed, weight loss between 70 °C and ~270 °C occurs in two overlapping steps and corresponds to the calculated value for loss of labile CO ligands as observed in other polymeric alkyne−$Co_2(CO)_6$ adducts.[23,24] For example, PS_{173}-$PPES_{67}[Co_2(CO)_6]_{61}$ shows weight loss (19%) from 20 to 270 °C in reasonably good agreement with the calculated value of 20.7% (Figure 2). This is consistent with the loss of the CO bands in IR spectra of samples heated at 110 °C for 23 h (see below and Figure 1).

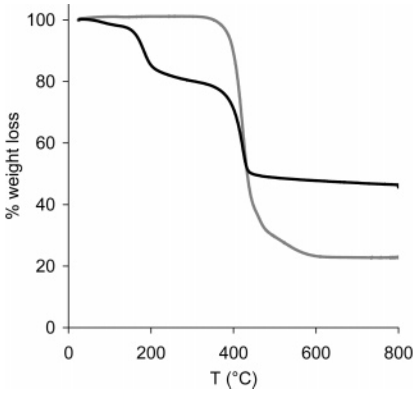

Figure 2. Thermogravimetric analysis at 10 °C/min under N_2 of PS_{173}-$PPES_{67}$ (gray trace) and PS_{173}-$PPES_{67}[Co_2(CO)_6]_{61}$ (black trace).

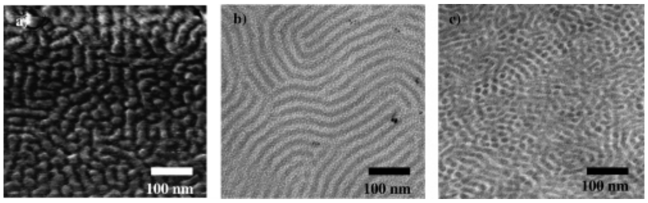

Figure 3. (a) AFM phase image of PS_{181}-$PPES_{56}[Co_2(CO)_6]_{50}$ dip-coated from toluene solution on freshly cleaved mica; (b) TEM image of PS_{181}-$PPES_{56}[Co_2(CO)_6]_{50}$ drop cast from toluene solution onto a C-coated Cu grid; (c) TEM image of microtomed bulk PS_{173}-$PPES_{67}[Co_2(CO)_6]_{61}$.

Microscopy studies were carried out to characterize phase separation in these composite materials in bulk and thin films. AFM and TEM images of samples of PS_{181}-$PPES_{56}[Co_2(CO)_6]_{50}$ and PS_{173}-$PPES_{67}[Co_2(CO)_6]_{61}$ show segregation of the two constituent blocks into what appears to be a cylindrical morphology independent of the sample preparation method: drop casting from toluene, spin casting from toluene, or microtomy of thicker solution-cast plugs (Figure 3). AFM images of PS_{181}-$PPES_{56}[Co_2(CO)_6]_{50}$ thin films spin cast on mica show the formation of cobalt-containing cylinders (Figure 3a). In spin-cast thin films (Figure 3b) and microtomed bulk samples (Figure 3c), both top and longitudinal views of the cylinders can be observed by TEM. The observation of phase separation in cobalt−copolymer adducts with these compositions is of interest as DSC studies of the parent diblock copolymer show a reasonably high degree of miscibility between PS and PPES blocks.[35] It is also somewhat remarkable that PS appears to make up the continuous phase in these samples despite the fact that PS blocks only account for 36−41% of the molecular weight of these cobalt-modified block copolymers and would be expected to exhibit discontinuous minority domains.[36] As the reported density of the model compound $Co_2(CO)_6C_2Ph_2$ is 1.58 g/cm^3, however, it is highly possible that this morphology results from a high degree of conformational asymmetry in the polymer.[37]

To investigate thermolysis of these materials in bulk, the loss of CO from PS-PPES$[Co_2(CO)_6]$ adducts at 110 °C under vacuum was monitored by IR spectroscopy. Over a 23 h period IR spectra show the disappearance of the CO bands (2048−2120 cm^{-1}) and the associated enhancement of bands appearing in the 1400−1610 cm^{-1} region (Figure 1). Bands at 1610, 1500, 1450, and 1420 cm^{-1} are similar to those present in the IR spectrum of PS-PPES or PS-PPES-$[Co_2(CO)_6]$. The insolubility of the resulting films in common solvents after heating suggests the occurrence of cross-linking. Intermolecular cycloaddition reactions promoted by cobalt carbonyl (with or without incorporation of CO) are a possible explanation for this observation. While TGA results (10 °C/min heating rate) show almost complete loss of CO, it is possible that isothermal heating at 110 °C allows competing incorporation of CO through cyclization reactions. A weak band appearing at 1560 cm^{-1} can be tentatively assigned to the C=O stretch that might arise from such a reaction.[38−44]

TEM studies on bulk thermolysis of Co−polymer adducts have also been carried out. PS_{173}-$PPES_{67}$-$[Co_2(CO)_6]_{58}$ (Table 1, Entry 4) was dissolved in toluene and cast into films (several mm thick). These bulk samples were further heated at 110 °C under vacuum for ∼18 h, embedded in epoxy, and microtomed for TEM imaging. TEM micrographs show that large domains of the initial cylindrical morphology (Figure 4a) remain largely intact after heating with little evidence of discrete nanoparticle formation, though micronscale regions of the polymer surface appear to have undergone heat-induced disruption (Figure 4b). Whether this disruption is an intermediate stage in the formation of cobalt nanoparticles or nanowires or just a surface effect is under further investigation. After heating, the Co−polymer adducts are no longer soluble in organic solvents, further suggesting that polymer cross-linking through thermally induced alkyne cyclization reactions occurs.

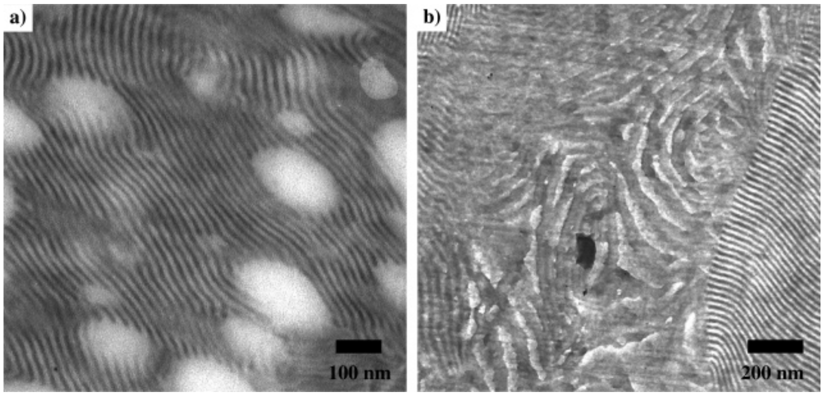

Figure 4. TEM micrographs of samples prepared from $PS_{173}PPES_{67}[Co_2(CO)_6]_{58}$ by microtome (a) before annealing and (b) after annealing at 110 °C under vacuum for 18.5 h.

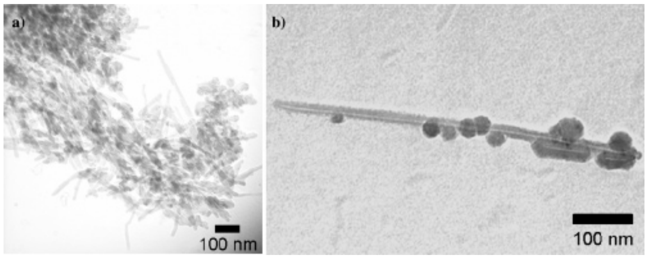

Figure 5. TEM images of (a) the toluene-insoluble residue formed by heating PS_{173}-$PPES_{67}[Co_2(CO)_6]_{58}$ to 800 °C at 10 °C/min under N_2 and (b) nanotubes and nanoparticles observed in toluene supernatant from TGA residue.

The effect of higher temperatures on these materials was studied by TEM analysis of the residual material from TGA experiments. TGA shows that significant amounts of material remain after heating to 800 °C for both the parent diblock copolymers and the cobalt adducts (Figure 2). The 22% ceramic yield observed for PS-PPES (Figure 2) most likely arises from the known cross-linking of pendant alkyne groups in polymers through aromatic rings to form char at high temperatures.[45−49] Thermolysis of diphenylacetylene−cobalt carbonyl adducts has been shown to lead to the formation of carbon nanotubes.[50] TEM analysis of the magnetic residue (~45%) formed by heating the cobalt-containing diblock copolymer up to 800 °C under N_2 suggests that it consists of carbonaceous material including what appear to be carbon nanotubes and colloidal cobalt including nanoparticles (Figure 5).

Conclusion

Block copolymers with alkyne-functional blocks enable localization of cobalt atoms as dicobalt carbonyl−alkyne adducts to specific domains of the microphase-segregated block copolymer. Heating the polymer−cobalt carbonyl adducts at moderate temperatures (110 °C) leads to loss of CO and formation of insoluble polymer cobalt composites, and high-temperature thermolysis of these materials leads to the formation of carbonaceous materials containing cobalt nanoparticles. Further studies into the effects of (1) relative PS and PPES block lengths, (2) structure of the alkyne functional monomer, and (3) extent of $Co_2(CO)_6$ group incorporation on phase separation and metal nanoparticle formation are currently underway.

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Supporting Information Available: FT-IR spectrum of $PS_{173}PPES_{67}[Co_2(CO)_6]_{61}$ after refluxing in toluene for 17 h. This material is available free of charge via the Internet at http://pubs.acs.org.

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