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Preparation and Phase Segregation of Block Copolymer Nanotube Multiblocks

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Abstract: Different nanotubes were prepared from two triblock copolymers. Chemistry was performed on the nanotubes so that one type contained amino terminal groups and the other bore carboxyl terminal groups. The amino and carboxyl groups were reacted by amidization to join the nanotubes head to tail to yield nanotube multiblocks. The block copolymer nanotube multiblocks (CONATUBLOCs) may be viewed as a macroscopic counterpart of block copolymers. Like block copolymers, the different blocks of the CONATUBLOCs segregated from one another not only in a block-selective solvent mixture but also in the solid state.

I. Introduction

Solvent-dispersible block copolymer nanotubes[1−4] have interesting chemical and physical properties. Hydrophobic nanotubes have, for example, been end-grafted to the surface of hydrophilic nanospheres to yield a "supersurfactant" with the nanotube comprising the "tail" and the nanosphere comprising the "head" of the surfactant.[5] Such supersurfactants may assemble analogously to the surfactant molecules to form micelles, which may help the ordering of molecules over several length scales from nanometers to micrometers.[6] The loading of magnetite or Ni into the core of block copolymer nanotubes yields polymer/inorganic superparamagnetic hybrid nanofiers that respond mechanically to magnetic fields and may serve as components of magnetomechanical nanodevices.[7] We report in this paper further new chemistry of block copolymer nanotubes, which involves the coupling of nanotubes of different compositions to yield block copolymer nanotube multiblocks (CONATUBLOCs). These CONATUBLOCs bear structural resemblance to semiconductor−semiconductor,[8] metal−metal,[9−10] metal−semiconductor,[11] or polymer−metal[12] multicblocks that may serve as components of nanoelectronic devices.[13,14] We also report the segregation of the different nanotube blocks in a block-selective solvent mixture and in the solid state akin to block copolymers.

The preparation of permanent block copolymer nanostructures normally involves taking advantage of the block segregation property of the polymers in either the solid state[15] or a block-selective solvent.[16] The block-segregated structures are then chemically processed,[17] invoking selective domain cross-linking and/or degradation, to yield stable nanostructures including nanofibers,[18] nanotubes,[1] and thin films containing nanochannels.[19−21] The nanotubes used in this study were prepared from poly(glyceryl methacrylate)-*block*-poly[(2-cinnamoyloxy-

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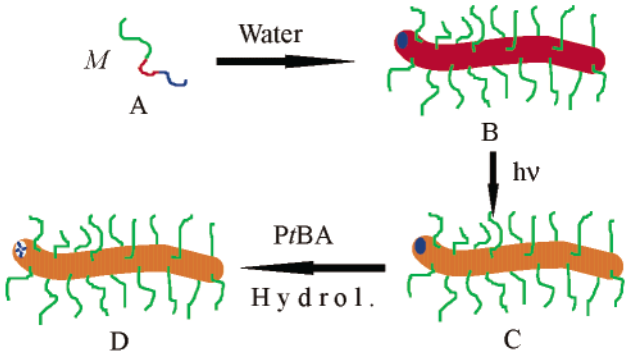
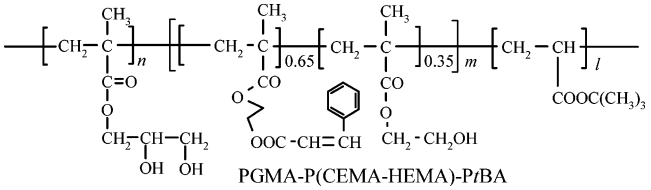
Scheme 1. Preparation of PGMA-P(CEMA-HEMA)-PAA Nanotubes



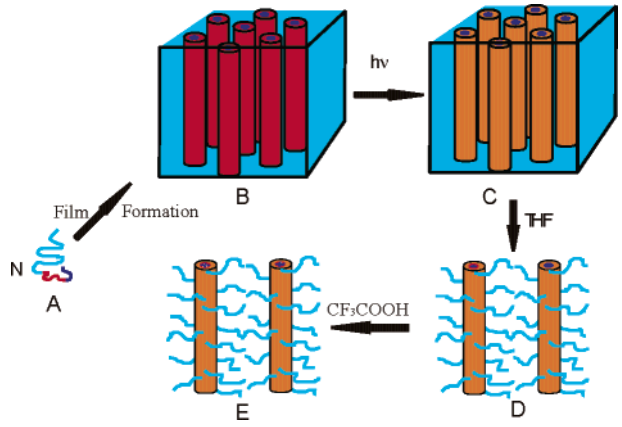
ethyl methacrylate)-*ran*-(2-hydroxyethyl methacrylate)]-*block*-poly(*tert*-butyl acrylate) or PGMA-P(CEMA-HEMA)-P*t*BA and



PS-PCEMA-P*t*BA, where PS denotes polystyrene. To prepare the PGMA-P(CEMA-HEMA)-P*t*BA nanotubes, the triblock was stirred in water, which is a good solvent for PGMA but a precipitant for P(CEMA-HEMA) and P*t*BA. This yielded cylindrical aggregates (A → B in Scheme 1) consisting of PGMA corona grafted onto the surface of the insoluble P*t*BA/P(CEMA-HEMA) core−shell cylinders. The cylinders were locked in structurally by photo-cross-linking the P(CEMA-HEMA) layer (B → C). Nanotubes with poly(acrylic acid)- or PAA-lined cores were obtained after P*t*BA hydrolysis (C → D). While the P*t*BA or PAA chains in Scheme 1 are shown to be end-exposed, they are so in reality only after nanotube shortening by ultrasonication.

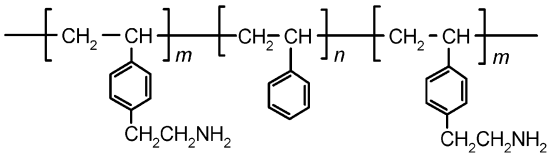
The preparation of the PS-PCEMA-PAA nanotubes has been reported before[5] and was achieved by taking advantage of the self-assembly of the triblock in the solid state. The volume fractions of different blocks were so adjusted that PCEMA and P*t*BA formed concentric shell−core cylinders dispersed in the continuous PS matrix (A → B in Scheme 2). The triblock solid film was then irradiated to cross-link the PCEMA shell cylinder (B → C). PS-PCEMA-P*t*BA nanofibers were obtained after separation of the cross-linked cylinders by solubilization of the PS matrix chains in THF (C → D). They were shortened by

Scheme 2. Preparation of PS-PCEMA-PAA Nanotubes



ultrasonication to expose the core P*t*BA chains at the fiber ends. PS-PCEMA-PAA nanotubes were obtained after the hydrolysis of the *tert*-butyl groups from the P*t*BA cores (D → E).

The two types of nanotubes can, in principle, be directly coupled or joined by a polymer spacer, poly[4-(2-aminoethyl)-styrene]-*block*-polystyrene-*block*-poly[4-(2-aminoethyl)styrene] or PAES-PS-PAES, if the length and composition of the



spacer are optimized. The PAES-PS-PAES sample that we used was synthesized for another project[5] and could not couple the nanotubes directly probably because the chains were too short. To overcome the difficulty, the end-exposed PAA chains of the PS-PCEMA-PAA nanotubes were reacted with an excess of PAES-PS-PAES (A → B in Scheme 3) first to yield nanotubes bearing amino end groups. The amino end groups of the PS-PCEMA-PAA tubes were then reacted with succinic anhydride to introduce carboxyl groups (B → C). PAES-PS-PAES thus serves in this case as a chain extender. The terminal carboxyl groups were finally reacted with the amino groups of PAES-PS-PAES, which have been grafted to the ends of the PGMA-PCEMA-PAA tubes, to couple the nanotubes (C → D).

II. Experimental Section

Materials and Reagents. Tetrahydrofuran (THF) was dried by refluxing with potassium and a small amount of benzophenone until a deep purple color developed and was distilled just before use. Pyridine was dried and distilled over CaH_2. *N*,*N*-Dimethylformamide (99.8%, EM Science) was used as received. 1,1-Diphenylethylene was purified by vacuum distillation in the presence of some *sec*-butyllithium (1.3 M in cyclohexane). Monomer solketal methacrylate was prepared following a literature method.[22] Initiator *sec*-butyllithium (1.3 M in cyclohexane) and monomers *tert*-butyl acrylate and 2-trimethylsiloxyethyl methacrylate (HEMA-TMS) were products of Aldrich. The monomers were purified by vacuum distillation first over calcium hydride and then in the presence of triethylaluminum before use.

Anionic Polymerization. Anionic polymerization was done in a 1 L three-neck round-bottomed flask attached to a vacuum line. Lithium

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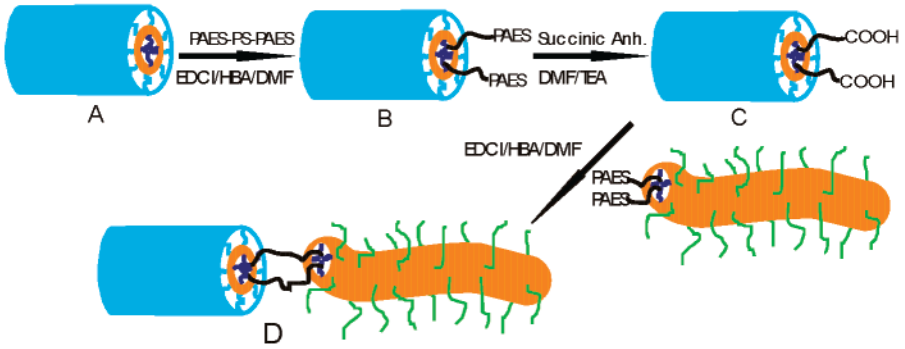
Scheme 3. Coupling of Different Nanotubes



chloride, 10 mg, was added into the flask before it was baked with a flame under vacuum. After refilling of the flask with high-purity argon (Praxair Co.), approximately 500 mL of THF was distilled into it. 1,2-Diphenylethylene, 4.8 μL or 0.26 mmol, was then added, and the flask was cooled in a dry ice/acetone bath at −78 °C. The impurities in the flask were titrated with *sec*-butyllithium until a faint pink color was observed. At this point, 0.126 mL of *sec*-butyllithium in cyclohexane or 0.16 mmol of initiator was added. This was followed by the injection of 14 mL of purified SMA, 4.3 mL or 22 mmol of HEMA-TMS, and 2.4 mL or 21 mmol of *t*BA with a time interval of 2 h between injections. After *t*BA had been polymerized for 2 h, the polymerization was terminated with the addition of degassed methanol containing drops of acetic acid. After being warmed to room temperature, the polymerization mixture was left stirring overnight to hydrolyze the P(HEMA-TMS) block to poly(2-hydroxyethyl methacrylate) or PHEMA. The resultant mixture was concentrated by rotaevaporation and added onto ice crystals to precipitate the polymer. The polymer was dried in a vacuum.

PSMA-PHEMA-P*t*BA Derivtization. To prepare PSMA-P(CEMA-HEMA)-P*t*BA, PSMA-PHEMA-P*t*BA, 2.0 g containing 2.3 mmol of hydroxyl groups, was mixed with 0.36 g or 2.16 mmol of cinnamoyl chloride (98%, Aldrich) and dissolved in 30 mL of dry pyridine. The mixture was stirred overnight before it was centrifuged to remove the salt precipitate. The supernatant was dropped onto ice crystals to precipitate the polymer. To fully cinnamate the PHEMA block to produce PSMA-PCEMA-P*t*BA, 1.5 molar equivalents of cinnamoyl chloride was used relative to the PHEMA hydroxyl groups. The polymer precipitate was rinsed with methanol before vacuum drying.

To hydrolyze the PSMA groups, 0.5 g of PSMA-P(CEMA-HEMA)-P*t*BA was dissolved in 10 mL of THF. To the solution was then added 2.5 mL of 6 M HCl in water. The mixture was stirred for 2 h before it was dialyzed against methanol (Spectra/Pro, molar mass cutoff 14000 g/mol) to remove water, HCl, and THF. The methanol solution was added into diethyl ether to precipitate PGMA-P(CEMA-HEMA)-P*t*BA.

PSMA-P(CEMA-HEMA)-P*t*BA Characterization. PSMA-P(CEMA-HEMA)-P*t*BA was better characterized by light scattering (LS) and size exclusion chromatography (SEC) in the PSMA-PCEMA-P*t*BA form due to the improved solubility of PCEMA relative to PHEMA in solvents such as THF and $CDCl_3$. SEC was performed using THF as the eluant. The Waters HT-4 column used was calibrated using poly(methyl methacrylate) standards. The refractive index difference Δn_r between the polymer solution and solvent THF was measured as a function of polymer concentration using a Phoenix Precision instrument. The weight-average molar mass was measured in THF using a light scattering instrument (Brookhaven model 9025) equipped with a 632.8 nm He−Ne laser. ^{1}H NMR spectra of PSMA-P(CEMA-HEMA)-P*t*BA and PSMA-PCEMA-P*t*BA were measured in $CDCl_3$ using a Bruker AC200 instrument.

PGMA-P(CEMA-HEMA)-PAA Nanotubes. PGMA-P(CEMA-HEMA)-P*t*BA, 500 mg and freshly precipitated in diethyl ether, was stirred in 200 mL of distilled water for 5−6 days. The resultant milky aqueous mixture was centrifuged at 1550*g* to separate the solid that did not disperse. The supernatant containing cylindrical aggregates of the triblock was irradiated in a Pyrex round-bottomed flask with a focused UV beam from a 500 W mercury lamp until PCEMA double bond conversion reached ∼30% as determined by UV absorption analysis at 276 nm.[23] The cross-linked cylindrical aggregates or nanofibers were shortened by ultrasonication in a Branson model 1200 R-C (voltage equals 117 V and current equals 1.3 A) ultrasonicator for 60 min. The solution was then dialyzed against methanol for solvent switch, and the methanol solution was added into diethyl ether to precipitate the nanofibers. To hydrolyze P*t*BA, 200 mg of the nanofibers, which were not fully dried, was dispersed in 16 mL of dichloromethane and 4 mL of trifluoroacetic acid. The suspension was stirred for 2 h before it was centrifuged at 1550*g* to settle the core-hydrolyzed nanofibers or nanotubes. The nanotubes were purified by repeating the procedure of dispersion in methanol and precipitation in diethyl ether twice. The nanotubes were stored under constant stirring as a DMF dispersion.

PS-PCEMA-PAA Nanotubes. The preparation of the PS-PCEMA-PAA nanotubes has been reported before.[5] The first step involved the preparation of a 15 wt % toluene solution of the triblock (150 mg) and a polystyrene homopolymer (60 mg, $M_n = 2500$ g/mol, $M_w/M_n = 1.07$). The solution was poured into a ring glued onto a leveled glass plate. The top of the ring was covered with another glass plate to slow toluene evaporation to 4−5 days. This yielded a film that was ∼50 μm thick. In step 2, the film was annealed at 120 °C under vacuum for 2 days to achieve more regular packing of the cylinders. In step 3, the film was irradiated with a focused beam, from a 500 W Hg lamp, that had passed a 302 nm cutoff filter to cross-link the PCEMA shell cylinders. In step 4, the irradiated films were stirred in 500 mL of THF for 4−5 days to separate the cross-linked cylindrical domains (nanofibers). The nanofibers were separated from the insoluble gels by centrifugation at 1350*g*. Methanol, ∼150 mL, was then added gradually into the supernatant to precipitate the nanofibers, which were separated from the solubilized PS homopolymer by centrifugation. In step 5, the nanofibers were redispersed in THF at ∼1.5 mg/mL and then shortened by ultrasonication for 8 h to expose the core chains at the ends. Finally, PS-PCEMA-PAA nanotubes were obtained after the *tert*-butyl groups were hydrolyzed from the P*t*BA cores of the nanofibers at 2 mg/mL in CH_2Cl_2 containing 25 vol % trifluoroacetic acid for 2 h. For solvent switching, the nanofibers were precipitated in methanol first and then dispersed in the second solvent without full drying of the fibers. The nanotubes were stored under constant stirring as a DMF dispersion.

Reaction between PS-PCEMA-PAA Nanotubes and PAES-PS-PAES. An example run involved mixing nanotubes (100 mg containing 0.149 mmol of carboxyl groups), DMF/water (v/v = 98/2, 20 mL), PAES-PS-PAES (0.20 g containing 0.224 mmol of NH_2 groups), triethylamine (TEA; 150 μL, 1.078 mmol), and 1-hydroxybenzotriazole (HBA; 40 mg, 0.296 mmol) with 1-[3-(dimethylamino)propyl]-3-

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ethylcarbodiimide hydrochloride (EDCI; 58 mg, 0.296 mmol). After the mixture was stirred at room temperature for 24 h, another 58 mg of EDCI and 40 mg of HBA were added, and the reaction was allowed to proceed for another 24 h. The mixture was added into a high excess of methanol and centrifuged at 1550*g* to settle the nanotubes. The precipitate was redispersed in THF. The THF solution was added into methanol again and centrifuged to precipitate the nanotubes. This redispersion and precipitation step was repeated five times. The purified PAES-PS-PAES-grafted nanotubes or PS-PCEMA-PAA-TUBE-NH_2 were last redispersed in Ar-bubbled DMF.

Reaction between PS-PCEMA-PAA-TUBE-NH_2 and Succinic Anhydride. PS-PCEMA-PAA-TUBE-NH_2, 20 mg, and succinic anhydride, 100 mg, were each dissolved in 2 mL of DMF. The succinic anhydride solution was then dropped into the nanotube solution. This was followed by the addition of 0.4 mL of triethylamine. The mixture was stirred overnight, before 15 mL of methanol was added to precipitate out the nanotubes. The nanotubes were redispersed in DMF and added into methanol to precipitate out the tubes. This procedure was repeated four times to purify the tubes.

Impregnation of PGMA-P(CEMA-HEMA)-PAA Nanotubes with Pd. A PGMA-P(CEMA-HEMA)-PAA nanotube dispersion in DMF at 10 mg/mL was bubbled with nitrogen for 10 min before a given amount of solid palladium chloride was added to enable a final concentration of ~5 mg/mL. Nitrogen bubbling was continued for another 10 min. The resultant solution was then capped and left stirring overnight. After that, the solution was dialyzed against water, which was changed 5−6 times, under the protection of bubbling nitrogen for 24 h. To reduce Pd^{2+} entrapped in the core, $NaBH_4$ at 2 molar equivalents relative to Pd^{2+} was added, and the mixture was stirred for 2 h. The excess reducing agent and impurities were removed by dialysis against distilled water and eventually against DMF for solvent switch. The resultant nanotubes are referred to as PGMA-P(CEMA-HEMA)-PAA/Pd nanotubes.

Reaction between PGMA-P(CEMA-HEMA)-PAA Nanotubes and PAES-PS-PAES. An example run involved mixing PGMA-P(CEMA-HEMA)-PAA nanotubes (100 mg containing 0.125 mmol of carboxyl groups), DMF/water (v/v = 98/2, 20 mL), PAES-PS-PAES (0.20 g containing 0.224 mmol of NH_2 groups), TEA (120 μL, 0.862 mmol), and HBA (34 mg, 0.251 mmol) with EDCI (48 mg, 0.246 mmol). After the mixture was stirred at room temperature for 24 h, another 48 mg of EDCI and 34 mg of HBA were added, and the reaction was allowed to proceed for another 24 h. The mixture was added into a high excess of THF and centrifuged at 1550*g* to settle the nanotubes. The precipitate was redispersed in DMF. The DMF solution was added into THF again and centrifuged to precipitate the nanotubes. This redispersion and precipitation step was repeated five times. The purified nanotubes or PGMA-P(CEMA-HEMA)-PAA-TUBE-NH_2 were last redispersed in Ar-bubbled DMF for storage. The reaction between PAES-PS-PAES and the PGMA-P(CEMA-HEMA)-PAA/Pd nanotubes was performed similarly to yield PGMA-P(CEMA-HEMA)-PAA-TUBE-NH_2/Pd.

Reaction between PGMA-P(CEMA-HEMA)-PAA-TUBE-NH_2 and Rhodamine B. The number of amino groups in a given PGMA-P(CEMA-HEMA)-PAA-TUBE-NH_2 sample was estimated by absorption measurement at 535 nm after their reaction with rhodamine B, which contains a carboxyl group. PGMA-P(CEMA-HEMA)-PAA-TUBE-NH_2, 10 mg, was dispersed in 2 mL of DMF. To the solution were then added rhodamine B (10 mg or 0.021 mmol), EDCI (8.0 mg or 0.042 mmol), HBA (5.6 mg or 0.042 mmol), triethylamine (29 μL or 0.21 mmol), and 40 μL of water. The mixture was stirred for 12 h before another batch of EDCI (8.0 mg) and HBA (5.6 mg) was added. The mixture was stirred for another 12 h. Then 10 mL of THF was added to precipitate the nanotubes, and the nanotubes were separated from the supernatant by centrifugation. The nanotubes were redispersed in DMF and reprecipitated with the addition of THF. This procedure was repeated five times before the nanotubes were dispersed in DMF and transferred into a dialysis tube with a molar mass cutoff of 14000 g/mol. The sample was dialyzed against DMF for 3 days with the solvent changed twice daily before absorbance measurement at 535 nm.

Reaction between PGMA-PCEMA-P*t*BA and Rhodamine B. The triblock copolymer (20 mg containing 0.143 mmol of hydroxyl groups) was dissolved in 5 mL of DMF. To it were added rhodamine B (137 mg or 0.286 mmol), EDCI (54.7 mg or 0.286 mmol), HBA (38.6 mg or 0.286 mmol), triethylamine (198 μL or 1.43 mmol), and 100 μL of water. The mixture was stirred for 12 h, before another batch of EDCI (54.7 mg) and HBA (38.6 mg) was added. After another 12 h, the mixture was transferred to a dialysis tube with a molar mass cutoff of 14000 g/mol. The mixture was dialyzed against methanol for 7 days with the solvent changed twice daily. The final polymer in the tube had no detectable rhodamine B absorption at 535 nm.

Nanotube Coupling. PS-PCEMA-PAA-TUBE-COOH, 10 mg, was mixed with 10 mg of PGMA-P(CEMA-HEMA)-PAA-TUBE-NH_2 in 5 mL of DMF containing 2 vol % water. Triethylamine (TEA, 40 μL, 0.316 mmol), HBA (7.5 mg, 0.055 mmol), and EDCI (10.8 mg, 0.055 mmol) were then added. After the mixture was stirred at room temperature for 24 h, another 10.8 mg of EDCI and 7.5 mg of HBA were added, and the reaction was allowed to proceed for another 24 h.

After the reaction, 5 mL of methanol, which dispersed PGMA-P(CEMA-HEMA)-PAA-TUBE-NH_2 selectively, was dropped in slowly. The mixture was centrifuged at 1550*g* to separate the supernatant which contained a majority of the unreacted PGMA-P(CEMA-HEMA)-PAA-TUBE-NH_2. The precipitate was redispersed in ~5 mL of DMF for several hours. THF, ~10 mL, was dropped in slowly and centrifuged to separate again the supernatant that contained the unreacted PS-PCEMA-PAA-TUBE-COOH. This was followed by the dispersion of the precipitate in DMF again with 2 days of stirring, the addition of methanol, and centrifugation to remove the supernatant containing more PGMA-P(CEMA-HEMA)-PAA-TUBE-NH_2. This procedure was repeated twice to remove PGMA-P(CEMA-HEMA)-PAA-TUBE-NH_2. After the purification, the yield defined as the ratio between the mass of the coupled product to the total initial mass of the PS-PCEMA-PAA-TUBE-COOH and PGMA-P(CEMA-HEMA)-PAA-TUBE-NH_2 for a reaction was determined to be 8%. Similar procedures were adopted for the coupling of PS-PCEMA-PAA-TUBE-COOH and PGMA-P(CEMA-HEMA)-PAA-TUBE-NH_2/Pd and the purification of the resultant product.

CONATUBLOC Aggregates in DMF/Toluene. Toluene was added by a syringe over a rate of ~10 mL/h into a CONATUBLOC solution in DMF at 0.8 mg/mL with stirring till the volume fraction of toluene reached 95%. The solution was kept stirring for another 2 h before aspiration onto a carbon-coated copper grid. The sample was stained with OsO_4 for 2 h before observation by transmission electron microscopy (TEM). TEM was performed using a Hitachi H-7000 instrument operated at 75 KV.

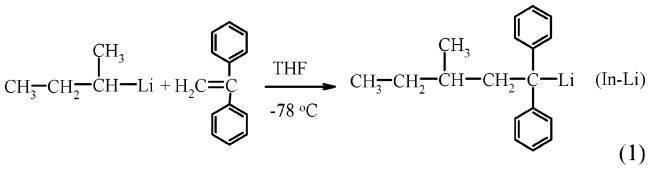
Morphology of a CONATUBLOC Solid Sample. CONATUBLOCs in DMF, 0.2 mL at 3 mg/mL, were mixed with homopolymers polystyrene (3.0 mg, M_w = 2500 g/mol, and M_w/M_n = 1.50) and PGMA (3.0 mg, M_w = 6000 g/mol, and M_w/M_n = 1.21). The resultant mixture was transferred into a loosely capped polyethylene capsule to allow the slow evaporation of the solvent over a 1 week span. A small piece of the thin film formed was sandwiched between two 2 mm thick polystyrene plates (Aldrich, bimodal distribution with M_w = 200000 and 4000 g/mol) that had been preheated to 120 °C and pressed at the temperature to promote adhesion. The sandwiched sample was then microtomed into 60 nm slices using an Ultracut-E Reichert-Jung instrument and stained by OsO_4 before TEM viewing.

III. Results and Discussion

Polymer Synthesis. Three polymers were used in this project. The procedures for PS-PCEMA-P*t*BA and PAES-PS-PAES

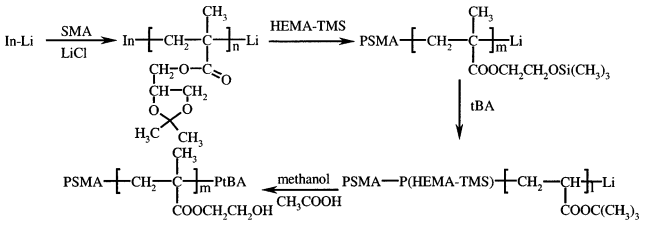
syntheses have been reported before.[5] All of the polymers were derived from precursors prepared by anionic polymerization.

PSMA-PHEMA-P*t*BA was derived from PSMA-P(HEMA-TMS)-P*t*BA. Although the anionic polymerization of the individual blocks of PSMA-P(HEMA-TMS)-P*t*BA has appeared in different combinations before, the preparation of this particular triblock has not been reported. The initiator used was 1,1-diphenyl-3-methylpentyllithium generated by reacting s*ec*-butyllithium with 1,1-diphenylethylene in THF at −78 °C. This sterically hindered initiator rather than s*ec*-butyllithium was used to minimize the nucleophilic attack of the SMA ester groups.



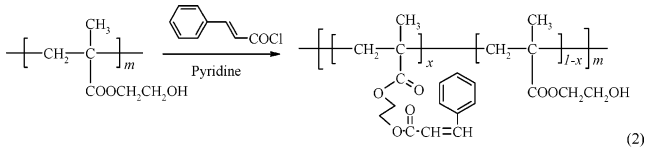
(1)

Each of the monomers was polymerized in THF at −78 °C for 2 h. The preparation of PSMA-PHEMA-P*t*BA involved the following reactions:



Lithium chloride was used in the polymerization to decrease sample polydispersity.[24] The PHEMA block was obtained after hydrolysis in THF/methanol containing drops of acetic acid.

PSMA-P(CEMA-HEMA)-P*t*BA was obtained from reacting the PHEMA block of PSMA-PHEMA-P*t*BA with a limiting amount of cinnamoyl chloride:



(2)

The partial cinnamation of the hydroxyl groups of the HEMA block was targeted to maintain the swellability of the cross-linked P(CEMA-HEMA) layer in water and thus to facilitate Pd^{2+} transport. This was deemed important, as loading of Pd^{2+} or Pd^0 would allow the ready differentiation of the PGMA-P(CEMA-HEMA)-PAA nanotubes from the PS-PCEMA-PAA nanotubes. The selective hydrolysis of PSMA to PGMA was accomplished in THF using hydrochloric acid as the catalyst.[1c]

Polymer Characterization. Table 1 shows the SEC, ^{1}H NMR, and LS characterization results for PSMA-PCEMA-P*t*BA, PS-PCEMA-P*t*BA, and P(AES-TMS)-PS-P(AES-TMS), where P(AES-TMS) denotes poly{4-[2-*N*,*N*-bis(trimethylsilyl)amino-ethyl]styrene} and is the precursor to PAES. PGMA-P(CEMA-HEMA)-P*t*BA was characterized by SEC and LS in the PSMA-PCEMA-P*t*BA form, because PSMA and PCEMA dissolved better than PGMA and P(CEMA-HEMA) in THF, the solvent used for SEC characterization. The characterization of PS-PCEMA-P*t*BA and P(AES-TMS)-PS-P(AES-TMS) has been described before[5] and will thus not be dwelt on further. The ^{1}H NMR spectrum of PSMA-PCEMA-P*t*BA is shown in Figure 1 together with peak assignments. For this sample, the e peaks of PCEMA and the f peaks of PSMA overlap. The intensities of peaks b, c, and d of PCEMA were used to estimate the area of the e peaks of PCEMA between 3.5 and 4.5 ppm. This was subtracted from the total area of peaks in this region to yield the area for f peaks of PSMA and thus *n*/*m*. From the known area for PSMA f peaks we then estimated the intensity of its g peaks between 1.2 and 1.7 ppm and subtracted it from the total area in this region to yield the area of the *tert*-butyl protons of P*t*BA, which yielded finally *n*/*m*/*l*. The molar fraction *x* of the CEMA units in the P(CEMA-HEMA) block was obtained from comparing the NMR spectra of PSMA-PCEMA-P*t*BA and PSMA-P(CEMA-HEMA)-P*t*BA to be 65%.

Table 1. Characteristics of the Polymers

sample	SEC M_w/M_n	LS $M_w \times 10^{-4}$ (g/mol)	NMR repeat unit number ratio	n	m	l
PSMA-PCEMA-P*t*BA	1.03	12.2	1.00/0.33/0.32	375	123	119
PS-PCEMA-P*t*BA	1.17	11.5	1.00/0.25/0.28	560	140	160
P(AES-TMS)-PS-P(AES-TMS)	1.17	2.0	7.2/1.00	115	16	

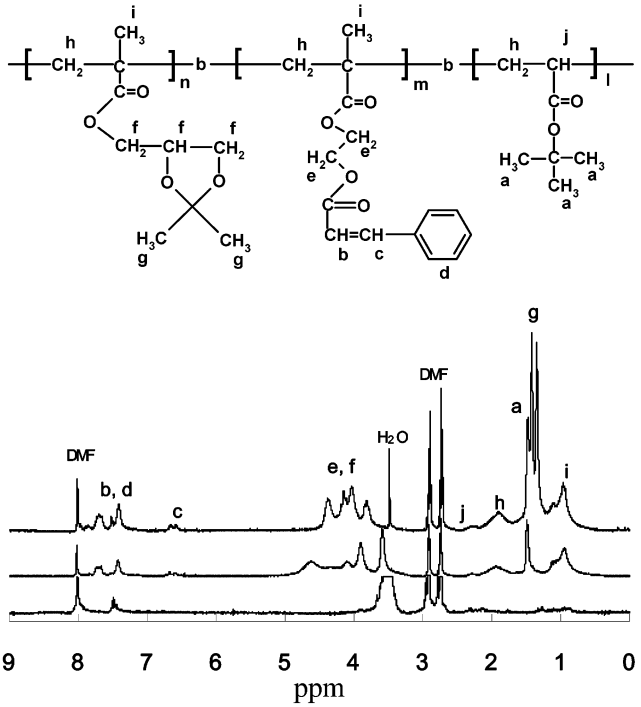


Figure 1. NMR spectra of PSMA-PCEMA-P*t*BA (top), PGMA-PCEMA-P*t*BA (middle), and the nanotube multiblocks (bottom) in DMF-d_7.

Also shown in Figure 1 is an NMR spectrum of PGMA-PCEMA-P*t*BA. The selective hydrolysis of PSMA under the acidic conditions described in the Experimental Section is evident by comparing the two top NMR spectra in Figure 1.

PGMA-P(CEMA-HEMA)-P*t*BA Aggregate Formation and Cross-Linking. Cylindrical aggregates were prepared from PGMA-P(CEMA-HEMA)-P*t*BA by stirring the triblock in water for several days. The solution was then irradiated to lock in the structure of the aggregates. An aliquot was taken and aspirated on a carbon-coated copper grid for TEM examination. Figure

(24) Creutz, S.; Teyssié, P.; Jérôme, R. *Macromolecules* **1997**, *30*, 6−9.

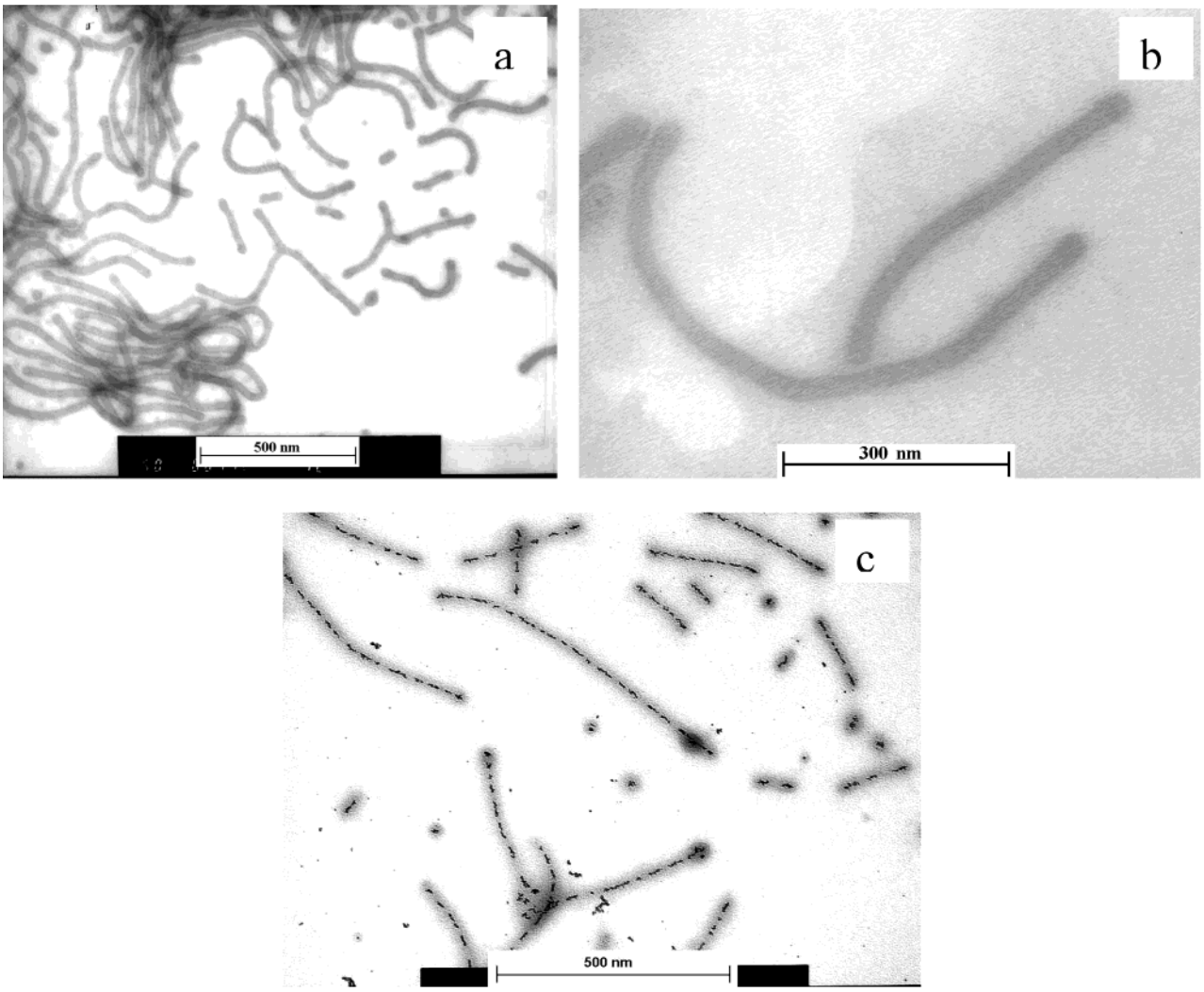


Figure 2. TEM images of cross-linked PGMA-P(CEMA-HEMA)-P*t*BA nanofibers before (a and b) ultrasonication aspirated from water. Also shown is an image of PGMA-P(CEMA-HEMA)-PAA nanotubes after Pd^0 loading (c) aspirated from water.

2a shows a TEM image of the nanofibers thus obtained after aspiration from water and CEMA staining with OsO_4 vapor. Simple and branched cylinders coexist in the sample.

The cylindrical aggregates could have formed for either kinetic or thermodynamic reasons. A thermodynamically stable aggregate is formed under a given set of conditions regardless of the formation pathway and is called a micelle. We prepared aqueous aggregates of the triblock also from dissolving the triblock molecularly in pyridine first and then adding water dropwise until the water volume fraction reached 95%. The residual pyridine was removed by dialysis against water. A TEM study revealed the formation of spherical aggregates in this case. The path-dependent product formation made the exact origin of the cylindrical aggregates unknown, and this is why they have been referred to as cylindrical aggregates rather than micelles.

P(CEMA-HEMA) cross-linked due to dimerization of CEMA groups of different polymer chains.[25] This reaction has been used by us to lock in many types of block copolymer nanostructures before. The effectiveness of the cross-linking reaction here was demonstrated by the structural stability of the cross-linked cylindrical aggregates in solvents such as pyridine and DMF that solubilized the precursory PGMA-P(CEMA-HEMA)-P*t*BA copolymer.

PGMA-P(CEMA-HEMA)-P*t*BA Nanofiber Shortening by Ultrasonication. Figure 2b shows a TEM image of the cross-linked PGMA-P(CEMA-HEMA)-P*t*BA aggregates or nanofibers before ultrasonication at a higher magnification than that in Figure 2a. The nanofibers had hemispherical end caps probably made of P(CEMA-HEMA) grafted with a layer of PGMA on the surface. To expose the P*t*BA core chains, the cross-linked PGMA-P(CEMA-HEMA)-P*t*BA aggregates or PGMA-P(CEMA-HEMA)-P*t*BA nanofibers were shortened by ultrasonication. The effectiveness of this treatment was established by measuring the lengths of the fibers before and after ultrasonication. For one sample, we established that the weight-average length L_w of 93 fibers before and after 1 h of ultrasonication were 2270 and 545 nm, respectively. The corresponding polydispersities L_w/L_n of the samples were 1.89 and 1.61.

(25) See, for example: Guillet, J. E. *Polymer Photophysics and Photochemistry—An Introduction to the Study of Photoprocesses in Macromolecules*; Cambridge University Press: Cambridge, 1985.

Table 2. Characteristics of the Nanotubes

tube sample	CEMA conv (%)	L_w (nm)	L_w/L_n
PS-PCEMA-PAA	23	390	1.41
PGMA-P(CEMA-HEMA)-PAA	30	545	1.61

PGMA-P(CEMA-HEMA)-PAA Nanotubes. PGMA-P(CEMA-HEMA)-PAA nanotubes were obtained after the hydrolysis of P*t*BA in a mixture of trifluoroacetic acid and methylene chloride.[26] The specific batch of PGMA-P(CEMA-HEMA)-PAA nanotubes used in this study has characteristics shown in Table 2.

The fact that the nanotubes possessed a PGMA corona was demonstrated by the observation of ^{1}H NMR signals from only the PGMA block in DMF-d_7. The signals of the PAA block were not observed as it stayed in the confined core caged by the cross-linked P(CEMA-HEMA) layer. Figure 2c shows a TEM image of the nanotubes after Pd loading. The Pd particles are obviously located in the center of the nanotubes, where the PAA chains reside.

PS-PCEMA-PAA Nanotubes. PS-PCEMA-PAA nanotubes were prepared by taking advantage of the block-segregation properties of the triblock copolymer in the solid state. PS homopolymer was mixed with PS-PCEMA-P*t*BA in toluene before film casting to ensure that the volume fractions of PCEMA and P*t*BA in the final solid were ~20% and ~10%, respectively, to facilitate shell−core cylinder formation.[27] The shell PCEMA cylinders were then cross-linked with UV light, and the cross-linked shell−core cylinders were separated from one another by PS chain solubilization in THF. The cylinders were shortened by ultrasonication to expose the P*t*BA core chains. Nanotubes with end-exposed PAA chains were prepared after P*t*BA core hydrolysis. The batch of PS-CEMA-PAA nanotubes that we used had an L_w of 390 nm and a polydispersity L_w/L_n of 1.41. Before ultrasonication, the L_n value of the nanofibers was ~5 μm. Thus, most of the nanotubes used had two exposed ends.

Reaction between PAES-PS-PAES and PS-PCEMA-PAA Nanotubes. The reaction conditions used to graft PAES-PS-PAES to the ends of PS-PCEMA-PAA nanotubes were established before.[5] The conditions used should allow the grafting of ~100 PAES-PS-PAES chains to each end of a nanotube.

Reaction between PAES-PS-PAES and PGMA-P(CEMA-HEMA)-PAA Nanotubes. We estimated the number of PAES-PS-PAES chains attached to each PGMA-P(CEMA-HEMA)-PAA nanotube end by spectrophotometry after the free amino groups of the grafted PAES-PS-PAES chains were reacted with rhodamine B. A model reaction between rhodamine B and PGMA-PCEMA-P*t*BA demonstrated that the hydroxyl groups of PGMA reacted negligibly with rhodamine B during this process. To relate the rhodamine B concentration with that of the grafted PAES-PS-PAES chains, we assumed that each grafted PAES-PS-PAES chain had only 16 free amino groups or only 1 PAES end block to react quantitatively with rhodamine B. While the number 16 is somewhat arbitrary, the quantitative reaction between amino and carboxyl groups has been validated before.[5] To arrive at the estimated molar mass M_n of 4.5×10^8 g/mol for the nanotubes, we made use of the fact that the sample had a number-average length L_n of 236 nm and the P(CEMA-HEMA)/P*t*BA layers had a TEM diameter of 32 nm. We further assumed that the density of the P(CEMA-HEMA)/P*t*BA layers was 1 g/cm^3. Combining the molar mass of the nanotubes and the rhodamine B absorbance data, we estimated that ~54 PAES-PS-PAES chains were grafted to each end of the PGMA-P(CEMA-HEMA)-PAA nanotubes.

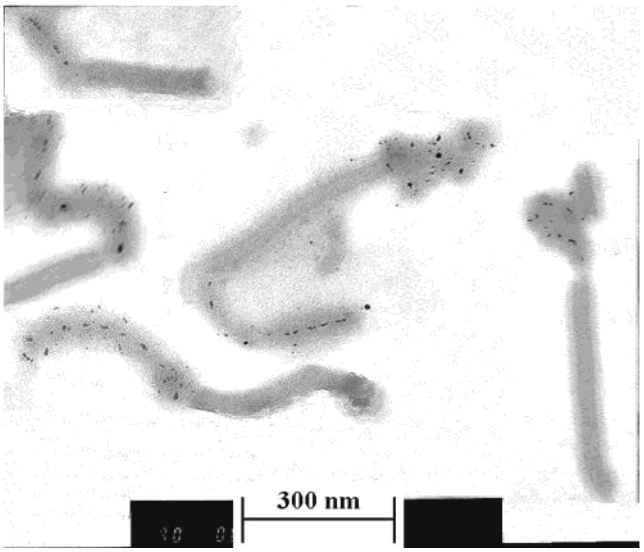


Figure 3. TEM image of the nanotube multiblocks aspirated from DMF.

Preparation of PS-PCEMA-PAA-TUBE-COOH. PS-PCEMA-PAA-TUBE-NH_2 was reacted with succinic anhydride to convert the terminal amino to carboxyl groups to yield PS-PCEMA-PAA-TUBE-COOH. The efficiency of this reaction was determined for a model system consisting of PAES-PS-PAES and succinic anhydride. Under similar reaction conditions, we found by NMR analysis that the amino groups of PEAS reacted quantitatively with the succinic anhydride.

Coupling of PS-PCEMA-PAA-TUBE-COOH and PGMA-P(CEMA-HEMA)-PAA-TUBE-NH_2. The nanotubes were joined via amide bond formation between their terminal carboxyl and amino groups. Our success in coupling the nanotubes in a head-to-tail fashion is clearly demonstrated by the TEM image in Figure 3. The PGMA-P(CEMA-HEMA)-PAA nanotubes are distinguished from the PS-PCEMA-PAA nanotubes, as the core of the former was loaded with some Pd nanoparticles. Also the PGMA-P(CEMAHEMA)-PAA tubes are more flexible. The coupling reaction produced not only nanotube diblocks but also some triblocks. Despite the success, the yield is currently low at a meager 8 wt %. We have tried to increase this yield in vain by changing reaction times and reactant concentrations.

We have also performed a solution NMR study of the nanotube multiblocks with the NMR spectrum shown in Figure 1. The signals of the phenyl rings at ~7.4 ppm and those of the methyl protons of PGMA at 0.9 ppm are low but are visible. The molar ratio between the styrene and GMA units was 1.00/0.55.

Aggregate Formation from CONATUBLOCs in a Block-Selective Solvent. The PS chains are soluble in toluene but not

(26) Lu, Z. H.; Liu, G. J.; Duncan, S. *Macromolecules* **2004**, *37*, 174−80.
(27) Breiner, U.; Krappe, U.; Abetz, V.; Stadler, R. *Macromol. Chem. Phys.* **1997**, *198*, 1051−83.

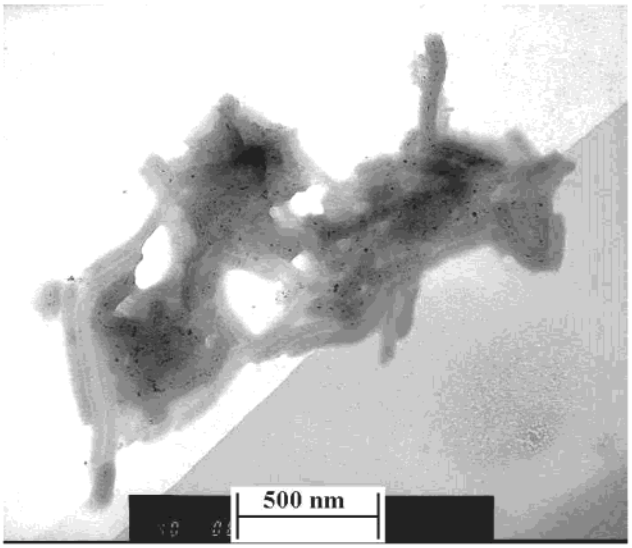


Figure 4. TEM image of the CONATUBLOCs aspirated from DMF/toluene containing 95% toluene.

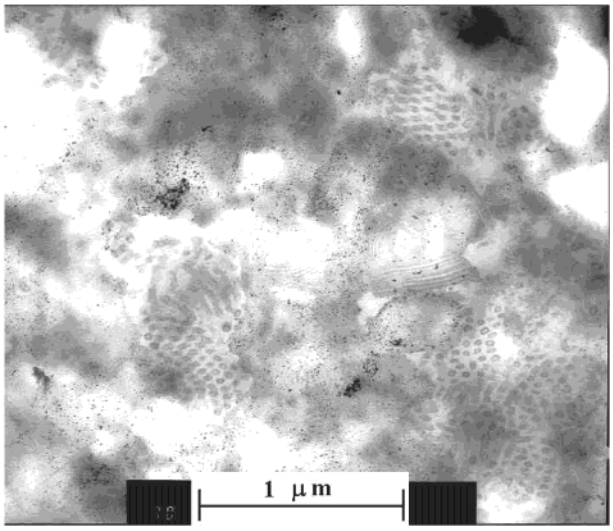


Figure 5. Thin-section TEM image of a CONATUBLOC solid consisting of 0.6 mg of CONATUBLOC, 3.0 mg of PS, and 3.0 mg of PGMA. The PGMA-P(CEMA-HEMA)-PAA nanotubes were loaded with Pd^0.

the PGMA chains. To check the behavior of the CONATUBLOCs in a block-selective solvent mixture, we first dispersed the CONATUBLOCs in DMF and added toluene slowly to a volume fraction of 95%. Figure 4 shows a TEM image of the resultant aggregates. The image shows that the PGMA-P(CEMA-HEMA)-PAA/Pd nanotube block concentrates mainly in the core and the PS-PCEMA-PAA nanotube block packs mostly along the periphery of the aggregate.We have also performed a control experiment involving the aspiration of a DMF/toluene solution containing physically mixed PGMA-PCEMA-PAA/Pd and PS-PCEMA-PAA nanotubes. The PGMA-PCEMA-PAA/Pd nanotubes were aggregated in contrast to the PS-PCEMA-PAA nanotubes, which remained isolated and scattered across the TEM images.

Images such as that shown in Figure 4 disappointed us initially, as the CONATUBLOCs did not form regularly shaped aggregates. Rather, the structures resembled very much those generated by computer simulation for unimolecular micelles.[28] The irregular structure may be due to the wide length distribution of the nanotubes used. Mirkin and co-workers[12] have recently reported the aggregation of gold−polypyrrole diblock rods. The metal and polymer blocks all had the same length, and the diblock rods packed regularly in water.

CONATUBLOC Segregation in the Solid State. Figure 5 shows a TEM image of the CONATUBLOCs dispersed at 9.1 wt % in PS and PGMA. The PS-PCEMA-PAA nanotubes, akin to block copolymers, segregate and form domains dispersed in the matrix of the other components. The detailed nanotube folding and packing mechanism and how the packing changes with relative lengths of the nanotube blocks remain to be elucidated.

IV. Conclusions

Nanofibers have been prepared from PGMA-P(CEMA-HEMA)-P*t*BA. Hydrolysis of the P*t*BA block yielded PAA-lined triblock nanotubes. The PAA core chains were end exposed after the nanotubes were shortened by ultrasonication. The end-exposed PAA chains reacted with PAES-PS-PAES to yield nanotubes bearing terminal amino groups. The amino groups were further reacted with carboxyl terminal groups of PS-PCEMA-PAA nanotubes to yield CONATUBLOCs. With the current PAES-PS-PAES chain design, we determined it ineffective in joining the two types of nanotubes directly. Rather, we had to go through a detour to extend the length of the PAA core chains of the PS-PCEMA-PAA nanotubes. This was achieved by reacting the end-exposed PAA chains of the PS-PCEMA-PAA nanotubes with PAES-PS-PAES to introduce terminal amino groups first. The amino groups were then reacted with succinic anhydride to reintroduce terminal carboxyl groups. The nanotube coupling yield is presently low at a meager 8 wt %. Despite this, we have demonstrated that the CONATUBLOCs, akin to block copolymers, segregated in a block-selective solvent mixture to form micelle-like aggregates. The different blocks also segregated in the solid state. Further research is ongoing to simplify the block design and block coupling chemistry.

Acknowledgment. NSERC of Canada is thanked for sponsoring this research.

JA0479890

(28) Khokhlov, A. R.; Khalatur, P. G. *Phys. Rev. Lett* **1999**, *82*, 3456−59.