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# End Coupling of Block Copolymer Nanotubes to Nanospheres

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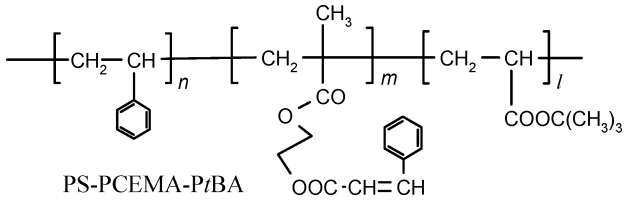
***Abstract:*** Triblock copolymer nanotubes bearing end-exposed poly(acrylic acid) or PAA core chains were prepared. The exposed PAA chains were reacted by amidization with a large excess of polystyrene spacer chains possessing amino end groups or amino-containing end blocks to graft the spacer chains. The amino groups at the other end of the spacer chains were then reacted with nanospheres bearing surface carboxyl groups to connect the nanotubes to nanospheres. The products from such a coupling reaction ranged from multiarm adduct to surfactant- and dumbbell-like objects. Product control using different strategies was explored. The products may have interesting properties and applications.

## Introduction

There have many reports in the past several years on the preparation of nanostructures from inorganic and organic compounds and from block copolymers. For the nanostructures to function as nanoelectronic devices, controlled coupling between different components is essential. There have been, to our knowledge, no reports on the coupling of different block polymer nanostructures. In this paper, we report on the end coupling of polystyrene-*block*-poly(2-cinnamoyloxyethyl methacrylate)-*block*-poly(acrylic acid) or PS−PCEMA−PAA nanotubes to nanospheres bearing surface carboxyl groups.

The preparation of permanent block copolymer nanostructures normally involves taking advantage of the block segregation property of the polymers in either the solid state[1] or a block-selective solvent.[2] The block-segregated structures are then chemically processed,[3] invoking selective domain cross-linking or degradation, to yield stable nanostructures including nanofibers,[4] nanotubes,[5] and thin films containing nanochannels.[6,7] The nanotubes used in this study were prepared from PS−PCEMA−P*t*BA following procedures reported before,[8] where P*t*BA denotes poly(*tert*-butyl acrylate).




The preparation of these nanotubes involved casting films from the triblock containing some PS homopolymer. In such films, P*t*BA and PCEMA formed hexagonally packed concentric core−shell cylinders dispersed in the PS matrix. The films were then irradiated to cross-link the PCEMA shell cylinders. PS−PCEMA−P*t*BA nanofibers were obtained after separating the cross-linked cylinders by solubilizing the PS matrix chains in THF. They were shortened by 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.

The nanospheres used in this study bear surface carboxyl groups and were prepared from emulsion polymerization or from PCEMA−PAA.[9] To couple the nanotubes to the nanospheres, the end-exposed PAA chains of the nanotubes were first reacted with an excess of a polymer spacer, which can be either poly[4-(2-aminoethyl)styrene]-*block*-polystyrene-*block*-poly[4-(2-aminoethyl)styrene], PAES−PS−PAES (Scheme 1), or poly-

† University of Calgary.
‡ Defence Research Development Canada.

(1) For block segregation patterns of di- and tri-block solids, see, for example: Bates, F. S.; Fredrickson, G. H. *Phys. Today* **1999**, *February, issue 32*.
(2) For block segregation patterns of diblocks in block-selective solvents, see, for example: Eisenberg, A. *Can. J. Chem.* **1999**, *77*, 1311.
(3) Liu, G. J. *Curr. Opin. Colloid Interface Sci.* **1998**, *3*, 200.
(4) See, for example: (a) Liu, G. J.; Qiao, L. J.; Guo, A. *Macromolecules* **1996**, *29*, 5508. (b) Liu, G. J.; Ding, J. F.; Qiao, L. J.; Guo, A.; Gleeson, J. T.; Dymov, B.; Hashimoto, T.; Saijo, K. *Chem.-Eur. J.* **1999**, *5*, 2740. (c) Massey, J.; Power, K. N.; Manners, I.; Winnik, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 9533. (d) Won, Y.-Y.; Davis, H. T.; Bates, F. S. *Science* **1999**, *283*, 960. (e) Templin, M.; Franck, A.; DuChesne, A.; Leist, H.; Zhang, Y. M.; Ulrich, R.; Schadler, V.; Wiesner, U. *Science* **1997**, *278*, 5344.
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(6) (a) Liu, G. J.; Ding, J. F.; Guo, A.; Herfort, M.; Bazett-Jones, D. *Macromolecules* **1997**, *30*, 1851. (b) Liu, G. J.; Ding, J. F. *Adv. Mater.* **1998**, *10*, 69. (c) Liu, G. J.; Ding, J. F.; Hashimoto, T.; Saijo, K.; Winnik, F. M.; Nigam, S. *Chem. Mater.* **1999**, *11*, 2233. (d) Liu, G.; Ding, J.; Stewart, S. *Angew. Chem.* **1999**, *38*, 835. (e) Hashimoto, T.; Tsutsumi, K.; Funaki, Y. *Langmuir* **1997**, *13*, 6869.
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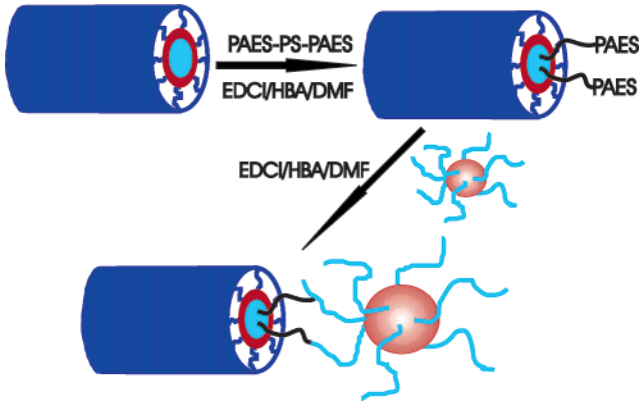
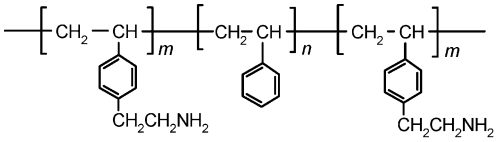
(8) (a) Liu, G. J.; Yan, X. H.; Qiu, X. P.; Li, Z. *Macromolecules* **2002**, *35*, 7742. (b) Yan, X. H.; Liu, G. J.; Liu, F. T. *Angew. Chem., Int. Ed.* **2001**, *40*, 3593.
(9) Henselwood, F.; Liu, G. J. *Macromolecules* **1997**, *30*, 488.

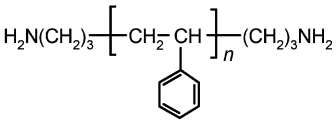
***Scheme 1.*** Coupling Nanotubes to Diblock Nanospheres




styrene end-labeled with amino groups, $NH_2-PS-NH_2$, to yield nanotubes containing amino end groups. The amino groups were then reacted with nanospheres bearing surface carboxyl groups (Scheme 1) to couple the nanotubes to nanospheres.



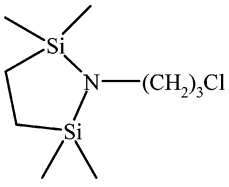
PAES-PS-PAES



$NH_2$-PS-$NH_2$

## Experimental Section

**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. Dry diethyl ether was obtained by refluxing and distillation over calcium hydride. Styrene was first filtered through an alumina column and then stirred with benzylmagnesium chloride at room temperature for 3 h. It was freshly distilled under reduced pressure just before polymerization. The anionic initiator lithium naphthalenide was prepared by the reaction of naphthalene with an excess of lithium in THF.[10] 2,2,5,5-Tetramethyl-1-(3-chloropropyl)-1-aza-2,5-disilacyclopentane was prepared following a literature method.[11]



2,2,5,5-tetramethyl-1-(3-chloropropyl)-1-aza-2,5-disilacyclopentane

***N,N*-Bis(trimethylsilyl)methoxymethylamine.**[12] A 500-mL three-neck round-bottomed flask was fitted with an addition funnel and purged with argon. To it was added 100 mL of a 1.0-M *N,N*-bis(trimethylsilyl)-lithium amide solution in hexane. The solution was cooled to 0 °C which resulted in the formation of a yellow precipitate. The precipitate was redissolved with the addition of 30 mL of dry THF. Chloromethyl methyl ether, 8.8 g or 110 mmol, was then added dropwise from the addition funnel. This caused the lithium chloride salt to precipitate shortly after from the reaction mixture. The mixture was left stirring for 8 h before the salt was filtered and the solvent was removed by rota-evaporation. The product was purified by vacuum distillation to give 16 g of clear liquid (80% yield).

**Grignard Reagent of 4-(Chloromethyl)styrene.**[13] To a 500-mL three-neck round-bottomed flask fitted with an addition funnel and purged with argon were added 150 mL of dry diethyl ether, 2.6 g or 107 mmol of magnesium, and a small iodine crystal. To the addition funnel was added 14.5 mL or 100 mmol of distilled 4-chloromethyl styrene in 50 mL of dry diethyl ether. Approximately 10 mL of the 4-chloromethyl styrene solution was added in one aliquot to the flask to start the reaction. The reaction mixture was heated to 40 °C, and stirring commenced. The remainder of the 4-chloromethyl styrene solution was added dropwise over 2 h. After that, the reaction was continued for another 30 min. The resultant solution contained a trace amount of residual magnesium and had a green color.

**4-[2-*N,N*-Bis(trimethylsilyl)amino ethyl]styrene.**[14,15] *N,N*-Bis(trimethylsilyl)methoxymethylamine, 20.7 g or 100 mmol, was added dropwise to the above Grignard reagent solution. The mixture was stirred at room temperature for 24 h. The salt was then filtered, and solvent was removed by rota-evaporation. The product was purified by vacuum distillation twice to give 4-[2-*N,N*-bis(trimethylsilyl)amino ethyl]styrene or TMS−AES as a colorless liquid with 50% yield.

**Polymerization.** Polymerization was done in a 1-L three-neck round-bottomed flask attached to a vacuum line. The flask was first evacuated and flamed. To it was distilled approximately 500 mL of THF. The flask was then cooled in a dry ice acetone bath at −78 °C. The impurities in THF were titrated with a 0.05-M lithium naphthalenide initiator solution until a faint green color of the initiator was observed. At this time, 20 mL of the initiator solution or 1.0 mmol of initiator was added. This was followed by the injection of 5.0 mL or 44 mmol of purified styrene. Styrene was polymerized for 1 h before 4.5 mL of TMS−AES was added and polymerized for 1 h. The polymerization was terminated with the addition of degassed methanol. After being warmed to room temperature, the polymerization mixture was concentrated by rota-evaporation and was added into methanol to precipitate out the polymer. The polymer was dried in vacuo.

$NH_2-PS-NH_2$ with protected amino end groups was prepared similarly. The polymerization was terminated by 2,2,5,5-tetramethyl-1-(3-chloropropyl)-1-aza-2,5-disilacyclopentane.

**Deprotection of the Amino Groups.** To hydrolyze P(TMS−AES)−PS−P(TMS−AES), 1.0 g of the triblock was dissolved in 15 mL of THF containing 1.0 mL of 2.0 M HCl. The mixture was stirred for 1 h before solvent was removed by rota-evaporation. The polymer was then washed with 1.0 M KOH aqueous solution and water and dried under vacuum at 40 °C overnight. The amino end groups of $NH_2-PS-NH_2$ were deprotected by stirring the sample in methanol overnight.

**Polymer Characterization.** The polymer PAES−PS−PAES was characterized in the P(TMS−AES)−PS−P(TMS−AES) form, because PAES did not dissolve well in organic solvents such as THF. The light scattering (LS) and size exclusion chromatography (SEC) measurements and the specific refractive index increment $dn_r/dc$ determination of the polymer spacers were all performed in THF. Proton NMR characterization was done in $CDCl_3$. The amino group content in $NH_2-PS-NH_2$ was determined by acid−base titration.[11]

The LS instrument used was a Brookhaven BI-200SM model equipped with 10-mW He−Ne laser operating at 632.8 nm. The

(10) Sorenson, W. R.; Sweeny, F.; Campbell, T. W. *Preparative Methods of Polymer Chemistry*, 3rd ed.; John Wiley & Sons: New York, 2001; p 295.
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determination of $dn_r/dc$ was achieved with a differential refractometer from Precision Instruments. SEC was performed on a Waters instrument using a Waters HT-4 broadband column. The SEC column was calibrated in THF using poly(methyl methacrylate) standards.

**PS−PCEMA−PAA Nanotube Synthesis.** 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 in a ring glued onto a leveled glass plate. The top of the ring was covered with another glass plate to slow the evaporation of toluene to 4−5 days. This yielded a film that was ∼50 $\mu$m thick. In step 2, the film was annealed at 120 °C under vacuum for 2 days to achieve more regular packing of the cylinders. Step 3 involved film irradiation 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.[16] 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 again by centrifugation. In step 5, the redispersed nanofibers in THF at ∼1.5 mg/mL were shortened by ultrasonication[17] in a Branson model 1200 R-C (voltage equals 117 V and current equals 1.3 A) ultrasonicator for 8 h to expose the core chains at the ends. Finally, PS−PCEMA−PAA nanotubes were obtained after hydrolyzing the *tert*-butyl groups 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 fully drying the fibers.

**Emulsion Nanospheres.** The emulsion spheres are of the core−shell type.[18] To prepare the core particles, 6.0 g of *tert*-butyl acrylate (*t*BA), 3.5 g of methyl methacrylate (MMA), 0.50 g of ethylene glycol dimethacrylate (EGDMA, cross-linker), 100 mL of water, 0.030 g of poly(ethylene glycol) monolaurate [$CH_3(CH_2)_{10}CO(OCH_2CH_2)_nOH$, Aldrich, $M_n \approx 600$ g/mol, emulsifier], and 0.12 g of potassium persulfate (Aldrich, initiator) were stirred at 150 rpm at room temperature for 5 min and then immersed into an oil bath preheated to 80 °C. The polymerization was allowed to proceed for 1.5 h. After that, 4.75 g of MMA, 0.25 g of EGDMA, and 0.020 g of poly(ethylene glycol) methacrylate [$CH_2{=}C(CH_3)CO(OCH_2CH_2)_nOH$, PEG−MA, Aldrich, $M_n \approx 526$ g/mol] mixed in one syringe were injected concurrently with 0.12 g of potassium persulfate solubilized in 50 mL of water in another syringe over a 2 h span to enable shell formation. The polymerization was continued for another 1 h after reagent addition. The spheres thus prepared were settled by centrifugation and cleaned by repeated washing with water, methanol, and THF. To convert the surface hydroxyl groups of PEG−MA to carboxyl groups, the spheres were reacted with a 100 molar excess of succinic anhydride in dry pyridine at 50 °C overnight.[19]

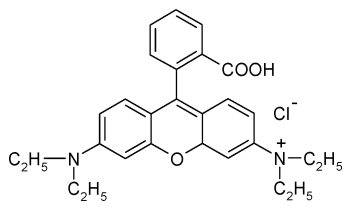
**PCEMA−PAA Nanospheres.** The second type of nanospheres was prepared from PCEMA−P*t*BA. Step 1 involved dissolving 200 mg of PCEMA−P*t*BA in 20 mL of THF. To the solution was then added 80 mL of 2-propanol, which is a precipitant for PCEMA, to induce formation of spherical micelles with PCEMA cores and P*t*BA coronas. Nanospheres were obtained after photolysis to achieve a CEMA double bond conversion of 31%. The P*t*BA coronal chains were hydrolyzed to PAA chains by stirring the spheres in $CH_2Cl_2$ containing 20 vol % trifluoroacetic acid for 4 h. The nanospheres after hydrolysis were separated from the supernatant by centrifugation and redispersed in DMF. The spheres were further purified by dialysis against DMF.

**Reaction between Nanotubes and Spacer Chains.** An example run involved first mixing nanotubes (45 mg containing 0.067 mmol of carboxyl groups), DMF/water (v/v = 98/2, 3.0 mL), $NH_2-PS-NH_2$ (0.60 g containing 0.085 mmol of $NH_2$ groups), and 1-hydroxybenzotriazole (HBA, 18 mg, 0.133 mmol) with 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDCI, 26 mg, 0.136 mmol). After the mixture was stirred at room temperature for 12 h, another 26 mg of EDCI and 18 mg of HBA were added, and the reaction was allowed to proceed for another 12 h. The nanotubes were then precipitated into methanol, and the precipitate was redispersed in THF. The THF solution was dialyzed in a dialysis tube (Spectra/Por, molar mass cutoff = 500 000 g/mol) against THF that was changed some 10 times over a week under nitrogen atmosphere to remove the coupling agent that was not chemically attached to the nanotubes. The purified nanotubes were precipitated into methanol, redispersed in DMF, and dialyzed in another tube (Spectra/Por, molar mass cutoff ∼14 000 g/mol) against DMF to remove the residual methanol under nitrogen atmosphere.

**Coupling Nanospheres and Nanotubes.** To connect the PAES−PS−PAES-treated nanotubes with the nanospheres, an example initial amidation mixture consisted of nanotubes (3.0 mg containing 4.5 $\mu$mol of carboxyl groups), the emulsion spheres (3.0 mg containing $7.6 \times 10^{-3}$ $\mu$mol of carboxyl groups), 1.0 mL of DMF/water (v/v = 98/2), triethylamine (4.5 mg, 45 $\mu$mol), EDCI (1.7 mg, 9 $\mu$mol), and HBA (1.2 mg, 9 $\mu$mol). The mixture was stirred for 12 h before another batch of EDCI (1.7 mg, 9 $\mu$mol) and HBA (1.2 mg, 9 $\mu$mol) was added, and the mixture was left stirring for another 12 h. After that, the mixture was diluted with more DMF and centrifuged at 1750 × *g* to settle the spheres and the coupled products. The precipitate was redispersed in DMF/THF (v/v = 80/20) and settled again by centrifugation. After this rinsing step was repeated three to four times, the sample was dispersed in DMF for characterization by transmission electron microscopy (TEM).

The product from coupling the nanotubes with PCEMA−PAA nanospheres was purified by dialysis against THF. This caused most of the nanospheres to precipitate due to their low solubility in THF. The aggregated nanospheres were separated from the supernatant containing the soluble nanotubes and the coupled products by centrifugation.

**Reaction between Rhodamine B and Grafted $NH_2-PS-NH_2$ Chains.** To label with Rhodamine B the free amino groups of the $NH_2-PS-NH_2$ chains that have been grafted to the nanotube ends, the initial amidation mixture consisted of 20 mg of nanotubes, 20 mg or 0.042 mmol of Rhodamine B (Aldrich, dye content ∼90%), 2 mL of DMF, 17.0 mg or 0.089 mmol of EDCI, and 11.5 mg or 0.085 mmol of HBA. The mixture was stirred for 12 h before another batch of EDCI (17.0 mg, 0.089 mmol) and HBA (11.5 mg, 0.085 mmol) was added, and the mixture was left stirring for another 12 h. After reaction, the sample was purified by precipitation into methanol and dialysis of the redispersed sample in THF against replenishing THF/methanol (v/v = 90/10) for 1 week and then THF until no further colored species left the tube. Absorption of Rhodamine B was analyzed at 543 nm.




Rhodamine B

**Reaction between $NH_2-PS-NH_2$ and Rhodamine B.** To react $NH_2-PS-NH_2$ with Rhodamine B, the amount of $NH_2-PS-NH_2$, Rhodamine B, EDCI, and HBA used initially was 40, 40, 32.8, and 22.8 mg, respectively. The amount of DMF used was 5.0 mL. Another

(16) For the CEMA double bond conversion determination, see, for example: Guo, A.; Tao, J.; Liu, G. J. *Macromolecules* **1996**, *29*, 2487.
(17) For length variation with ultrasonication time, see, for example: Liu, G. J.; Yan, X. H.; Duncan, S. *Macromolecules* **2002**, *35*, 9788.
(18) See, for example: (a) Westby, M. J. *Colloid Polym. Sci.* **1988**, *266*, 46. (b) Levesque, G.; Moitie, V.; Bacle, B.; Depraetere, P. *Polymer* **1988**, *29*, 2271.
(19) Li, Z.; Liu, G. J.; Law, S.-J.; Sells, T. *Biomacromolecules* **2002**, *3*, 984.

***Table 1.*** Characteristics of the Polymers

| sample | SEC $M_w/M_n$ | $dn_r/dc$ (mL/g) | LS $M_w \times 10^{-4}$ (g/mol) | NMR repeat unit number ratio | *n* | *m* | *l* |
|---|---|---|---|---|---|---|---|
| PS−PCEMA−P*t*BA | 1.17 | 0.151 | 11.5 | 1.00/0.25/0.28 | 560 | 140 | 160 |
| PCEMA−P*t*BA | 1.18 | 0.121 | 26 | 0.95/1.00 | 660 | 700 | |
| P(AES−TMS)−PS−P(AES−TMS) | 1.17 | 0.184 | 2.0 | 7.2/1.00 | 115 | 16 | |
| $NH_2$−PS−$NH_2$ | 1.26 | 0.195 | 1.42 | | 140 | | |

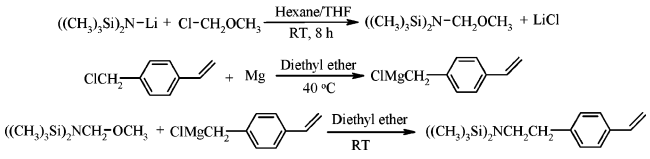
batch of catalysts equal in amounts to the first was added 12 h after the first one, and a total of 24 h was allowed for the reaction. After reaction, the polymer was precipitated into methanol and washed with methanol several times to remove most of the excess Rhodamine B. The precipitate was redispersed in distilled THF and dialyzed against THF/methanol (v/v = 90/10) (Spectra/Pro, molar mass cutoff = 1000 g/mol) for 4 days. It was finally dialyzed against distilled THF, and the resultant solution was used for visible absorption measurement.

**Transmission Electron Microscopy.** All transmission electron microscopy (TEM) studies were performed on a Hitachi H-7000 instrument operated at 75 kV. Specimen of the PCEMA−PAA nanospheres and their coupled products were prepared by aspirating methanol and THF solutions of the two on carbon-coated copper grids using a home-built device.[20] TEM specimens of the emulsion spheres and their coupled products were prepared by aspirating DMF solutions of the samples onto water surface. The films on water surface were then picked up by carbon-coated copper grids. All samples except the emulsion sphere sample were stained with $OsO_4$ vapor for 4 h before being viewed by TEM.

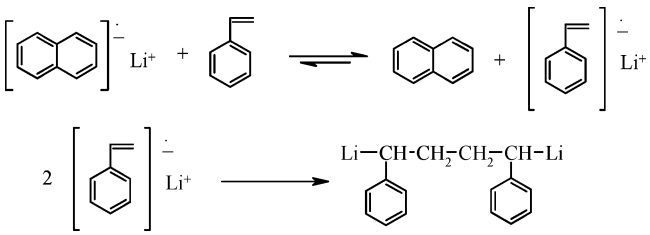
## Results and Discussion

**Polymer Synthesis.** A total of four polymers were prepared for this project. The procedures for PS−PCEMA−P*t*BA[8] and PCEMA−P*t*BA[9] syntheses were not given in the Experimental Section, as they have been reported before. Briefly, PS−PCEMA−P*t*BA was derived from PS−P(HEMA−TMS)−P*t*BA, where HEMA−TMS denotes 2-trimethylsiloxyethyl methacrylate, and PCEMA−P*t*BA was derived from P(HEMA−TMS)−P*t*BA. Both PS−P(HEMA−TMS)−P*t*BA and P(HEMA−TMS)−P*t*BA were prepared by anionic polymerization.

The polymer spacer PAES−PS−PAES was obtained from hydrolyzing P(TMS−AES)−PS−P(TMS−AES). Monomer TMS−AES was prepared following a literature method invoking the following reactions:[12−15]




P(TMS−AES)−PS−P(TMS−AES) was prepared by living anionic polymerization at −78 °C in THF using lithium naphthalenide as the initiator following the procedure of Nakahama and co-workers.[15] The initiation mechanism was:




The polymer grew at both ends of the initiating molecule. Styrene polymerization should essentially complete within minutes, but we allowed 1 h for the process. The resultant polystyrene dianions were then used to initiate TMS−AES polymerization,[14] which was also given 1 h to complete. The polymerization was terminated by the addition of some methanol.

To prepare $NH_2$−PS−$NH_2$, the styrene polymerization was also initiated with lithium naphthalenide.[11] The polymerization was terminated by 2,2,5,5-tetramethyl-1-(3-chloropropyl)-1-aza-2,5-disilacyclopentane, and the amino groups were deprotected by 2,2,5,5-tetramethyl-1-aza-2,5-disilacyclopentane ring opening in methanol.[11] An acid−base titration experiment showed that the end labeling of the PS chains by amino groups was higher than 95%.[11] The preparation procedure for 2,2,5,5-tetramethyl-1-(3-chloropropyl)-1-aza-2,5-disilacyclopentane was not described in any detail in the Experimental Section, because it was well documented in ref 11.

**Polymer Characterization.** All polymers were carefully characterized by LS, $^1$H NMR, and SEC. LS allowed the determination of the weight-average molar masses $M_w$ of the samples. Analysis of the intensity ratios of the $^1$H NMR peaks of the different blocks yielded the relative lengths of the blocks. The weight-average number of repeat units for each block was obtained by combining the LS and NMR results. SEC was used mainly to obtain $M_w/M_n$ as a measure for the width of the molar mass distribution of the samples, where $M_n$ denotes the number-average molar mass of a sample. The polymer characterization results thus obtained are summarized in Table 1. The *n*, *m*, and *l* values denote the numbers of repeat units for the appropriate blocks with their definition given in the formulas for the block copolymers.

**Nanotubes.** The 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. At such ratios, PCEMA and P*t*BA formed shell−core cylinders dispersed in the PS matrix.[21] 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. Following this approach, several batches of nanotubes were prepared. The CEMA conversion of the nanotubes was typically ∼23% unless otherwise specified.

Figure 1a shows a TEM image of a nanotube sample prepared from the hydrolysis of the PS−PCEMA−P*t*BA nanofibers that

(20) Ding, J. F.; Liu, G. J. *Macromolecules* **1999**, *32*, 8413.
(21) Breiner, U.; Krappe, U.; Abetz, V.; Stadler, R. *Macromol. Chem. Phys.* **1997**, *198*, 1051.

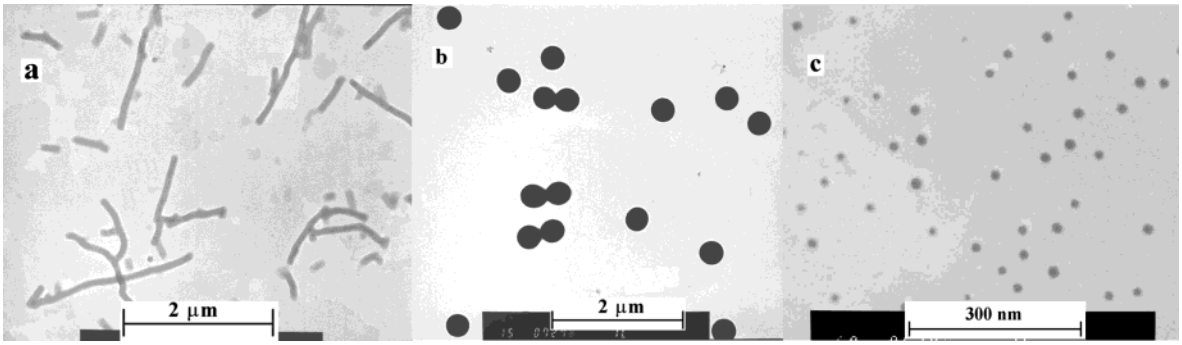



***Figure 1.*** TEM images of (a) the nanotubes, (b) emulsion spheres, and (c) the diblock nanospheres.

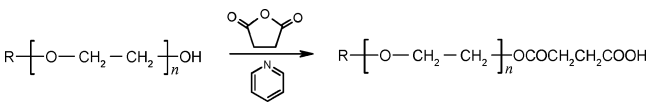
***Table 2.*** Effect of Varying [$NH_2$−PS−$NH_2$] and CEMA Double Bond Conversion on $n_c$

| nanotube sample | $L_n$ (nm) | $10^{-8} \times M_n$ (g/mol) | CEMA conversion | [$NH_2$–PS–$NH_2$] (g/mL) | $n_c$ |
|---|---|---|---|---|---|
| 1 | 410 | 4.0 | 41% | 0.075 | 38 |
| | | | | 0.30 | 74 |
| 2 | 460 | 4.5 | 23% | 0.075 | 92 |
| | | | | 0.30 | 104 |

had been ultrasonicated for 8 h. Better TEM images and spectroscopic evidence for nanotube preparation can be found in a prior publication.[8b] Statistical analysis of the lengths of 188 tubes for the sample shown in Figure 1a yielded the weight- and number-average lengths $L_w$ and $L_n$ of 701 and 515 nm, respectively. Another two batches of samples obtained under similar conditions possessed $L_n$ values of 410 and 460 nm (Table 2), respectively. Before ultrasonication, the $L_n$ value of the nanofibers was ∼5 $\mu$m. Thus, most of the nanotubes used in this study had two exposed ends.

The number-average molar masses $M_n$ of the nanotubes were obtained from multiplying the TEM $L_n$ and the unit length molar mass $M_u$ of $9.7 \times 10^5$ g/(mol·nm) for nanotubes. $M_u$ was estimated following procedures detailed in ref 8a. Column 3 of Table 2 gives the $M_n$ values for two nanotube samples that will be invoked in a later discussion.

**Emulsion Nanospheres.** The emulsion spheres used are of the core−shell type prepared for another project. The core consisted of a copolymer of MMA and *t*BA cross-linked with EGDMA. The shell was made of cross-linked PMMA. PEG−MA was used as the surfactant in shell formation and got anchored chemically on the nanosphere surface. The hydroxyl group at the other end of the immobilized PEG−MA chains was converted to a carboxyl group via the following reaction:[19]




The efficiency of this reaction should be high as succinic anhydride reacted with poly(ethylene glycol) monolaurate under similar conditions quantitatively.

Figure 1b shows a TEM image of the emulsion spheres. The average diameter is 365 ± 6 nm. As described in the Experimental Section, the spheres were prepared by reacting 15.0 g of various monomers with 0.020 g or $3.8 \times 10^{-5}$ mol of PEG−MA. Assuming a density of 1.0 g/mL for the spheres, the quantitative grafting of PEG−MA onto the nanosphere surface, and the quantitative conversion of the hydroxyl groups of PEG−MA to carboxyl groups, we estimated an upper bound of 40 000 carboxyl groups per nanosphere.

**PCEMA−PAA Nanospheres.** This type of sphere was prepared by taking advantage of PCEMA−P*t*BA micelle formation in the block-selective solvent mixture THF/2-propanol. Such micelles possess cores made of the insoluble PCEMA block and coronas of the soluble P*t*BA block. Nanospheres were prepared after PCEMA core cross-linking by photolysis. PAA coronal chains were obtained after P*t*BA hydrolysis. Figure 1c shows a TEM image of the PCEMA−PAA nanospheres stained with $OsO_4$. The core diameter averaged over 78 spheres is 28 ± 4 nm. Using this core diameter and assuming a density of 1.0 g/mL for the core, we estimated an aggregation number of ∼40 for the nanospheres. Because the number of repeat units for PAA is 700, the total number of carboxyl groups per PCEMA−PAA nanosphere is ∼28 000.

**Amidation.** Four kinds of amidation experiments were performed. The first type involved reaction between PAA chains of the nanotubes and the amino groups of the polymer spacers, and the second type was between the amino groups of the spacers that have been grafted to the nanotubes and the surface carboxyl groups of the nanospheres. In the third and fourth types, amid bonds were formed between the carboxyl group of Rhodamine B and the amino groups of either free $NH_2$−PS−$NH_2$ chains or $NH_2$−PS−$NH_2$ chains that have been grafted to the nanotube ends by one end only. While the receipts used differed, the general experimental protocol was the same. It involved first mixing carboxyl- and amino-containing components in a solvent with the catalysts EDCI and HBA each at 2 molar equivalents relative to the carboxyl groups.[22] When PAES−PS−PAES was involved, the solvent used was DMF/water (v/v = 98/2), where water was used to increase PAES solubility. Otherwise, the solvent used was DMF. In the second type of amidation experiment, triethylamine at 10 molar excess relative to the carboxyl groups was also used to ensure that the amino groups to be reacted were in the neutral form. The initial amidation mixture was stirred at room temperature for 12 h before another batch of EDCI and HBA equal in amount to the first batch was added. The mixture was then allowed to react for another 12 h.

**Reaction between the Spacer Chains and Nanotubes.** The first step in the preparation of the nanotube−nanosphere-coupled products involved grafting either $NH_2$−PS−$NH_2$ or PAES−

(22) See, for example: Zeng, H.; Miller, R. S.; Flowers, R. A.; Gong, B. *J. Am. Chem. Soc.* **2000**, *122*, 2635.

PS−PAES chains to the ends of PS−PCEMA−PAA nanotubes. To estimate the number $n_c$ of $NH_2-PS-NH_2$ chains attached to each nanotube end, we made use of the fact that $NH_2-PS-NH_2$ was used in a large excess and assumed that $NH_2-PS-NH_2$ reacted with the nanotubes by only one amino group or one end. Thus, $n_c$ determination was reduced to the measurement of the amino group content. To determine the amino group content, the amino groups were reacted with a large excess of Rhodamine B for their quantitative labeling by Rhodamine B. The validity of the quantitative labeling assumption was deduced from the quantitative reaction of the amino groups in a control experiment involving the free $NH_2-PS-NH_2$ chains and a 10 molar excess of Rhodamine B under identical conditions. After removal of the unreacted Rhodamine B from the nanotubes by prolonged dialysis, the amount of Rhodamine B groups that were chemically attached to the grafted $NH_2-PS-NH_2$ chains was analyzed by visible absorption spectrophotometry. To ensure that the Rhodamine B that was detected by visible absorption spectrophotometry was chemically attached to the amino groups of the grafted $NH_2-PS-NH_2$ chains, we have also performed one more control experiment. This involved stirring Rhodamine B under identical conditions in the presence of EDCI, HBA, and nanotubes that were not end-grafted with $NH_2-PS-NH_2$. After nanotube purification by dialysis, the amount of Rhodamine B that was retained with the nanotubes inside the dialysis tube was negligible in this case.

Table 2 shows the variation in $n_c$ thus determined as a function of $NH_2-PS-NH_2$ concentration and PCEMA shell cross-linking density while holding the other parameters of the amidation protocol constant as described in the Experimental Section. The data suggest that $n_c$ increased with increasing $NH_2-PS-NH_2$ concentration and decreasing nanotube cross-linking density. A lower PCEMA cross-linking density leads to a larger $n_c$ because the PAA core swells more under this condition and a larger core cross-section facilitates the grafting of more $NH_2-PS-NH_2$ chains. Increasing bulk concentration of $NH_2-PS-NH_2$ helps to reduce the spacer chain concentration gradient between the grafted $NH_2-PS-NH_2$ layer and the bulk and thus favors a higher grafting density. Under the typical conditions of $[NH_2-PS-NH_2] = 0.30$ g/mL and a CEMA conversion of ~23%, $n_c$ is ~100. We expect the $n_c$ values for PAES−PS−PAES to be similar, because the $n_c$ value is limited mainly by the number of chains that can be squeezed into the grafted layer and not by the reactivity between the amino and carboxyl groups. The fact that the grafted layer is crowded and has a "brush" conformation can be easily appreciated by performing calculations following procedures detailed before.[23]

**Performance of Different Polymer Spacers.** $NH_2-PS-NH_2$ was the first polymer spacer that we prepared and used. This polymer was ineffective in coupling the nanotubes to the emulsion spheres. When this polymer was used to couple the nanotubes to the PCEMA−PAA spheres, the fraction of nanotube ends that were labeled by nanospheres as seen by TEM was ~30%. The coupling efficiency improved in the latter case probably due to the much higher local concentration of carboxyl groups in the PAA coronas than in the emulsion sphere coronas.

The second polymer spacer PAES−PS−PAES was designed and prepared to increase the amino group concentrations at the ends of the spacer-grafted nanotubes. The PS backbone design was retained to increase its compatibility with the PS nanotube coronal chains and to prevent the penetration of the coupling agent into the PAA-lined channels. Using this agent, we determined that the efficiency of coupling between the nanotubes and the PCEMA−PAA nanospheres increased only slightly to ~40%. The increase in the efficiency of coupling between the nanotubes and the emulsion spheres was, however, much more dramatic as demonstrated by the abundance of the coupled products. We could not estimate the coupling efficiency in this case, as nanotubes that did not couple with the nanospheres did not settle with the emulsion spheres during the centrifugation purification step.

**Coupled Products.** Figure 2a−c shows the typical products from coupling the PAES−PS−PAES-treated nanotubes with the emulsion nanospheres. The product in Figure 2a resulted from the coupling between one tube and one sphere. Because the spherical "head" is water-dispersible and the tube "tail" is hydrophobic, this structure may be viewed as a macroscopic counterpart of a surfactant molecule or a "supersurfactant". There is a light aura around each sphere in this image and also in images 2b and 2c probably due to the fact that the spheres extended out of the plane of focus.

Figure 2b shows the attachment of two tubes to one sphere, which has fused with another sphere probably during TEM specimen preparation. The attachment of one tube to two spheres at the opposite ends is seen in Figure 2c. The products depicted in Figure 2a−c coexisted regardless of how we changed the tube to microsphere mass ratio from 20/1 to 1/20. At the high tube to emulsion sphere mass ratio of 20/1, the supersurfactant and dumbbell-shaped species were the major products. At the mass ratio of 1/1 and 1/20, the dumbbell-shaped product dominated. Other than product control by adjusting the stoichiometry, an effective method to eliminate the dumbbell-shaped product was to use nanotubes labeled with spacer chains at only one end. These tubes were obtained by breaking up nanotubes that contained end-grafted polymer spacer chains by ultrasonication. For example, the ultrasonication of the PAES−PS−PAES-grafted nanotubes for 8 h reduced $L_w$ of a nanotube sample from 701 to 252 nm and $L_n$ from 515 to 187 nm. The reaction between the shortened tubes and the nanospheres at the tube to sphere mass ratio of 1/20 yielded almost exclusively the supersurfactant structure with unreacted nanospheres. The content of the multiarmed structure increased as the mass ratio increased.

An effective method to eliminate the multiarmed structure is to use smaller spheres. Figure 2d shows a TEM image of products formed from coupling the nanotubes to the much smaller PCEMA−PAA spheres. Multitube attachment to the same sphere was not seen after the examination of many TEM images. It appears that the smaller surface area of these spheres impeded multitube attachment.

**Potential Applications.** The supersurfactants shown in Figure 2a may self-assemble like surfactant molecules to form micelles and help order molecules on the micrometer size scale. Alternatively, a supersurfactant with a sufficiently long fluorescent tail may be studied by the optical tweezers method to

(23) See, for example: (a) Ding, J. F.; Tao, J.; Guo, A.; Stewart, S.; Hu, N.; Birss, V. I.; Liu, G. J. *Macromolecules* **1996**, *29*, 5398. (b) Tao, J.; Guo, A.; Liu, G. J. *Macromolecules* **1996**, *29*, 1618.

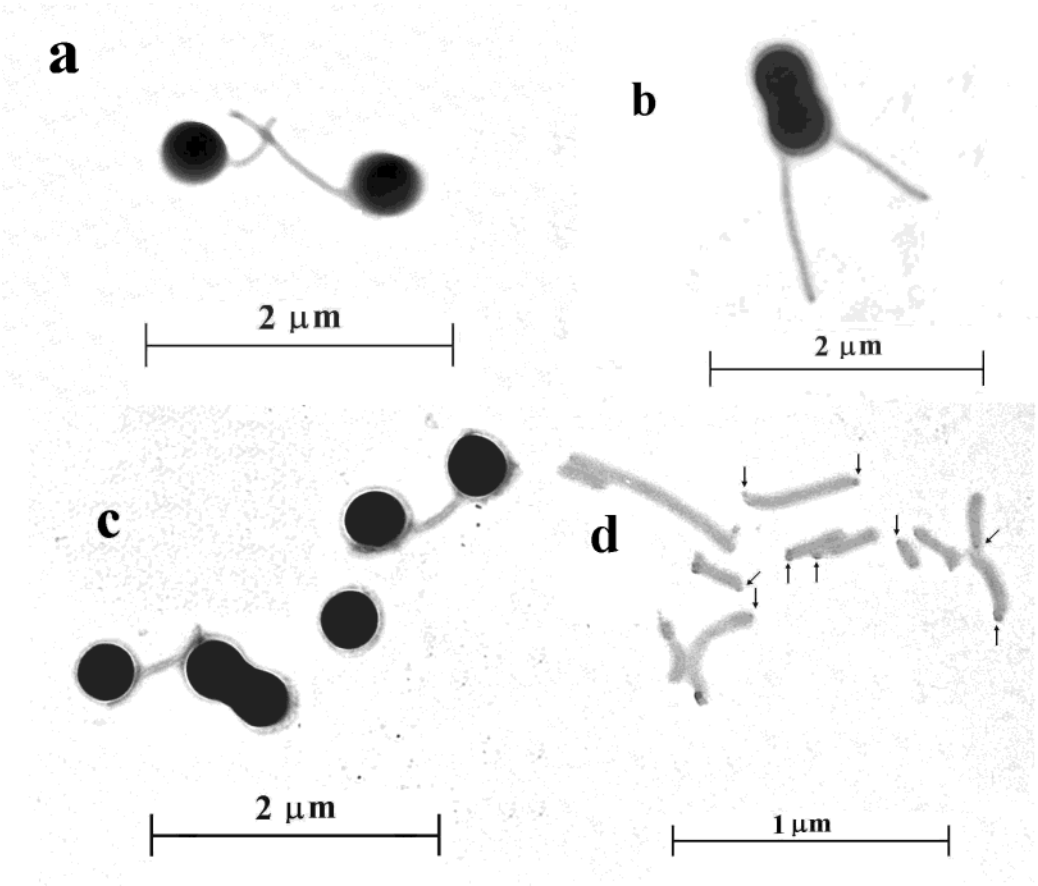



***Figure 2.*** TEM images of nanotube and nanosphere coupling products. The arrows indicate nanosphere attachment.

interrogate the dynamics of the nanotubes.[24] Such studies will help verify if the dynamic theories developed for polymer chains would still apply to large objects such as nanotubes.

The structure of Figure 2b will be of particular interest if the nanotubes are replaced with $Fe_2O_3$-impregnated PS−PCEMA−PAA nanotubes or PS−PCEMA−PAA/$Fe_2O_3$ hybrid nanofibers. The hybrid nanofibers are superparamagnetic as demonstrated previously.[8b] They attracted one another in a magnetic field due to magnetization and demagnetized once the field was off. After their attachment to a sphere to form the structure in Figure 2b, the closing motion of the fibers or "fingers" in a magnetic field may serve as the basis for a magnetic nanohand.

## Conclusion

Four polymers PS−PCEMA−P*t*BA, PAES−PS−PAES, $NH_2$−PS−$NH_2$, and PCEMA−P*t*BA were prepared and characterized. The P*t*BA and PCEMA blocks of PS−PCEMA−P*t*BA formed concentric core−shell cylinders dispersed in the continuous PS matrix in films of the triblock containing PS homopolymer. Photo-cross-linking the PCEMA shell cylinders and separating the cross-linked cylinders by solubilizing the PS matrix chains in THF yielded PS−PCEMA−P*t*BA nanofibers with an average length of ∼5 $\mu$m. The fibers were shortened by ultrasonication to expose the P*t*BA core chains at the fiber ends. PS−PCEMA−PAA nanotubes were obtained after hydrolyzing the *tert*-butyl groups from the P*t*BA cores. Reacting the end-exposed PAA chains with excess PAES−PS−PAES or $NH_2$−PS−$NH_2$ yielded nanotubes containing amino end groups. The number of coupling chains that were attached to each nanotube end under our typical reaction conditions was ∼100. The amino groups were then reacted with nanospheres bearing surface carboxyl groups prepared from PCEMA−PAA or emulsion polymerization to couple the nanotubes to nanospheres. The products from such coupling reaction ranged from multiarm adduct to surfactant- and dumbbell-like objects and may have interesting properties and applications. The coupling products can be controlled either by changing the nanotube to nanosphere mass ratio or by changing the size of the nanospheres. The use of nanotubes labeled with the coupling agent at only one end helped to eliminate the dumbbell-shaped product.

**Acknowledgment.** NSERC of Canada and Defence Research Development Canada are cordially acknowledged for sponsoring this research.

JA034847H

(24) See, for example: Perkins, T. T.; Quake, S. R.; Smith, D. E.; Chu, S. *Science* **1994**, *264*, 822.