A sample (0.104 g) of the binary alloy "KGe_4", prepared by high-temperature reactions of pure elements (Aldrich) within sealed Nb tubing, was dissolved in neat en (5 mL), forming a dark green solution. A separate solution of [18]crown-6 (0.048 g, 0.182 mmol) in neat toluene (4 mL) was slowly added and layered on the alloy solution. Formation of transparent light blue-green rodlike crystals was observed after two weeks. The moisture-sensitive crystals were preserved in mother liquor and were found to be of compound **1** (yield 30–40 %).

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[1] a) L. E. Brus, P. F. Szajowski, W. L. Wilson, T. D. Harris, S. Schuppler, P. H. Citrin, *J. Am. Chem. Soc.* **1995**, *117*, 2915; b) K. M. Ho, A. A. Shvartsbyrg, B. Pan, Z.-Y. Lu, C.-Z. Wang, J. G. Wacker, J. L. Fye, M. F. Jarrold, *Nature* **1998**, *392*, 582.

[2] a) M. J. Wagner, J. L. Dye in *Comprehensive Supramolecular Chemistry, Vol. 1* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, J.-M. Lehn), Pergamon, Oxford, **1996**; b) G. Schmid, *Cluster and Colloids*, VCH, Weinheim, **1994**.

[3] a) M. L. Steigerwald in *Inorganometallic Chemistry* (Ed.: T. P. Fehlner), Plenum, New York, **1992**, pp. 333–358; b) M. O. Watanabe, T. Miyazawa, T. Kanayama, *Phys. Rev. Lett.* **1998**, *81*, 5362.

[4] a) J. D. Corbett, *Struct. Bonding (Berlin)* **1997**, *87*, 157; b) H.-G. von Schnering, *Angew. Chem.* **1981**, *93*, 44; *Angew. Chem. Int. Ed. Engl.* **1981**, *20*, 33.

[5] a) R. A. Bley, S. M. Kauzlarich, *J. Am. Chem. Soc.* **1996**, *118*, 12461; b) L. Brus, *J. Phys. Chem.* **1994**, *98*, 3575.

[6] C. H. E. Belin, J. D. Corbett, A. Cisar, *J. Am. Chem. Soc.* **1977**, *99*, 7163.

[7] a) C. Belin, H. Mercier, V. Angilella, *New J. Chem.* **1991**, *15*, 931; b) T. F. Fässler, M. Hunziker, *Inorg. Chem.* **1994**, *33*, 5380.

[8] J. Campbell, G. J. Schröbilgen, *Inorg. Chem.* **1997**, *36*, 4078.

[9] L. Xu, S. C. Sevov, *J. Am. Chem. Soc.* **1999**, *121*, 9245.

[10] P. Kirchner, G. Huttner, K. Heinze, G. Renner, *Angew. Chem.* **1998**, *110*, 1754; *Angew. Chem. Int. Ed.* **1998**, *37*, 1664.

[11] a) V. Queneau, S. C. Sevov, *Angew. Chem.* **1997**, *109*, 1818; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1754; b) H. G. von Schnering, M. Baitinger, U. Bolle, W. Carrillo-Cabrera, J. Curda, Y. Grin, F. Heinemann, J. Llanos, K. Peters, A. Schmeding, M. Somer, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1037; c) M. Somer, W. Carillo-Cabrera, E. M. Peters, K. Peters, H. G. von Schnering, *Z. Anorg. Allg. Chem.* **1998**, *624*, 1915.

[12] T. F. Fässler, U. Schutz, *Inorg. Chem.* **1999**, *38*, 1866.

[13] T. F. Fässler, R. Hoffmann, *Angew. Chem.* **1999**, *111*, 526; *Angew. Chem. Int. Ed.* **1999**, *38*, 543.

[14] Crystal structure data for **1**: $M_r = 1320.24$, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 11.2796(7)$, $b = 14.7049(9)$, $c = 27.8321(17)$ Å, $V = 4616.4(5)$ Å^3, $Z = 4$, $\rho = 1.900\ \text{g cm}^{-3}$, $\mu = 6.003\ \text{mm}^{-1}$, $\lambda = 0.71073$ Å ($Mo_{K\alpha}$), $2\theta_{max} = 46.5°$; of 20849 total reflections, 6629 were independent and 6605 were observed ($> 3\sigma_I$); 455 total variables; final R indices $R1 = 0.0328$, $wR2 = 0.0772$ ($I > 4\sigma(I)$) and $R1 = 0.0488$, $wR2 = 0.0978$ (all data). The analysis, using a Siemens SMART diffractometer equipped with a CCD area detector, was carried out at −50 °C. Empirical absorption correction was applied on a hemisphere of data, and redundant reflections were averaged. The structure was solved by direct methods and refined by full-matrix least-squares calculations. One of the two crown ether molecules is disordered over two different positions (50:50). The potassium atom K2 attached to it binds to an en solvent molecule, which is also disordered. Owing to disorder, the exact amount of en cannot be determined. One en molecule per K2 atom was assumed for all the calculations. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-133996. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[15] a) W. B. Pearson, *The Crystal Chemistry and Physics of Metals and Alloys*, Wiley, New York, **1972**; b) K. Wade, *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

[16] Z. Tang, C. Downie, A. M. Guloy, unpublished results.

[17] a) J. R. Heath, *Science* **1992**, *258*, 1131; b) L. Brus, *Adv. Mater.* **1993**, *5*, 286.

[18] a) L. Lohr, *Inorg. Chem.* **1981**, *20*, 4229; b) J. Campbell, D. A. Dixon, H. P. A. Mercier, G. J. Schröbilgen, *Inorg. Chem.* **1995**, *34*, 5798.

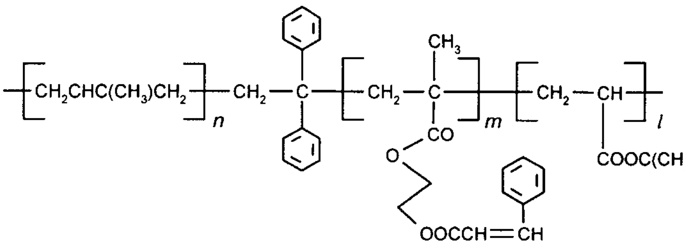
[19] a) C. Belin, M. Tillard-Charbonnel, *Prog. Solid State Chem.* **1993**, *22*, 59; b) J. K. Burdett, E. Canadell, *J. Am. Chem. Soc.* **1990**, *112*, 7207; c) Z. Xu, A. M. Guloy *J. Am. Chem. Soc.* **1998**, *120*, 7349.

[20] a) T. Ogawa, T. Takagahara, *Phys. Rev. B* **1991**, *43*, 14325; b) F. Rossi, E. Molinari, *Phys. Rev. Lett.* **1996**, *76*, 3642.

Block Copolymer Nanotubes[**]

Sean Stewart and Guojun Liu[*]

The preparation of nanometer-sized structures with well-defined shape and narrow size distribution, "nanostructures", has attracted much attention mainly to meet the demand for smaller electronic devices.[1] Nanostructures are also useful in the preparation of strong nanocomposite materials or sensors that may imitate enzymes in molecular recognition. Nanostructures of block copolymers[2] are interesting because they span the size range from 5 to 500 nm and fill the gap between nanostructure sizes obtainable from traditional lithographic techniques and those from small-molecule self-assembly processes. In this communication we report the preparation of solvent-dispersible nanotubes from a triblock copolymer, polyisoprene-*block*-poly(2-cinnamoylethyl methacrylate)-*block*-poly(*tert*-butyl acrylate), PI-*b*-PCEMA-*b*-P*t*BA (**1**), with 130 isoprene, 130 CEMA, and 800 *t*BA units.



1, PI-*b*-PCEMA-*b*-P*t*BA

Although there have been many reports in the past decade on the preparation and study of nanotubes, our nanotubes are unique in composition and properties. Excluding those dealing with nanochannels formed in inorganic oxides,[3–6] glass,[7] metals,[8] or polymer matrices,[9, 10] the majority of publications in the past eight years have been on carbon[11–14] or metal

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oxide nanotubes.[15, 16] Nanotubes have been reported to derive from lipids,[17] amino acids,[18, 19] tubulin templates,[20] organic precursors,[21, 22] or polymers.[23, 24] For polymeric nanotube preparation, alumina membranes with cylindrical pores were used as the template.[23] The resultant tubes are generally made of conductive polymers and are not dispersible in any solvents. More recently Eisenberg and coworkers[24] reported tubule formation due to the self-assembly of polystyrene-*block*-poly(ethylene oxide) in water. The tubules were not crosslinked and are different from our nanotubes not only in preparation methodology but also in their structural stability in different solvents.

The approach utilized here, illustrated in Figure 1, is similar to that used extensively in our research group for the preparation of nanochannels in thin films,[9, 25] nanofibers,[26, 27] and hollow[28, 29] or shaved[30] nanospheres. This approach has also been utilized by Lee et al.[10] for the preparation of porous films and Huang et al.[31] for the preparation of hollow nanospheres from diblocks. The approach involves molecular design, block copolymer synthesis, self-assembly of block copolymers, the interlocking of the self-assembled nanostructure by crosslinking the shell, and the selective domain degradation, "nanosculpturing", of the crosslinked nanostructure. The triblock self-assembly occurred in methanol to form cylindrical micelles with a PI core, a PCEMA shell, and a P*t*BA corona. Cylindrical structure interlocking was achieved by photocrosslinking the PCEMA shell. Nanotubes of PCEMA-*block*-P*t*BA (**2**) were obtained by degrading the PI core of crosslinked micelles of **1**.

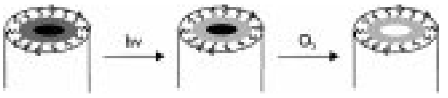


Figure 1. Schematic presentation of the process involved in the preparation of nanotubes. The PCEMA shell is photocrosslinked (dark gray to light gray), then ozonolysis decomposes the PI core (black to white). The P*t*BA corona chains (wavy lines) render solvent dispersibility to the nanotubes.

The precursor to the triblock was synthesized by anionic polymerization with the detailed procedure described elsewhere.[32–35] The triblock **1** was characterized by light scattering (LS), ^1H NMR, and gel-permeation chromatography (GPC) (Table 1). LS was used to determine the molar mass of the PI block. NMR analysis of the triblock yielded monomer ratios $n/m/l = 1.00/0.97/6.0$. GPC analysis suggests narrow molar mass distributions for both the PI block and **1** as a whole.

Formation of cylindrical micelles from **1** in methanol was confirmed by transmission electron microscopy (TEM) results shown in Figure 2a. The cylinders have a diameter of about 22 nm with a dark-gray core-shell structure. Since P*t*BA is soluble in methanol and is not stained by OsO_4, the P*t*BA has formed an "invisible" corona. The core and shell of micelles of **1** (Figure 2a) should consist of PI and PCEMA. PI should look darker, as demonstrated by Ding and Liu,[36] under these conditions because each gram of PI contains approximately four times more stain-susceptible double bonds than PCEMA. The cylinders reach micrometer lengths but with a broad length distribution.

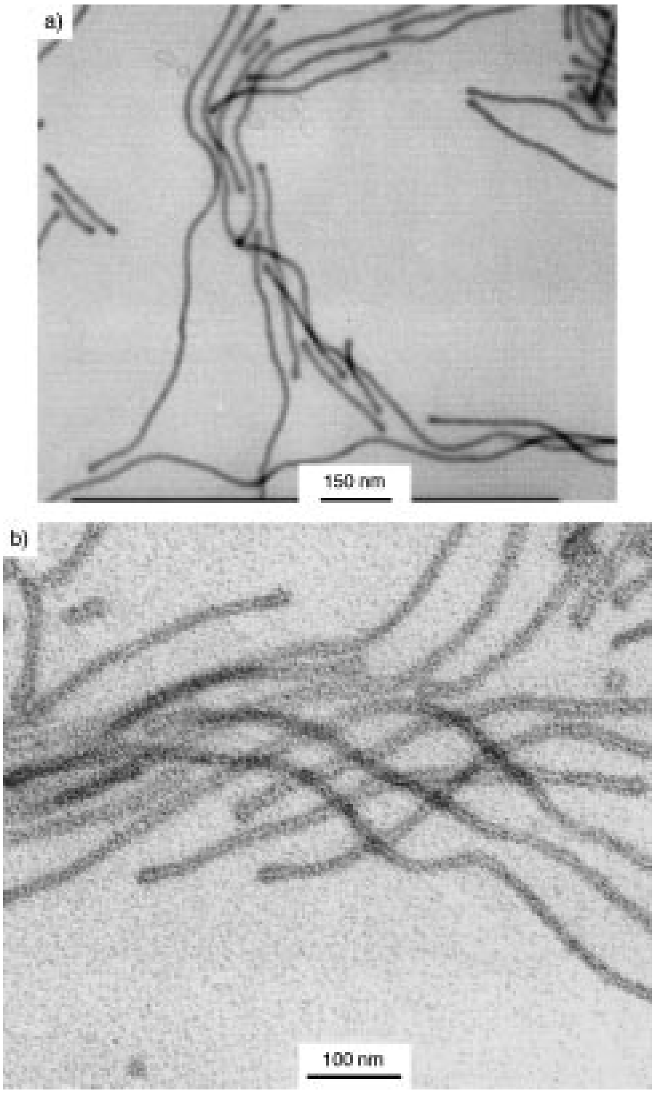


Figure 2. TEM images of a) cylindrical micelles of **1** and b) nanotubes **2**. The micelles were stained with OsO_4, the nanotubes with RuO_4.

Although there have been many studies of ABC triblock copolymer morphology in the solid state,[37] the study of their morphologies in block-selective solvents has been rare.[29, 38–40] This may represent the second report of cylindrical micelle

Table 1. Characteristics of the polymers.

			PI block				Triblock	
Sample	d*n*/d*c* [mL g^{-1}]	$\overline{M}_w$ (LS) [g mol^{-1}]	$\overline{M}_w/\overline{M}_n$ (GPC)	1,4-PI [%]	*n*	*m*	*l*	$\overline{M}_w/\overline{M}_n$ (GPC)
1	0.104	9.0×10^3	1.05	92	130	130	800	1.08
1′	0.104	20×10^3	1.06	93	290	220	770	1.30

formation of a triblock copolymer in a block-selective solvent following Yu and Eisenberg.[38]

The crosslinking of the cylindrical micelles of **1** to produce **2** was achieved by irradiating the sample with UV light (500 W Hg lamp) that had passed through a 260 nm cut-off filter. The filter was used to minimize light absorption by PI and its consequent crosslinking. The loss of CEMA double bonds was followed by absorbance decrease from either IR (1631 cm^{-1}) or UV (274 nm) where the converted CEMA groups absorb negligibly. PCEMA crosslinked due to the dimerization of CEMA groups from different chains in the shell.[41, 42] A typical CEMA conversion of 40 to 50 % was used for locking the cylindrical micelle structure. PCEMA crosslinking did not perturb the structure of the cylindrical micelles as judged from TEM images. The crosslinking, however, made the structure immutable as demonstrated by the stability not only in methanol but also in THF, $CHCl_3$, and CH_2Cl_2 which dissolves PI, P*t*BA, and uncrosslinked PCEMA.

Due to the structural stability of the crosslinked micelles and the fact that PCEMA crosslinking stabilized but did not change the micelle morphology, it was more convenient to use the crosslinked micelles or nanofibers for demonstrating their core–shell corona structure. This was done using ^{1}H NMR spectroscopy and TEM. When a nanofiber sample of **1** was analyzed by NMR in $CDCl_3$, no signals were observed from the PCEMA block and the intensity of the PI peaks was substantially reduced relative to that of the P*t*BA signals. The absence of PCEMA signals suggests PCEMA crosslinking and lowered mobility of PCEMA chain segments. The enhanced signals of P*t*BA relative to PI suggest that the P*t*BA chains exist in a relatively unhindered environment, such as in the corona. Signals were seen from PI because PI is a rubbery polymer at room temperature and segmental motion was possible in the PI phase of the nanofibers.

For the TEM study, another triblock **1′** (Table 1) was used because this sample had an overall higher molar mass, and formed much larger straight or branched cylindrical micelles (Figures 3 a and 3 b), thus facilitating the differentiation of the various sub-domains. Unfortunately, this sample had a greater polydispersity arising presumably from nonuniform chain growth due to the high viscosity of the mixture at the later stage of the polymerization. Also, **1′** formed mainly branched rather than straight cylindrical micelles due to the different relative block lengths. Despite these differences, the straight or branched cylindrical micelles formed from this triblock should have the same core–shell–corona structure as **1** due to their similar preparation.

Like the cylindrical micelles of **1**, the branched cylindrical micelles of **1′** have distinctively a dark PI core and gray PCEMA shell in the TEM images independent of the staining by OsO_4 (Figure 3 a) or RuO_4 (Figure 3 b). The presence of an unstained P*t*BA layer was confirmed by the following experiment. After spraying from CH_2Cl_2 and staining with OsO_4, the crosslinked branched or straight cylindrical micelles of **1′** had a diameter of approximately 65 nm. This value increased to about 79 nm when the sample was sprayed from a trimethylsilyl idodide solution in CH_2Cl_2. The diameter of the crosslinked micelles increased, because trimethylsilyl idodide stained the P*t*BA corona through reaction (1).

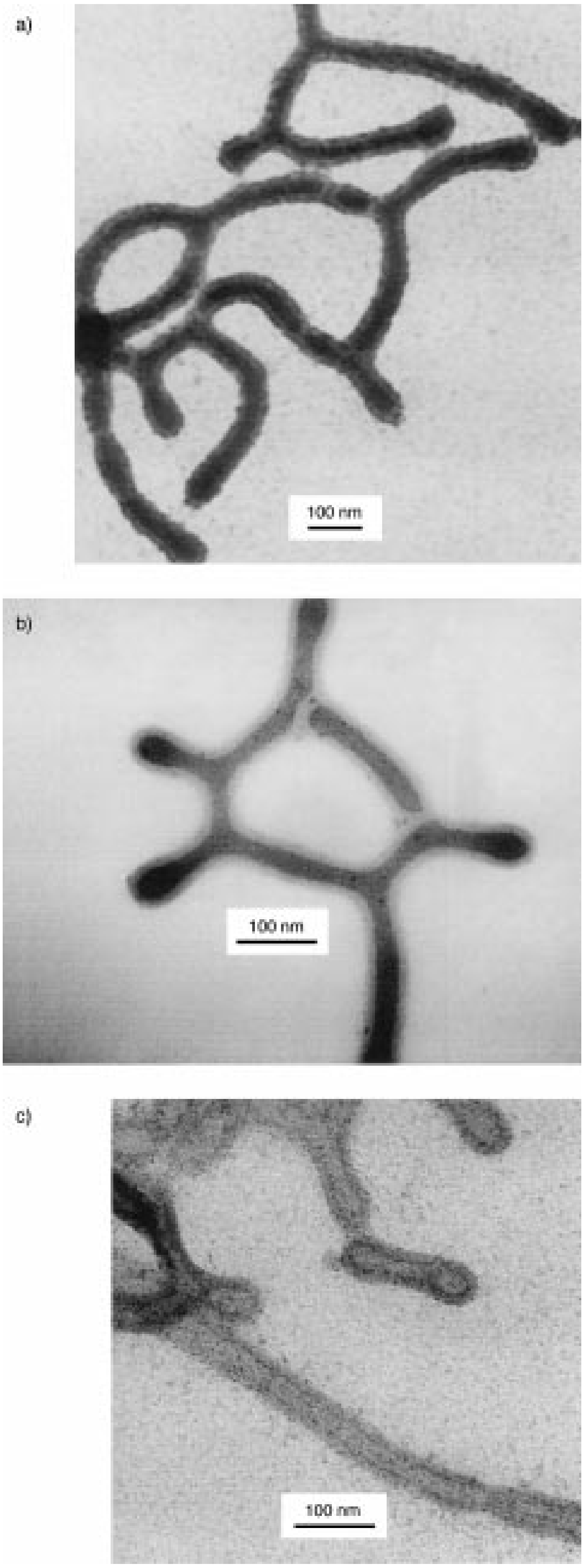
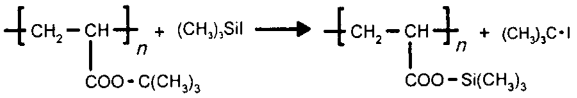


Figure 3. TEM images of straight or branched cylindrical micelles of **1′** stained with a) OsO_4 and b) RuO_4. Shown in c) is the TEM image of nanotubes **2′** stained with RuO_4.



$$\left[\mathrm{CH_2}-\underset{\mathrm{COO-C(CH_3)_3}}{\mathrm{CH}}\right]_n + \mathrm{(CH_3)_3SiI} \longrightarrow \left[\mathrm{CH_2}-\underset{\mathrm{COO-Si(CH_3)_3}}{\mathrm{CH}}\right]_n + \mathrm{(CH_3)_3C{\cdot}I} \qquad (1)$$

The PI block of nanofibers (**1** or **1′**) was decomposed by ozonolysis to form nanotubes (**2** or **2′**, respectively). The complete decomposition of the PI block is demonstrated by the almost quantitative disappearance of the characteristic IR absorption for double bonds at 1631 cm^{-1} (Figure 4). Shown in Figures 2b and 3c are TEM images of such straight **2** or branched **2′** nanofibers stained with RuO_4. Comparing Figures 3b and 3c, a light stripe in the center of each cylinder in Figure 3c unambiguously suggests the formation of nanotubes. A similar light stripe can be seen in each cylinder in Figure 2b but it is not as clear due to its small size.

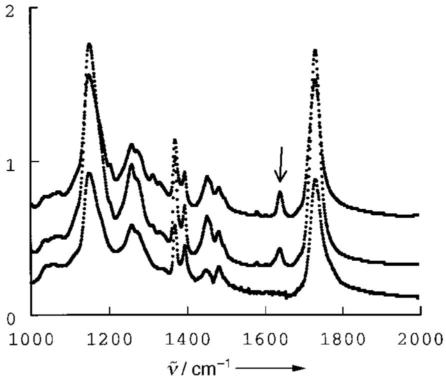


Figure 4. Comparison between the FTIR spectra of micelles of **1** (top), crosslinked micelles of **1** (middle), and nanotubes **2** (bottom).

The formation of nanotubes from **1** was also confirmed from a rhodamine B (RB) loading experiment. RB loading was achieved by refluxing either nanofibers of **1** or nanotubes **2** with a RB solution in methanol (ca. 10%) for 24 h and then evaporating off the methanol. RB impregnated the tubes and fibers presumably to eliminate a concentration gradient between the bulk phase and the fiber or tube phase. The distinct IR absorption peaks at 1590 and 845 cm^{-1} for RB and *tert*-butyl groups of the nanotubes and nanofibers, respectively, were used to estimate RB loading density. Under the same conditions, each gram of nanotube or nanofiber was impregnated with 0.065 and 0.021 g of RB, respectively. The much higher RB loading for the nanotubes suggests the presence of a hollow space left behind by PI degradation. Since the mass ratio of PI to PCEMA and P*t*BA in the triblock **1** is 0.066, the excess loading density of 0.044 $g\,g^{-1}$ for the nanotube **2** relative to that of the nanofiber of **1** suggests the high utilization of the hollow space in **2**. This high space utilization is possible because of methanol evaporation. As methanol evaporates, the RB concentration increases until it reaches the saturation limit. After that, RB crystallizes inside and outside of the tube. The crystallization of RB inside the tube will decrease the local RB concentration and lead to the diffusion of more RB into the tube. This process continues until all the methanol evaporates.

The loading of RB into the nanotube hollow space is evident from the TEM image shown in Figure 5. A sample from the reflux of **2** with RB in methanol was aspirated onto a carbon-coated copper grid. The grid was equilibrated with a drop of water for 20 s to dissolve most of the free RB on the grid or adsorbed on the nanotube outer surfaces, and this excess water was removed by adsorption onto filter paper. The RB-loaded **2** was stained with RuO_4, and the TEM image of the cylinders do not show the light stripes in agreement with RB filling of the nanotubes.

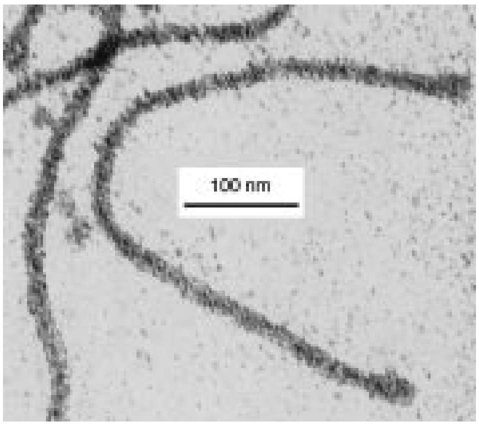


Figure 5. TEM image of nanotubes **2** loaded with rhodamine B, and stained with RuO_4.

In summary, we have demonstrated cylindrical micelle formation in methanol from sample **1**. The cylindrical micelles consisted of a P*t*BA corona, PCEMA shell, and PI core. Nanotubes **2** were obtained after PCEMA crosslinking and PI core degradation. The potential of using molecules **2** as microvials has been demonstrated by RB loading. Other potential applications of **2** include the use as templates for metal or semi-conductor nanowire production. Such insulated nanowires should be of use in nanometer-sized electronic devices. Nanotube **2** can also be pyrolyzed to yield carbon or metal-carbide nanotubes, which could be useful in nanocomposite preparation.[1]

Experimental Section

The polymerization of isoprene was performed in dry hexane (1 d). A slight excess of diphenyl ethylene over *sec*-butyl lithium was added to convert the polyisoprene anion to the terminal diphenyl ethylene anion and an aliquot of the PI block was taken for molar mass determination. After the introduction of THF by cryodistillation, the second monomer 2-trimethylsiloxyethyl methacrylate (HEMA-TMS) was polymerized at $-78\,^\circ C$ for 2 h, then the third monomer *t*BA for 4 h. Polymerization was terminated by the addition of methanol. The methanol also hydrolysed the trimethylsilyl group from HEMA-TMS to yield poly(2-hydroxylethyl methacrylate), PHEMA. PI-*b*-PHEMA-*b*-P*t*BA was purified by precipitation from methanol/water ($\approx 7/3$) at ca. $-10\,^\circ C$. **1** was obtained by reacting PI-*b*-PHEMA-*b*-P*t*BA with excess cinnamoyl chloride in pyridine overnight at room temperature. Polymer **1** was purified by repeated precipitation from methanol/water (see above). Residual PI homopolymer in the triblock was removed through three extractions with hexanes (room temperature, 1 d). The extracted sample was dissolved in THF and added into a large excess of methanol; once the THF evaporated, the micellar sample was finally added into ice to induce precipitation.

The specific refractive index increment d*n*/d*c* of the PI block in cyclohexane at 488 nm was determined to be 0.104 $g\,mL^{-1}$. The molar masses of the PI blocks were determined from a Brookhaven Model 9025 light-scattering instrument. The GPC analysis was performed using a Waters HT-4 ultra-styragel column and polystyrene as calibrant.

To prepare cylindrical micelles, triblock copolymer (100 mg) was dissolved in THF (≈ 2 mL), the THF was evaporated and the sample dried at 85°C for 2 h. Methanol (50 mL) was added to redisperse the polymer.

To prepare nanotubes, ozone generated (Welsback generator) was bubbled into a nanofiber solution in CH_2Cl_2 at −78°C for 10 min. Excess ozone was purged with nitrogen. An excess of trimethylphosphite was added and the mixture was stirred for 3 h at −78°C to reduce the ozonides formed to low molar mass aldehyde or ketone groups.[43]

TEM images were obtained using a Hitachi-7000 instrument operated at 100 kV. TEM specimens were prepared by aspirating a liquid sample onto a carbon-coated Cu grid and staining with OsO_4 or RuO_4. For staining P*t*BA with $(CH_3)_3SiI$, nanofibers of **1′** were mixed with a 0.14 M $(CH_3)_3SiI$ solution in CH_2Cl_2 for 1 h, followed by aspirating onto a carbon-coated copper grid. Excess $(CH_3)_3SiI$ was removed with a drop of dry CH_2Cl_2 and adsorption onto tissue.

For RB impregnation, nanotubes or nanofibers (40 mg) were mixed with RB (470 mg) and methanol (6 mL). The mixture was refluxed for 24 h. Then the methanol was evaporated. The remaining solid was suspended in water, filtered, and washed repeatedly with hot water before drying. The dried RB-loaded nanotube or nanofiber aggregates were ground with KBr for FTIR measurements.

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[1] G. M. Chow, K. E. Gonsalves, *Nanotechnology—Molecularly Designed Materials* (*ACS Symp. Ser.* **1996**, *622*).
[2] G. Liu, *Curr. Opin. Colloid Interface Sci.* **1998**, *3*, 200.
[3] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710.
[4] For a review, see J. Y. Ying, C. P. Mehnert, M. S. Wong, *Angew. Chem.* **1999**, *111*, 58; *Angew. Chem. Int. Ed.* **1999**, *38*, 56.
[5] C. R. Martin, *Science* **1994**, *266*, 1961.
[6] P. Hoyer, *Langmuir* **1996**, *12*, 1411.
[7] D. H. Pearson, R. J. Tonucci, *Science* **1995**, *270*, 68.
[8] H. Masuda, K. Fukuda, *Science* **1995**, *268*, 1466.
[9] G. Liu, J. Ding, *Adv. Mater.* **1998**, *10*, 69.
[10] J.-S. Lee, A. Hirao, S. Nakahama, *Macromolecules* **1989**, *22*, 2602.
[11] S. Iijima, *Nature* **1991**, *354*, 56.
[12] S. Iijima, T. Ichihashi, *Nature* **1993**, *363*, 603.
[13] A. Thess, R. Lee, P. Nikolaev, H. Dai, P. Petit, J. Robert, C. Xu, Y. H. Lee, S. G. Kim, A. G. Rinzler, D. T. Colbert, G. E. Scuseria, D. Tomanek, J. E. Fischer, R. E. Smalley, *Science* **1996**, *273*, 483.
[14] For a review, see S. Subramoney, *Adv. Mater.* **1998**, *10*, 1157.
[15] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, *Langmuir* **1998**, *14*, 3160.
[16] B. C. Satishkumar, A. Govindaraj, E. M. Voli, L. Basumallic, C. N. R. Rao, *J. Mater. Res.* **1997**, *12*, 604.
[17] J. M. Schnur, *Science* **1993**, *262*, 1669.
[18] N. Khazanovich, J. R. Granja, D. E. McRee, R. A. Milligan, M. R. Ghadiri, *J. Am. Chem. Soc.* **1994**, *116*, 6011.
[19] J.-H. Fuhrhop, D. Spiroski, C. Boettcher, *J. Am. Chem. Soc.* **1995**, *115*, 1600.
[20] M. Mertig, R. Kirsch, W. Pompe, *Appl. Phys. A* **1998**, *66*, 723.
[21] A. Harada, J. Liu, M. Kamachi, *Nature* **1993**, *364*, 516.
[22] M. F. M. Roks, R. J. M. Nolte, *Macromolecules* **1992**, *25*, 5398.
[23] J. P. Spatz, B. Lorenz, K. Weishaupt, H. D. Hochheimer, V. P. Menon, R. V. Parthasarathy, C. R. Martin, J. Bechtold, P.-H. Hor, *Phys. Rev. Lett.* **1994**, *50*, 14888.
[24] K. Yu, A. Eisenberg, *Macromolecules* **1998**, *31*, 3509.
[25] G. Liu, J. Ding, A. Guo, M. Herfort, D. Bazett-Jones, *Macromolecules* **1997**, *30*, 1851.
[26] G. Liu, L. Qiao, A. Guo, *Macromolecules* **1996**, *29*, 5508.
[27] G. Liu, *Adv. Mater.* **1997**, *9*, 437.
[28] J. Ding, G. Liu, *Chem. Mater.* **1998**, *10*, 537.
[29] S. Stewart, G. Liu, *Chem. Mater.* **1999**, *11*, 1049.
[30] J. Tao, G. Liu, J. Ding, M. Yang, *Macromolecules* **1997**, *30*, 4084.
[31] H. Huang, E. E. Remsen, T. Kowalewski, K. L. Wooley, *J. Am. Chem. Soc.* **1999**, *121*, 3805.
[32] J. Ding, G. Liu, *J. Phys. Chem.* **1998**, *102*, 6107.
[33] F. Henselwood, G. Liu, *Macromolecules* **1997**, *30*, 488.
[34] G. Wang, F. Henselwood, G. Liu, *Langmuir* **1998**, *14*, 1554.
[35] G. Liu, J. Ding, S. Stewart, *Angew. Chem.* **1999**, *111*, 884; *Angew. Chem. Int. Ed.* **1999**, *38*, 835.
[36] J. Ding, G. Liu, *Macromolecules* **1997**, *30*, 655.
[37] For a review, see F. S. Bates, G. H. Fredrickson, *Phys. Today* **1999** (February), 32.
[38] K. E. Yu, A. Eisenberg, *Macromolecules* **1998**, *31*, 5546.
[39] J. Kriz, B. Masar, J. Plestil, Z. Tuzar, H. Pospisil, D. Doskocilova, *Macromolecules* **1998**, *31*, 41.
[40] C. S. Patrickios, C. Forder, S. P. Armes, N. C. Billingham, *J. Polym. Sci. Part A*: *Polym. Chem.* **1997**, *35*, 1181.
[41] J. E. Guillet, *Polymer Photophysics and Photochemistry—An Introduction to the Study of Photoprocesses in Macromolecules*, Cambridge University Press, Cambridge, **1985**.
[42] A. Guo, G. Liu, J. Tao, *Macromolecules* **1996**, *29*, 2487.
[43] See, for example: S. H. Pine, J. B. Hendrickson, D. J. Cram, G. S. Hammond, *Organic Chemistry*, 4th ed., McGraw-Hill, New York, **1980**.

A Dicubane-Like Tetrameric Nickel(II) Azido Complex**

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Over the last few years, considerable research has been directed at the preparation of molecule-based magnets, especially nanoscale magnets in which each microcrystal behaves as a single domain. A method of preparing nanomagnets involves single molecules having ground electronic states with a large number of unpaired electrons.[1] A variety of blocking organic ligands has been used for the preparation of these cluster compounds, most of which provide oxo bridges between metal centers.[2]

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