Articles

Controlled RAFT Synthesis of Polyacrylonitrile-*b*-poly(acrylic acid) Diblocks as Precursors of Carbon Nanocapsules with Assistance of Gold Nanoparticles

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A new strategy for the synthesis of carbon nanocapsules has been developed, based on the preparation of well-defined polyacrylonitrile-*b*-poly(acrylic acid) (PAN-*b*-PAA) block copolymers followed by their micellization in basic water to form spherical micelles with a PAN core and PAA shell. The PAN is then cross-linked by the use of gold nanoparticles. After pyrolysis, carbon nanocapsules are produced by graphitization of the PAN core and diffusion of the molten gold nanoparticles out of the nano-objects.

Introduction

Much attention is paid nowadays to micro- and nanosized carbon materials because of unique chemical, mechanical, and electrical properties and potential applications[1] in nanocomposites,[2] gas storage media,[3] supported catalysis,[4] drug delivery,[5] and protection of enzymes and proteins.[6] As an answer to the steadily growing demand for carbon nanocapsules, a variety of templating methods have been developed for their preparation, such as colloids,[7] dendrimers,[8] vesicles,[9] and block copolymers micelles.[10]

Recently, Matyjaszewski and co-workers reported an interesting method for the preparation of carbon nanospheres by pyrolysis of cross-linked micelles of a poly(acrylic acid)-*b*-polyacrylonitrile (PAA−PAN) copolymer.[11] The carbon nano-objects were actually templated by the micelles formed by the copolymer in water at high pH, thus in a non solvent for PAN and a good solvent for PAA. The polyacrylonitrile (PAN) core was the precursor of carbon, whereas the poly(acrylic acid) (PAA) shell was the sacrificial block. Upon pyrolysis, the PAN core of the micelles was progressively converted into graphitic carbon and the sacrificial phase was volatilized. The prerequisite for the success of this approach was that the PAA and PAN domains remained unchanged all along the thermal treatment. This was achieved by the cross-linking of the PAA shell by 2,2′-(ethylenedioxy)-bis(ethylamine).

Experimental Section

Materials. 2-Dodecylsulfanylthiocarbonylsulfanyl-2-methyl propionic acid (DMP) was synthesized according to Lai et al.[12a] Acrylic acid (AA) and acrylonitrile (AN) were purified by distillation under reduced pressure. Dimethylformamide (DMF), azo-bis-isobutyronitrile (AIBN), trimethylsilyldiazomethane, and anisole were used as received.

Analysis. Conversions were determined by gas chromatography (GC), with anisole as an internal standard and a VARIAN 3900 model equipped with Chrompack capillary columns (15 m, 0.25 mm, and 0.25 μm). Molecular weight and polydispersity index (M_w/M_n) were determined by size exclusion chromatography (SEC), using a 25 mM solution of LiBr in DMF as the eluent at 50 °C. The columns were calibrated with polystyrene standards. The ^{1}H

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(1) Burchell, T. D. *Carbon materials for advanced technologies*; Pergamon: Amsterdam, 1999.

(2) Shchukin, D. G.; Sukhorukov, G. B.; Mohwald, H. *Angew. Chem., Int. Ed.* **2003**, *42*, 4472.

(3) Che, G.; Lakshmi, B. B.; Fiser, E. R.; Martin, C. R. *Nature* **1998**, *393*, 346.

(4) Morris, C. A.; Anderson, M. L.; Stroud, R. M.; Merzbacher, C. I.; Rolison, D. R. *Science* **1999**, *284*, 622.

(5) Donath, E.; Sukhorukov, G. B.; Caruso, F.; Davis, S. A.; Mohwald, H. *Angew. Chem., Int. Ed.* **1998**, *37*, 2202.

(6) Gill, I.; Ballesteros, A. *J. Am. Chem. Soc.* **1998**, *120*, 8587.

(7) Marinakos, S. M.; Novak, J. P.; Brousseau, L. C., III; House, A. B.; Edeki, E. M.; Feldhaus, J. C.; Feldheim, D. L. *J. Am. Chem. Soc.* **1999**, *121*, 8518.

(8) Wendland, M. S.; Zimmerman, S. C. *J. Am. Chem. Soc.* **1999**, *121*, 1389.

(9) Hubert, D. H. W.; Jung, M.; German, A. L. *Adv. Mater.* **2000**, *12*, 1389.

(10) Harada, A.; Kataoka, K. *Science* **1999**, *283*, 65.

(11) (a) Tang, C.; Qi, K.; Wooley, K. L.; Matyjaszewski, K.; Kowalewski, T. *Angew. Chem., Int. Ed.* **2004**, *43*, 2783. (b) Kowalewski, T.; Tsarevsky, N. V.; Matyjaszewski, K. *J. Am.Chem. Soc.* **2002**, *124*, 10632. (c) Tang, C.; Dufour, B.; Bombalsky, L.; Matyjaszewski, K.; Kowalewski, T. *Polym. Prepr.* **2005**, *46* (2), 497. (d) Tang, C.; Qi, K.; Tsarevsky, N. V.; Jia, S.; Dufour, B.; Bombalski, L.; Legeleiter, J.; Wooley, K. L.; Matyjaszewski, K.; Kowalewski, T. *Polym. Prepr.* **2004**, *45* (1), 745.

(12) (a) Lai, J. T.; Filla, D.; Shea, R. *Macromolecules* **2002**, *35*, 6754. (b) Couvreur, L.; Lefay, C.; Belleney, J.; Charlleux, B.; Guerret, O.; Magnet, S. *Macromolecules* **2003**, *36*, 8260.

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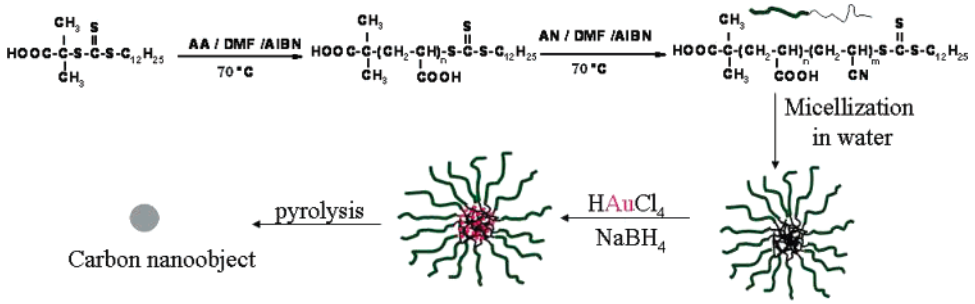
Scheme 1. General Strategy for the Preparation of Carbon Nanoparticles[a]



[a] (1) Synthesis of the PAA block by RAFT. (2) Synthesis of the PAA-*b*-PAN copolymer. (3) Micellization of the diblock in an aqueous medium. (4) Stabilization of the PAN core of the micelles by in situ formation of strongly interacting gold nanoparticles. (5) Formation of carbon nanoparticles by pyrolysis.

NMR spectra were recorded with a 400 MHz Bruker spectrometer. TEM images were collected with a Philips CM-100 microscope, at an accelerating voltage of 100 kV. The images were recorded by a camera. Samples were prepared by deposition of 1 drop of an appropriately diluted solution onto the holey carbon film on copper grid and drying of it in air. The diameter of the micelles was measured by dynamic light scattering (DLS) with a Malvern Instrument (Model CGS-3) at 633 nm (He−Ne laser). The nanoparticules were also observed by atomic force microscopy (tapping mode) with a Dimension 3100 microscope controlled by Nanoscope III electronics (Digital Instruments) with silicon nitride cantilevers. The Raman scattering spectroscopy was carried out with a LabRam spectrometer (Jobin-Yvon) equipped with a confocal microscope and a liquid-N_2-cooled open electrode CCD.

Polymerization of AN and AA by RAFT. ***PAN.*** Azo-bis-isobutyronitrile (0.007 g, 4.27×10^{-5} mol), 0.073 g of DMP (2×10^{-4} mol), 5 mL of AN (4.54×10^{-2} mol), 15 mL of DMF, and 0.4 mL of anisole (internal standard for GC) were mixed together in a 50 mL Schlenk flask. The mixture was degassed by four freeze−pump−thaw cycles and heated in an oil bath at 70 °C for 4 h. The reaction mixture was dissolved in DMF, and the polymer was precipitated by addition of the solution into ether. The solid product was dried in vacuo until constant weight. M_n was determined by ^{1}H NMR in DMSO ($M_n = 3xI_{3.1}/I_{0.8} + 364$), where $I_{0.8}$ and $I_{3.1}$ are the intensity of the proton resonances at 0.8 ppm (CH_3-$C_{11}H_{22}$, t) and 3.1 ppm (*CH*-CN, m), respectively. Moreover, in the course of polymerization, samples were picked out from the medium, diluted with DMF and analyzed by SEC and GC. The monomer conversion was measured by GC with anisole as an internal standard.

PAA. 0.012 g azo-bis-isobutyronitrile (7.31×10^{-5} mol), 1.09 g DMP (3×10^{-3} mol), 15 mL of AA (1.98×10^{-1} mol) and 15 mL of DMF were mixed together in a 250 mL Schlenk flask. The mixture was degassed by four freeze−pump−thaw cycles. This reaction mixture was heated in an oil bath at 70 °C for 4 h. The polymer was precipitated by addition of the solution to ether, and dried in vacuo up to constant weight. The molecular weight was determined by ^{1}H NMR in DMSO ($M_n = 3xI_{2.44}/I_{0.8} + 364$), where $I_{0.8}$ and $I_{2.44}$ are the intensity of the proton resonances at 0.8 ppm ($CH_3-C_{11}H_{22}$, t) and 2.44 ppm (*CH*−COOH, m), respectively. Polydispersity was measured by SEC.

Synthesis of PAA-*b*-PAN by RAFT. PAA-*b*-PAN: A mixture of 1 g of trithiocarbonate-capped PAA (2.5×10^{-4} mol; M_n (NMR) $= 4000$ and $M_w/M_n = 1.05$), 2.65 g of AN (0.05 mol), 4 mg of azo-bis-isobutyronitrile (2.5×10^{-5} mol), and 16 mL of DMF was degassed by four freeze−pump−thaw cycles and heated in an oil bath at 75 °C. The copolymer was precipitated into ether and dried in vacuo up to constant weight. Molecular weight was determined by ^{1}H NMR in DMSO, from the relative intensity of the resonances at 2.21 ppm (CH_2−CH−CN) and at 1.5 ppm (CH_2−CH−COOH), respectively. Polydispersity was determined by SEC in DMF after methylation of the carboxylic acid groups of PAA by trimethylsilyldiazomethane as reported by Couvreur et al.[12b]

Micellization and Cross-linking of PAA-*b*-PAN. PAA-*b*-PAN block copolymer (0.06 g) was dissolved in 5 mL of DMF under stirring, followed by addition of 15 mL of water (pH = 8) with a syringe pump (∼30 mL/h). A micellar solution (pH ∼ 6) was formed and maintained under stirring for 2 h. The micellar solution was transferred into a porous membrane tubing (cutoff ∼6000−8000 Da) that was immersed into deionized water and dialyzed under gentle stirring for 2 days. After dialysis, the micellar solution was added with 5 mg of $HAuCl_4$ that dissolved within the core of the micelles. It was reduced by a freshly prepared $NaBH_4$ aqueous solution, with the formation of gold nanoparticles within the micelles.

Pyrolysis Conditions. Approximately one milliliter of the gold-containing micellar solution was transferred to the platinum cell of the TGA equipment (TA instruments TGAQ500) and allowed to dry in air. The sample was heated from room temperature to 900 °C at a 5 °C/min rate under nitrogen. The TGA cell was then dipped into DMF and ultrasonicated to recover the carbon nanoobjects.

Results and Discussion

This paper aims at reporting on a new and simple method for the fast preparation of well-defined carbon nanocapsules (Scheme 1). The strategy is based on the micellization of PAA-*b*-PAN copolymers in water at high pH, followed by formation of gold nanoparticles within the PAN core. The strong interaction of the cyano (−CN) groups of PAN with the surface of the gold nanoparticles results in the cross-linking of the PAN core of the micelles. Upon pyrolysis at 900 °C, the gold nanoparticles are molten within the PAN core and the metal diffuses out of the particles with formation of an inner cavity. So the gold nanoparticles that cross-link the core of the micelles are promoters of carbon nanocapsules in one step (Scheme 1), thus without need of chemical leaching of the cavity promoter.

Reversible addition fragmentation chain-transfer (RAFT) polymerization has proven to be an extremely versatile, controlled radical polymerization technique. RAFT is indeed applicable to a wide-range of monomers, under mild reaction conditions with formation of polymers with predetermined molecular weight, narrow molecular weight distribution, complex architectures, and various functionalities. Therefore,

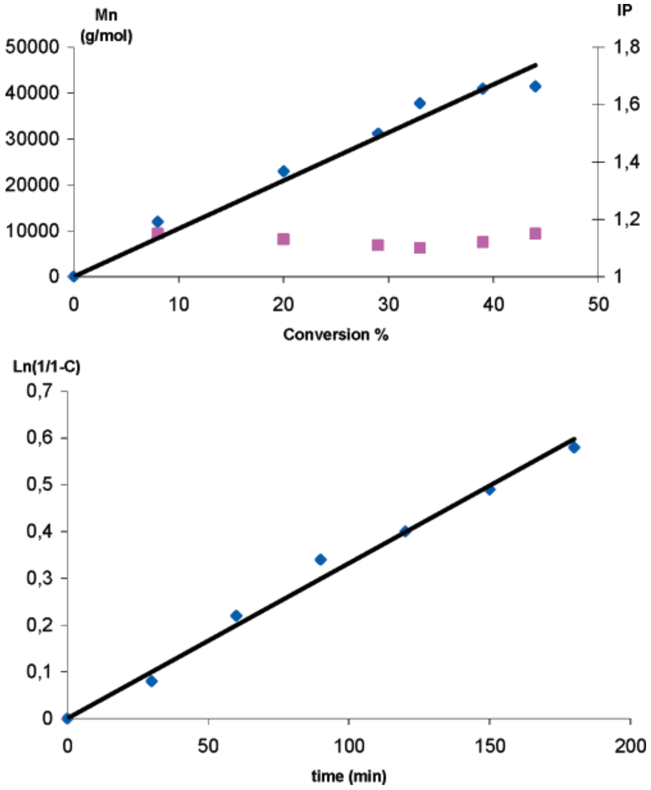


Figure 1. (a) Dependence of the number-average molecular weight (determined by SEC) and polydispersity of PAN on monomer conversion. RAFT polymerization of AN was initiated by AIBN in the presence of DMP as a transfer agent, in DMF at 70 °C. [AN]/[DMP]/[AIBN] = 376:1:0.2 (solid line is a linear fit). (b) Time dependence of $\ln(1/(1 - C))$ for the RAFT polymerization of AN initiated by AIBN in the presence of DMP as a transfer agent, in DMF at 70 °C. C stands for the weight fraction of converted monomer. [AN]/[DMP]/[AIBN] = 376:1:0.2.

RAFT has been considered in this study for the block copolymerization of AA and AN. Interestingly enough, acrylic acid does not need protection for being polymerized by RAFT, in contrast to the strategy proposed by Matyjaszewski and co-workers for the preparation of the PAA-*b*-PAN copolymers, which was based on the polymerization of *tert*-butylacrylate as precursor of acrylic acid.[11] Lai et al. reported that 2-dodecylsulfanylthiocarbonylsulfanyl-2-methyl propionic acid (DMP) is an effective chain-transfer agent for the AA polymerization.[12a,13a] In this work, controlled radical polymerization of AN with DMP has been carried out by RAFT with formation of polymers with a narrow molecular weight distribution and a predictable molecular weight at high conversion. This control has been extended to the block copolymerization of AN with AA.

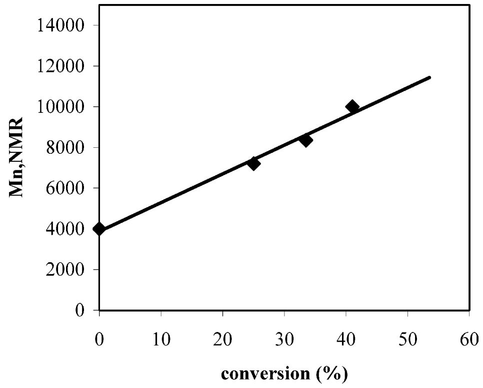


Figure 2. Dependence of the number-average molecular weight (determined by ^{1}H NMR) of PAA-*b*-PAN on AN conversion. RAFT polymerization of AN was initiated by a PAA macroinitiator ($M_{n,NMR}$ = 4000 g/mol; M_w/M_n = 1.05) in DMF at 75 °C ([AN]/[PAA]/[AIBN] = 2000:10:1; [AN] = 3 M (solid line is a linear fit).

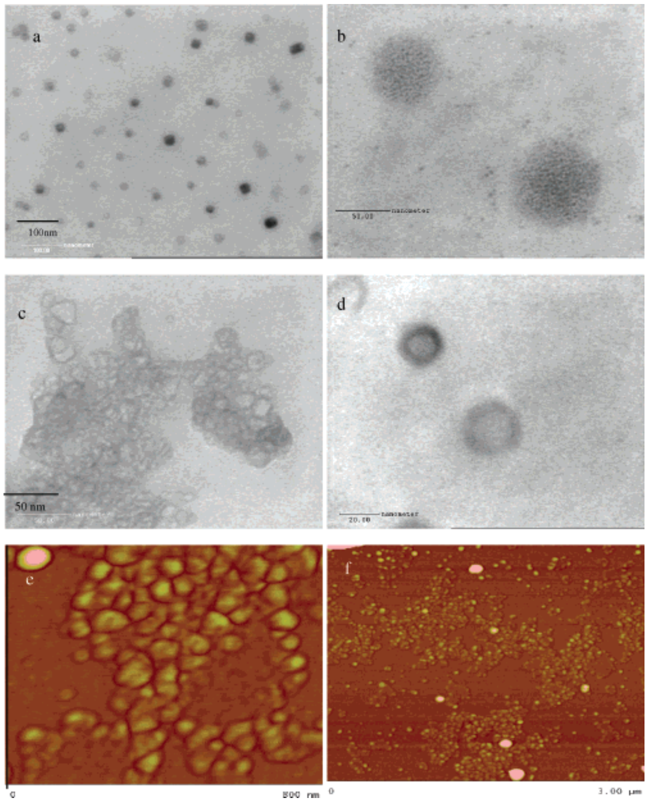


Figure 3. Transmission electron micrographs of (a) $PAA_{(40)}$-*b*-$PAN_{(128)}$ micelles, (b) $PAA_{(40)}$-*b*-$PAN_{(128)}$ micelles after the gold loading of the PAN core, (c,d) carbon nanocapsules after pyrolysis, and (e,f) atomic force microscopy (tapping mode) of the carbon nano-objects deposited onto an ozonolized silicon wafer.

Figure 1 shows that the acrylonitrile radical polymerization is well-controlled when initiated by azo-bis-isobutyronitrile (AIBN) in the presence of DMP, in DMF at 70 °C ([AN]/[DMP]/[AIBN] = 376:1:0.2). The apparent molecular weight

Table 1. Synthesis of PAA-*b*-PAN Copolymers by RAFT

	first block			diblock copolymer					
	PAA			PAA-*b*-PAN^c					
entry	$M_{n,SEC}$^{a}	$M_{n,NMR}$^{b}	M_w/M_n	time (h)	conv. (%)	DP_{NMR}^{b} PAN	DP_{theo} PAN	$M_{n,SEC}$^{d}	M_w/M_n
1	20000	4000	1.05	3	25	60	50	63000	1.35
				5	34	82	68	66000	1.36
				8	41	113	82	104000	1.38
2	11500	3000	1.10	7	47	128	132	82500	1.20

[a] Entry 1: in DMF/LiBr (0.025 M); calibration with polystyrene standards. Entry 2: in a phosphate buffer (pH = 7.4); calibration with poly(ethylene oxide) standards. [b] In deuterated DMSO. [c] Entry 1: [AN]/[PAA]/[AIBN] = 2000:10:1, 75 °C, DMF ([AN] = 3 M). Entry 2: [AN]/[PAA]/[AIBN] = 2830:10:1, 75 °C, DMF ([AN] = 2.83 M). [d] In DMF/LiBr (0.025 M); calibration with polystyrene standards.

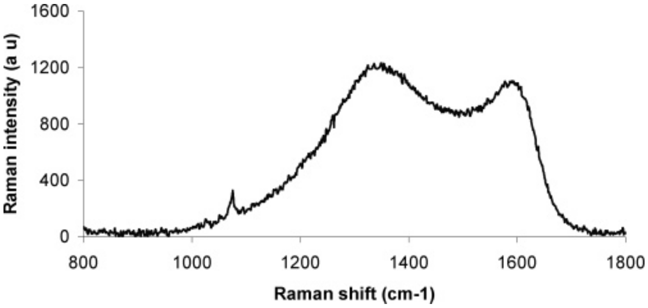


Figure 4. Raman spectrum for the carbon nanocapsules prepared by pyrolysis at 900 °C.

that was determined by SEC in DMF with polystyrene standards increases linearly with monomer conversion (measured by gas chromatography (GC)). The polydispersity index (M_w/M_n) for all the samples is lower than 1.15. The time dependence of $\ln([M]_0/[M])$ is linear, indicating a constant concentration of radicals in the polymerization medium (Figure 1b). All these observations give consistency to a controlled RAFT process[13b,c] and confirm that DMP is quite an appropriate chain-transfer agent for the controlled polymerization of AN.

PAA-*b*-PAN block copolymers have been prepared (Table 1) by using PAA macroinitiators that were previously prepared by RAFT with DMP as reported elsewhere.[12a,13a] The PAA chains were purified by precipitation to eliminate the unreacted monomer, before polymerization of AN was initiated in DMF at 75 °C. In one experiment (M_n PAA $=$ 4000 g mol^{-1}, PDI $=$ 1.05), M_n of the PAN block was measured at several conversions. Figure 2 shows a linear dependence of the total molecular weight of the diblock on the AN conversion.

The amphiphilic block copolymer, PAA$_{40}$-*b*-PAN$_{128}$ (Table 1, entry 2) was tested as a precursor of carbon nanocapsules according to the strategy shown in Scheme 1. This block copolymer is dissolved in DMF, followed by the slow addition of water (~30 mL/h) at pH ~ 8, until formation of a micellar solution. The carboxylic acid groups of the PAA block are thus at least partially deprotonated, which provides the corona with a negative charge and stabilizes the micelles by electrostatic repulsion. The PAA$_{(40)}$-*b*-PAN$_{(128)}$ micelles are nearly monodisperse in size (polydispersity $=$ 0.3) with a number-average hydrodynamic diameter of 35 nm, as measured by dynamic light scattering (DLS) and confirmed by TEM analysis (Figure 3a).

Nitriles are known for σ-type coordination to metal atoms and ions by donation of the lone electrons pair of nitrogen.[14] So, added to the micellar solution, a gold salt ($HAuCl_4$) is expected to accumulate within the micellar core as a result of strong complexation by the cyano (−CN) groups of PAN. This is quite a favorable situation for the production of small gold nanoparticles with a very narrow size distribution.[14] Actually, the gold salt has been dissolved in the micellar solution and the gold ions have been reduced by a freshly prepared $NaBH_4$ aqueous solution. TEM images confirm the formation of gold nanoparticles with a 3 nm diameter within the core of the micelles (Figure 3b). The major effect of the high affinity of the cyano groups of PAN for the gold surface[15] is the stabilization of the micellar core, particularly during pyrolysis. In this respect, a few drops of the gold-stabilized micellar solution have been transferred to the platinum cell of TGA equipment, allowed to evaporate in air, and then heated from room temperature to 900 °C at a 5 °C/min rate under nitrogen. To confirm the graphitization of the PAN block and the pyrolysis of the sacrificial PAA block, the TGA cell was immersed into DMF under ultrasonication, and the carbon nano-objects were collected for analysis by Raman spectroscopy. Figure 4 shows the strong and relatively narrow band around 1600 cm^{-1}, characteristic of graphitic species (G-band) and a broader band centered around 1350 cm^{-1}, typical of the defect-mode species (D-band).[11a,b,d]

Morphology and size distribution of the carbon nanoparticles formed by pyrolysis have been observed by TEM.[16] The TEM images (Figure 3c,d) show spherical carbon nano-objects with a diameter of approximately 30 nm. These nano-objects are actually carbon nanocapsules, mainly aggregated by $\pi-\pi$ interaction of the graphite layers. They have been

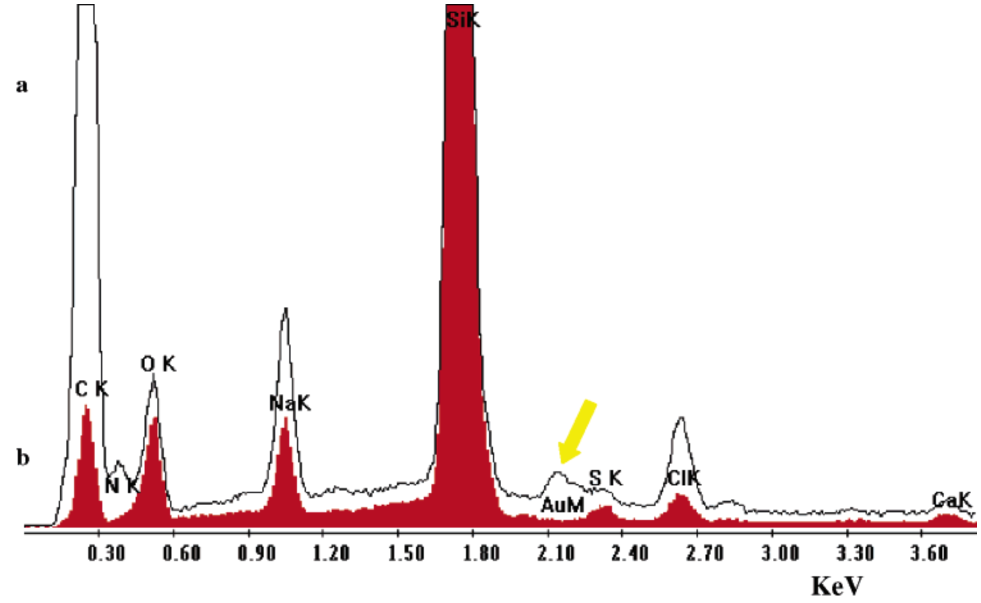


Figure 5. EDAX analysis for (a) the gold-loaded PAA-*b*-PAN micelles and (b) the carbon nanocapsules after pyrolysis, deposited on a silicon wafer.

deposited onto an ozonolized silicon wafer from a DMF suspension and analyzed by atomic force microscopy (AFM) in the tapping mode (Figure 3e,f). The larger diameter observed by AFM for these nano-objects (70 nm instead of 30 nm by TEM) is an artifact due to the exceedingly large size of the AFM tip.[17] Clearly, pyrolysis of PAA-*b*-PAN micelles loaded by gold nanoparticles is a straightforward way to carbon nanocapsules. A reasonable explanation is that, during pyrolysis, the gold nanoparticles preformed in the PAN core of the micelles are molten and diffuse out of the graphitizing micelles, leaving an inner cavity within the carbon nano-objects. Supporting information may be found in the EDAX analysis of the nano-objects which cannot detect any residual gold, such as the peak at 2.12 eV typical of Au Mα (Figure 5b), although this characteristic peak was observed for the PAA-*b*-PAN micelles before pyrolysis (Figure 5a).

Conclusions

In conclusion, carbon nanocapsules were successfully prepared by a novel method based on the pyrolysis of PAA-*b*-PAN micelles, whose PAN core was previously loaded by gold nanoparticles. The well-defined PAA-*b*-PAN block copolymer was prepared in a controlled manner by RAFT with 2-dodecylsulfanylthiocarbonylsulfanyl-2-methyl propionic acid (DMP) as a transfer agent, in DMF. The gold nanoparticles have a dual role. They indeed stabilize the PAN core of the micelles by the strong interaction with the nitrile substituents of the chains, whereas at a high enough temperature, they diffuse out from hollow graphitized nano-objects.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) (a) Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M.; Thang, S. H. *Macromolecules* **2003**, *36*, 2273. (b) Quanfu, A.; Jinwen, Q.; Liyun, Y.; Yingwu, L.; Xinzhi, L. *J. Polym. Sci., Part A: Polym. Chem.* **2005**, *43* (9), 1973. Vana, c-P.; Davis, T. P.; Barner-Kowollik, C. *Macromol. Theory Simul.* **2002**, *11* (8), 823.

(14) Teranishi, T.; Kiyokawa, I.; Miyake, M. *Adv. Mater.* **1998**, *10*, 596. Richardson, D. E.; Taube, H. *J. Am. Chem. Soc.* **1983**, *105*, 40.

(15) Tamoto, N.; Adachi, C.; Nagai, K. *Chem. Mater.* **1997**, *9*, 1077.

(16) Samples were prepared by spreading a drop of a dilute dispersion of nanoparticles onto a carbon-coated copper grid.

(17) Ma, Q.; Remsen, E. E.; Kowalewski, T.; Wooley, K. L. *J. Chem. Soc.* **2001**, *123*, 4627.