Nanoparticles Built of Cross-Linked Heterotelechelic, Amphiphilic Poly(dimethylsiloxane)-*b*-poly(ethylene oxide) Diblock Copolymers

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ABSTRACT: Novel short chain α,ω-heterotelechelic amphiphilic poly(dimethylsiloxane)-*b*-poly(ethylene oxide) diblock copolymers (PDMS−PEO) with total molecular weights below 10 000 g/mol are synthesized, characterized, and used as basic constituent parts for functionalized nanoparticles. The self-assembly of the amphiphilic diblock copolymer in water as a solvent selective for the PEO block leads to the formation of spherical and cylindrical micellar structures with diameters between 10 and 25 nm. The core of the micelles is built of the hydrophobic PDMS chains, whereas the corona is set up by the hydrophilic PEO blocks. By using α,ω-heterotelechelic diblock copolymers, it is possible to fix the core of the micelles by cross-linking of the PDMS-sided (α) methacrylic end groups. The resulting nanoparticles possess the PEO-sided (ω) functional end groups introduced during the synthesis of the amphiphilic diblock copolymer. In the present study, these functionalities are hydrophilic, uncharged hydroxy end groups (−OH), hydrophilic, charged carboxylate (−COOH) end groups, or hydrophobic benzylic end groups ($-CH_2C_6H_5$).

Introduction

Nanoparticles are of rapidly growing interest because of their size-coupled properties. They possess a highly specific surface area, which, combined with their smallness, makes them interesting candidates for various applications, e.g., for the encapsulation of sensitive substances, for drug delivery,[1] or as nanoreactors.[2−4] In general, it should be possible with the help of appropriate functionalities to equip the nanoparticles with special interaction properties. By doing this, the nanoparticles could serve as carrier system or as fundamental part for even more complex supramolecular assemblies.[5]

One possible way to generate the nanoparticles is to use the self-assembly of block copolymers into micelles as "mold". The solution properties of amphiphilic diblock copolymers have recently gained growing attention. When dissolved in a selective solvent for one block, self-assembly takes place. The observed micellar morphologies are the topics of increasing research activities. Eisenberg et al. have found different morphologies formed by block copolymers cast from solution. The structures they investigated were spheres, cylinders, tubules, vesicles, large compound vesicles, lamellae, and other even more complex morphologies.[6−8] Förster et al. have used amphiphilic diblock copolymers to generate and stabilize metal and semiconductor colloids inside the core of spherical micelles.[9−11] A similar approach has been used by Möller and co-workers to obtain metal structures in diblock copolymers forming cylindrical domains.[12] Due to their amphiphilic character, amphiphilic diblock copolymers have the possibility to dissolve nonpolar substances in a polar solvent, and vice versa. Together with the low rate of intermicellar chain exchange,[13,14] this makes them interesting candidates for the applications mentioned above, e.g., as carrier system for drug delivery.[1] The intermicellar chain exchange is mainly a function of the type of blocks, i.e., their relative polarity, the overall chain length, and relative block lengths. To obtain stable micelles with small radii of only some 10 nm, these micelles have to be stabilized further.

One way to achieve this is to cross-link either the core or the shell of the micelles. Examples for the cross-linking of the micellar core are given by Liu et al.[15,16] They have used poly(2-cinnamoylethyl methycrylate) as the core-forming block and subsequent photo-cross-linking to form covalently stabilized micellar architectures. Bates et al. report on the synthesis of cross-linked poly(butadiene)-*b*-poly(ethylene oxide) diblock copolymers in aqueous solution. They obtained cylindrical structures in water as selective solvent for PEO.[28] Iijima et al. performed a linear polymerization of end-functionalized poly(ethylene glycol)-*b*-poly(lactide) in water.[29]

Cross-linking of the shell of amphiphilic diblock copolymer micelles has been presented by Wooley and co-workers.[17,18] They used for example poly(acrylic acid) as shell-forming block and subsequent intramicellar cross-linking by amidation with di- and multifunctional amino linkers. These examples show the use of cross-linking reactions for the formation of nanoparticles built of amphiphilic diblock copolymers.

A possible strategy to introduce specific functionalities to the nanoparticles is to use amphiphilic diblock copolymers carrying the desired functionalities as end groups. In this case the average number of functional groups per particle is defined by the average aggregation number per micelle,[19] which is again mainly influenced by the length of the diblock copolymer and the relative block lengths.

The present paper deals with the synthesis of cross-linked micelles built on the basis of heterotelechelic, amphiphilic poly(dimethylsiloxane)-*b*-poly(ethylene oxide) diblock copolymers (PDMS-*b*-PEO). The choice of poly(dimethylsiloxane) as hydrophobic block has the advantage that the PDMS is at room temperature still

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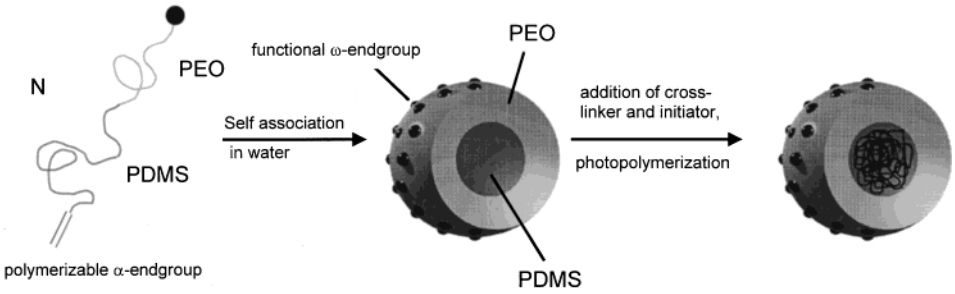

Figure 1. Schematic representation of the micelle formation in aqueous solution (PDMS = poly(dimethylsiloxane), PEO = poly(ethylene oxide)).

far above its glass transition temperature of −123 °C. This guarantees that the formation of micellar structures is not kinetically hindered by a glassy block, and no cosolvent is needed. "Heterotelechelic" is used to describe the fact that the diblock copolymers possess two different functional end groups, α at the PDMS side and ω at the PEO side. The synthesis of the diblock copolymers by anionic polymerization allows the defined introduction of functionalized end groups. The PDMS-sided α-end group is a polymerizable methacrylic group, and the PEO-sided ω-end group is either a hydrophilic, but nonionic, hydroxy group, a hydrophilic and ionic carboxylate group, or a hydrophobic benzyl group. These amphiphilic diblock copolymers build the basic constituent parts of the nanoparticles through their self-association in water, a solvent selective for the PEO block. A schematic representation is given in Figure 1. Subsequent "swelling" of the micellar core with a small amount of hydrophobic cross-linker and initiator, followed by photo-cross-linking of the hydrophobic core, is used to obtain the desired functional nanoparticles possessing either hydroxy, carboxylate, or benzylic functionalities.

Experimental Section

Materials. Benzene, tetrahydrofuran (THF), and diethyl ether were distilled over $LiAlH_4$ for 48 h under argon atmosphere before being degassed. Water was purified with a Milli-Q deionizing system. Triethylamine, dimethylchlorosilane, and allyl alcohol were distilled before use. Ethylene oxide and hexamethylcyclotrisiloxane were stirred over calcium hydride for 1 h before being condensed/distilled.

Methacryloxypropyldimethylchlorosilane, benzyl bromide, acetamide, naphthalene, potassium, toluene, dichloromethane, methanol, 2-propanol, 12-crown-4, 18-crown-6, lithium hydride, lithium aluminum hydride, calcium hydride, succinic anhydride, platinum divinyltetramethyldisiloxane catalyst (3−3.5% Pt concentration), and phenothiazine were used as received in p.a. grade.

Polymers were synthesized by standard anionic ring-opening polymerization under argon. All necessary precautions were taken against any inadvertent exposure of the reactants to air.

Synthesis. The boldface numbers refer to Figure 2, a schematic representation of the synthetic route.

Initiator Preparation (PDMS).[20] **(i) Methacryloxypropyldimethylsilanol (3).** A mixture of 3.12 g (53 mmol) of acetamide and 4.37 g (43 mmol) of triethylamine in 80 mL of benzene was heated to 90 °C to yield a clear solution and then cooled to 70 °C. A 8.83 g (40 mmol) sample of methacryloxypropyldimethylchlorosilane (**1**) was added dropwise. After stirring for 1 h at 75 °C precipitated diethylamine hydrochloride was removed at 0 °C. The solvent was evaporated to yield 7.70 g of (acetamido)methacryloxypropyldimethylsilane (**2**) as an oil.

Methacryloxypropyldimethylsilanol (**3**) was prepared by hydrolysis of the oil in 30 mL of ice water stirring for 30 min. After separation of the organic layer and extraction of the water layer twice with 15 mL of diethyl ether, the organic layers were collected and the diethyl ether was evaporated. The residue was distilled in a vacuum under addition of phenothiazine to afford 5.33 g (26 mmol) of methacryloxypropyldimethylsilanol (**3**) (66%) at 94 °C (0.1 mbar).

(ii) Lithium Methacryloxypropyldimethylsilanolate (4). A 3.44 g (17 mmol) sample of methacryloxypropyldimethylsilanol (**3**) in 50 mL of THF was stirred with 0.135 g (17 mmol) of lithium hydride and 3.52 g (20 mmol) of 12-crown-4 at 45 °C overnight (initiator solution).

Homopolymer Preparations (PDMS).[25] **(iii) α-Methacryloxypropyl-ω-hydropoly(dimethylsiloxane) (7a, 7b, 7c).** The initiator solution in THF was filtered through a 0.22 μm Millipore filter into the reaction flask. After 15 min of ultrasonic irradiation, followed by cooling in an ice bath, 63 g (0.283 mol) of hexamethylcyclotrisiloxane (**5**) in 150 mL of THF was added at once, and polymerization was performed at 0 °C for 24 h. After warming to room temperature 4.83 g (51 mmol) of the terminating agent dimethylchlorosilane (**6**) was added, followed by 15 min of ultrasonic irradiation and several hours of further stirring. Precipitated LiCl was removed, and the resulting solution was dropped into methanol at −60 °C to afford an oily liquid. The poly(dimethylsiloxane) MA-PDMS65 (**7a**) was freeze-dried in benzene to yield 48 g (71%). M_n^{GPC} = 5000 g/mol (M_w/M_n = 1.14, PS with a calibration factor of 0.717).

The preparation of MA-PDMS59 (**7b**) and MA-PDMS49 (**7c**) was performed under the same reaction conditions. MA-PDMS59: M_n^{GPC} = 4600 g/mol (M_w/M_n = 1.17, PS with a calibration factor of 0.717). MA-PDMS49: M_n^{GPC} = 4000 g/mol (M_w/M_n = 1.15, PS with a calibration factor of 0.717). ^{1}H NMR in $CDCl_3$, δ (ppm): 6.08 [s, 1H, H−CH=C(CH_3)−], 5.52 [s, 1H, H−CH=C(CH_3)−], 4.68 [se, 1H, −Si(CH_3)$_2$-H], 4.08 [t, 2H, −O−CH_2−CH_2−], 1.92 [s, 3H, H_2C=C(CH_3)−], 1.68 [q, 2H, −O−CH$_2$−CH_2−CH_2−], 0.55 [m, 2H, −CH_2−Si(CH_3)$_2$O−], 0.25 to −0.15 [m, 6yH, −(Si(CH_3)$_2$O)$_{y-1}$−Si(CH_3)$_2$H].

Homopolymer Preparations (PEO). (iv) (a) α-Allyl-ω-hydropoly(ethylene oxide) (13). A 0.87 g (15 mmol) sample of allyl alcohol, 4.5 g (17 mmol) of 18-crown-6, and 30 mL of a 0.5 M potassium naphthalene solution in THF were added to 100 mL of THF under argon atmosphere. By means of a condenser 41 g (0.93 mol) of ethylene oxide (**9**) was dropped into the solution at room temperature. Polymerization of ethylene oxide proceeded for 48 h. The termination reaction was performed by addition of 2 mL of methanol and stirring for several hours. The polymer was precipitated into 2-propanol at −10 °C, and the waxy solid was freeze-dried in benzene to yield 35 g (85%) of PEO56-H (**13**), a white powder. M_n^{GPC} = 3500 g/mol (M_w/M_n = 1.04, PS), M_n^{MALDI} = 2500 g/mol. ^{1}H NMR in $CDCl_3$, δ (ppm): 5.85 [m, 1H, CH_2=CH−CH_2−], 5.20 [dd, 2H, CH_2=CH−CH_2−], 3.80−3.45 [m, 4xH, −O−(CH_2−CH_2−O)$_x$−].

(iv) (b) α-Allyl-ω-carboxylate−Poly(ethylene oxide) (11). This polymer was prepared by the same procedure as α-allyl-ω-hydropoly(ethylene oxide) (**13**) with 0.87 g (15 mmol) of allyl alcohol, 4.5 g (17 mmol) of 18-crown-6, 30 mL of a 0.5 M potassium naphthalene, and 50.0 g (1.14 mol) of ethylene oxide (**9**). The termination reaction was performed by addition

of 4.50 g (45.0 mmol) of succinic anhydride (**10**) and stirring for several hours. The polymer was precipitated into 2-propanol at −10 °C, and the waxy solid was freeze-dried in benzene to obtain 38 g (72%) of PEO64-COOK (**11**), a white powder. M_n^{GPC} = 3900 g/mol (M_w/M_n = 1.04, PS), M_n^{MALDI} = 3000 g/mol. ^{1}H NMR in $CDCl_3$, δ (ppm): 5.85 [m, 1H, CH_2=C*H*−CH_2−], 5.20 [dd, 2H, CH_2=CH−CH_2−], 4.23 [t, 2H, −(C=O)−O−CH_2−CH_2−], 3.80−3.45 [m, 4xH, −O−(CH_2−CH_2−O)$_x$−].

(iv) (c) α-Allyl-ω-benzylpoly(ethylene oxide) (19). This polymer was prepared by the same procedure as α-allyl-ω-hydropoly(ethylene oxide) (**13**) with 0.87 g (15 mmol) of allyl alcohol, 4.5 g (17 mmol) of 18-crown-6, 30 mL of a 0.5 M potassium naphthalene, and 45.3 g (1.03 mol) of ethylene oxide (**9**). The termination reaction was performed by addition of 5.13 g (30 mmol) of benzyl bromide and stirring for several hours. The polymer was precipitated into 2-propanol at −10 °C, and the waxy solid was freeze-dried in benzene to obtain 35 g (73%) of PEO55-Bz (**19**), a white powder. M_n^{GPC} = 3400 g/mol (M_w/M_n = 1.04, PS), M_n^{MALDI} = 2600 g/mol. ^{1}H NMR in $CDCl_3$, δ (ppm): 7.30 [m, 5H, −CH_2−*Ph*], 5.85 [m, 1H, CH_2=C*H*−CH_2−], 5.20 [dd, 2H, CH_2=CH−CH_2−], 4.55 [s, 2H, −CH_2−Ph], 3.80−3.45 [m, 4xH, −O−(CH_2−CH_2−O)$_x$−]; 1.9 traces of water.

Diblock Copolymer Preparations.[21] **(v) α-Methacryloxypropyl-ω-carboxylate−Poly(dimethylsiloxane)-*b*-poly(ethylene oxide) (14).** The homopolymers are coupled by a hydrosilylation reaction. A 10.0 g (2.0 mmol) sample of α-methacryloxypropyl-ω-hydropoly(dimethylsiloxane) (**7a**), 7.9 g (2.6 mmol) of α-allyl-ω-carboxylpoly(ethylene oxide) (**11**), and 0.2 g (1 mmol) of phenothiazine were dissolved in 60 mL of dichloromethane. The hydrosilylation reaction was initiated by adding 500 mg of Pt−divinyltetramethyldisiloxane catalyst complex and stirring for 3 h at 45 °C. M_n^{GPC} = 11 500 g/mol (M_w/M_n = 1.11, PS), M_n^{MALDI} = 8500 g/mol. [Pt]/[Si−H] = 4 mol %. ^{1}H NMR in $CDCl_3$, δ (ppm): 6.08 [s, 1H, *H*−CH=C(CH_3)−], 5.52 [s, 1H, *H*−CH=C(CH_3)−], 4.23 [t, 2H, −(C=O)−O−CH_2−CH_2−]4.08 [t, 2H, −O−CH_2−CH_2−], 3.80−3.45 [m, 4xH, −O−(CH_2−CH_2−O)$_x$−], 1.92 [s, 3H, H_2C=C(CH_3)−], 1.68 [q, 2H, −O−CH_2−CH_2−CH_2−], 0.55 [m, 2H, −CH_2−Si(CH_3)$_2$O−], 0.25 to −0.15 [m, 6yH, −(Si(CH_3)$_2$O)$_{y-1}$−Si(CH_3)$_2$−].

α-Methacryloxypropyl-ω-hydropoly(dimethylsiloxane)-*b*-poly(ethylene oxide) (15). Same as (**14**) with 16.2 g (3.5 mmol) of MA-PDMS59 (**7b**) and 10.8 g (4.3 mmol) of PEO56-H (**13**) in 80 mL of dichloromethane. M_n^{GPC} = 8700 g/mol (M_w/M_n = 1.15, PS), M_n^{MALDI} = 6600 g/mol. [Pt]/[Si−H] = 2 mol %. ^{1}H NMR in $CDCl_3$, δ (ppm): 6.08 [s, 1H, *H*-CH=C(CH_3)−], 5.52 [s, 1H, *H*−CH=C(CH_3)−], 4.08 [t, 2H, −O−CH_2−CH_2−], 3.80−3.45 [m, 4xH, −O−(CH_2−CH_2−O)$_x$−], 1.92 [s, 3H, H_2C=C(CH_3)−], 1.68 [q, 2H, −O−CH_2−CH_2−CH_2−], 0.55 [m, 2H, −CH_2−Si(CH_3)$_2$O−], 0.25 to −0.15 [m, 6yH, −(Si(CH_3)$_2$O)$_{y-1}$−Si(CH_3)$_2$−].

α-Methacryloxypropyl-ω-benzylpoly(dimethylsiloxane)-*b*-poly(ethylene oxide) (20). Same as (**14**) with 8 g (2.0 mmol) of MA-PDMS49 (**7c**) and 8 g (3.1 mmol) of PEO55-Bz (**19**) in 60 mL of dichloromethane. M_n^{GPC} = 10 300 g/mol (M_w/M_n = 1.15, PS), M_n^{MALDI} = 6200 g/mol. [Pt]/[Si−H] = 4 mol %. ^{1}H NMR in $CDCl_3$, δ (ppm): 7.30 [m, 5H, −CH_2−*Ph*], 6.08 [s, 1H, *H*−CH=C(CH_3)−], 5.52 [s, 1H, *H*−CH=C(CH_3)−], 4.55 [s, 2H, −CH_2−Ph], 4.08 [t, 2H, −O−CH_2−CH_2−], 3.80−3.45 [m, 4xH, −O−(CH_2−CH_2−O)$_x$−], 1.92 [s, 3H, H_2C=C(CH_3)−], 1.68 [q, 2H, −O−CH_2−CH_2−CH_2−], 0.55 [m, 2H, −CH_2−Si(CH_3)$_2$O−], 0.25 to −0.15 [m, 6yH, −(Si(CH_3)$_2$O)$_{y-1}$−Si(CH_3)$_2$−].

IR spectroscopy was used to monitor the progress of the block coupling hydrosilylation reaction of poly(dimethylsiloxane) and poly(ethylene oxide) by following the decrease in intensity of the Si−H valence and deformation vibration at ν = 2124 and 913 cm^{-1}. Therefore, 0.1 mL of the reaction solution was placed directly between NaCl plates. After 30 min the Si−H bands disappeared completely.

Purification of Block Copolymers.[27] A 32 g sample of silica gel was added to the dichloromethane solution of block copolymer and unreacted homopolymer under stirring. The solvent was evaporated to afford the polymer-coated silica gel as a dry powder which was added on the top of a chromatography column 15 cm in diameter filled with 25 cm silica gel in toluene. Elution started with toluene taking fractions of each 100 mL. With toluene only the PDMS homopolymer was eluted, and then solvent was changed to a mixture of THF/methanol 8.5:1.5 (v:v) to afford fractions with pure PDMS−PEO diblock copolymer followed by unreacted PEO. Compositions of fractions were checked with size exclusion chromatography and ^{1}H NMR. Yields of pure diblock copolymers were about 30%.

Instrumentation. Proton NMR spectra were recorded on Bruker AC or AM spectrometers operating at a frequency of either 200 or 400 MHz.

IR spectra were run on a Perkin-Elmer 283B spectrometer.

Size exclusion chromatography was performed on a system with a Waters 510 HPLC pump equipped with Styragel polymer columns (10^2 Å, 5 × 10^2 Å, 10^3 Å nominal pore diameter for homo and block copolymers or 10^3 Å, 10^4 Å, 10^5 Å, 10^6 Å for the cross-linked block copolymers) in THF at a flow of 1 mL/min at 40 °C and refractive index detection with a Waters 410 differential refractometer.

Atomic force micrographs were recorded with a Nanoscope III instrument (Digital Instruments, St. Barbara, CA) operating in tapping mode at a resonance frequency of the tip of about 300 kHz. One drop of the block copolymer solutions in water or tetrahydrofuran was placed on freshly cleaved mica or graphite and spin-cast. The pictures are processed with Image-Pro Plus V. 4.0 (Media Cybernetics Inc.), yielding the particle diameters or heights, respectively. The results have not been desmeared to correct for the tip dimension.

Transmission electron microscopy (TEM) studies of negatively stained air-dried specimens were performed at ambient temperature using a Zeiss EM900, operated at 80 kV. Electron micrographs were recorded on a Kodak type 4489 electron image film.

For preparation of negatively stained specimens the single droplet procedure (20 μL) was used, with consecutive application of polymer solution and negative stain (2% (w/v) uranyl acetate in water) to glow-discharged treated carbon support films on 400 mesh copper EM grids. Excess sample and stain were removed carefully by touching the grid edge to the edge of a filter paper wedge.

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectra were recorded with a Micromass TofSpecE in reflectron mode. Samples have been prepared on a target using 1 μL of 5:5:2 mixed solutions of a 1 g/L solution of the polymer, 10 g/L dithranol, and silver trifluoroacetate, each in THF.

Photopolymerization. A 10 mL aliquot of aqueous diblock copolymer solution was irradiated with an AMKO (Mod.03-MKLS0200-X, Tornesch, Germany) monochromatic Hg−UV lamp (HBO 100 W) at a wavelength of 366 nm in a quartz tube. Concentrations of polymer, initiator, and cross-linker were 0.407 g/L (6.17 × 10^{-5} mol/L), 1.23 × 10^{-6} and 6.17 × 10^{-6} mol/L for MA-PDMS59-PEO56-H, 1.55 g/L (1.83 × 10^{-4} mol/L), 1.83 × 10^{-6} and 9.13 × 10^{-6} mol/L for MA-PDMS65-PEO64-COOK, and 0.55 g/L (8.84 × 10^{-5} mol/L), 8.42 × 10^{-7} and 4.21 × 10^{-6} mol/L for MA-PDMS49-PEO55-Bz. About 10 μL of initiator and cross-linker in separate benzene solutions was added to the aqueous polymer solution by means of a syringe, and the whole solution was degassed in ultrahigh vacuum to remove traces of oxygen before irradiation.

Results and Discussion

Synthesis of the Diblock Copolymers. The synthesis of the heterotelechelic, amphiphilic diblock copolymers is achieved by chain−chain coupling of the homopolymers. These have been synthesized by anionic polymerization of hexamethylcyclotrisiloxane and ethylene oxide, respectively. A schematic representation of the reaction pathways is given in Figure 2. The anionic ring-opening polymerization of hexamethylcyclotrisiloxane (**5**) is initiated by the methacryloylic functionalized silanolate (**4**). The growing chains are terminated using dimethylchlorosilane (**6**) to give the heterotelechelic

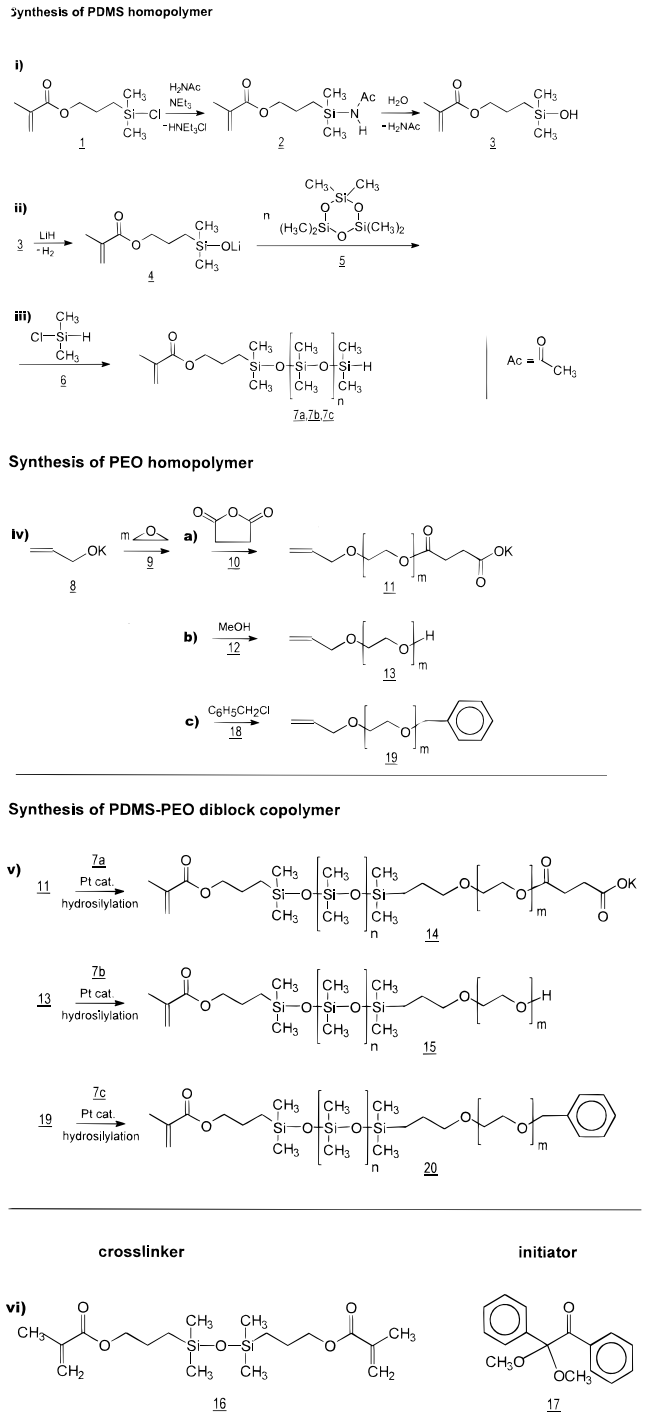

Figure 2. Synthesis of the diblock copolymers: (i−iii) anionic synthesis of poly(dimethylsiloxane); (iv) anionic synthesis of poly(ethylene oxide); (v) hydrosilylation coupling reaction; (vi) cross-linker and UV initiator.

PDMS homopolymers MA-PDMS65 (**7a**), MA-PDMS59 (**7b**), and MA-PDMS49 (**7c**). MA describes the methacryloylic α-end group; the numbers indicate the average degree of polymerization P_n, as determined by GPC (Figure 3a). Anionic polymerization is also used to synthesize the PEO homopolymers. The allyl alcoholate (**8**) is used as initiator for the polymerization of ethylene oxide (**9**). Termination is achieved by adding either methanol (**12**) to give PEO56-H (**13**), bearing a hydroxy ω-end group, succinic anhydride (**10**) to give PEO64-COOK (**11**), possessing a carboxylate ω-end group, or benzyl chloride (**18**) to give PEO55-Bz (**19**), having a benzylic ω-end group. The GPC elugrams are given in Figure 3b. Again, the numbers indicate the average degree of polymerization, as determined by MALDI-TOF mass spectrometry (Figure 4).

The homopolymers are coupled by a hydrosilylation reaction. The progress of the reaction is monitored by infrared spectroscopy, using the decreasing band corresponding to the Si−H bond. The resulting three diblock copolymers under investigation, MA-PDMS59-PEO56-H (**15**), MA-PDMS65-PEO64-COOK (**14**), and MA-PDMS49-PEO55-Bz (**20**), are of comparable block length and relative block ratio. The numbers indicate the mean degree of polymerization of each block. The main difference is the PEO sided ω-end group, in the first case a hydroxy group, indicated by ω = H, in the second case a carboxylate group, indicated by ω = COOK, and in the third case a benzylic group, indicated by ω = Bz. Table 1 summarizes the data characterizing the diblock copolymers. The GPC traces are shown in Figure 5.

One important issue is the degree of end group functionalization of each diblock copolymer given in Table 1. These end group functionalities are found to be >90% for all three diblock copolymers, making the reasonable assumption that the hydrosilylation reaction does not influence the degree of end group functionalization, which is in fact in good agreement with the NMR data.

Nonfixed Micelles. The diblock copolymers are dispersed in water and form micellar aggregates above the critical micelle concentration (cmc) due to the good solubility of the PEO block and the fact that the PDMS block is insoluble in aqueous solution. Typically, the cmc for PDMS−PEO diblock copolymers is on the order of 10^{-6}−10^{-5} mol/L.[31] All investigations of structures formed in solution are done above the cmc. The structure of diblock copolymers in a selective solvent has been studied for example by Förster et al.[22] From the results obtained it can be deduced that in aqueous solution the hydrophobic PDMS should be collapsed and forms the micellar core whereas the PEO should be swollen with water and forms the corona of the micelles.

Atomic force microscopy (AFM) is used to determine the structure and dimensions of the aggregates formed in aqueous solution. Therefore, the solutions of the diblock copolymers were spin-cast on freshly cleaved mica for MA-PDMS59-PEO56-H and MA-PDMS65-PEO64-COOK and on graphite for MA-PDMS49-PEO55-Bz. The results are presented in Figures 6−8.

Figure 6a shows structures of MA-PDMS59-PEO56-H with circular shapes. The diameter of the objects varies between 6 and 18 nm with a mean diameter of 10.0 nm (average of 14 particles, standard deviation 3.0 nm). The same block copolymer spin-cast from a tetrahydrofuran solution, a good solvent for both blocks, results in completely structureless AFM pictures. In this case the mica surface is homogeneously covered by the diblock copolymers. Nevertheless, the average height of a section obtained perpendicular to the surface of the substrate in Figure 6a is about 1.5 nm, which is an indication that the structures formed in solution are collapsed during the process of spin-casting and drying of the solution and might in addition to this also be destroyed. Therefore, a quantitative analysis of this AFM micrographs before cross-linking can only be tentative. Qualitatively, the dimensions of the larger

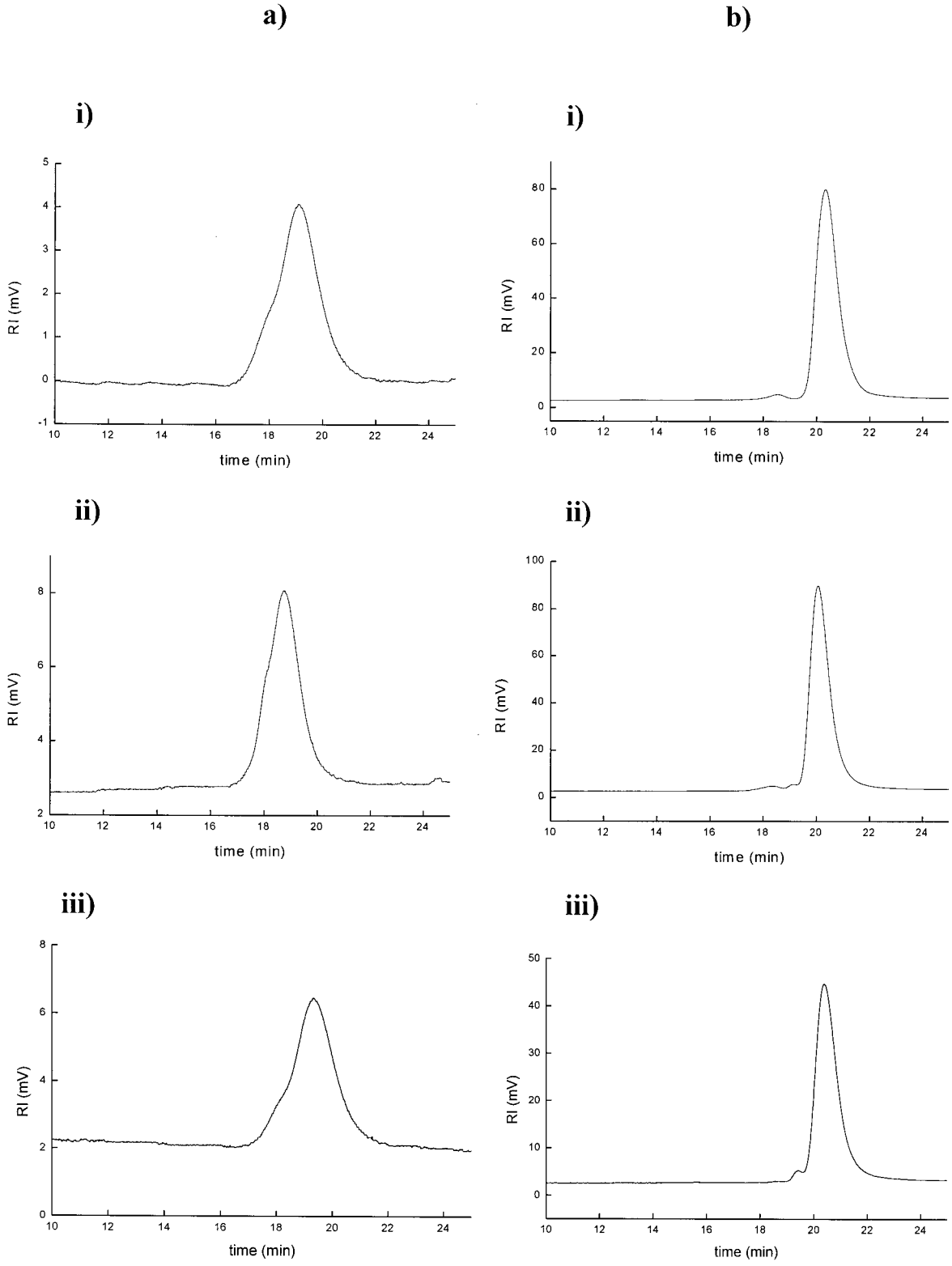

Figure 3. Size exclusion chromatograms of the PDMS and PEO homopolymers: a-i: MA-PDMS59; a-ii: MA-PDMS65; a-iii: MA-PDMS49; b-i: PEO56-H; b-ii: PEO64-COOK; b-iii: PEO55-Bz.

objects correspond to collapsed spherical micelles with PDMS as hydrophobic core and PEO as hydrophilic corona.

To check the generality of the presented synthetic route, PDMS−PEO diblock copolymers of comparable size but with different additional ω-end groups, an ω-carboxylate or an ω-benzylic end group, have been synthesized. The micelles formed by the diblock copolymer MA-PDMS49-PEO55-Bz were spin-cast from dilute aqueous solution on graphite (Figure 8a,b). In this case, particles are visible, which have diameters comparable to collapsed spherical micelles ($\langle D \rangle = 16.0$ nm) with a broader size distribution compared to MA-PDMS59-PEO56-H and show average heights of 1.5 nm. Besides this, larger particles that consist of aggregated micelles are found, which mainly contribute to the broader size distribution. As third species cylindrical objects can be identified on the AFM pictures. These cylindrical objects

Table 1. Characterization of the Homopolymers and Diblock Copolymers

	GPC		MALDI-TOF				
polymer[a]	M_n [g/mol]	M_w/M_n	M_n [g/mol]	M_w/M_n	mol % PEO[d]	wt % PEO[e]	functionality[g]
MA-PDMS59	4600[b]	1.17					>0.90
MA-PDMS65	5000[b]	1.14	5400	1.06			>0.90
MA-PDMS49	4000[b]	1.15					>0.90
PEO56-H	3500[c]	1.04	2500[f]	1.03			>0.95
PEO64-COOK	3900[c]	1.04	3000[f]	1.02			>0.90
PEO55-Bz	3400[c]	1.04	2600[f]	1.02			>0.90
MA-PDMS59-PEO56-H	8700[c]	1.15	6600	1.04	48.7	35.2	>0.90
MA-PDMS65-PEO64-COOK	11500[c]	1.1	8500	1.03	49.6	37.5	>0.90
MA-PDMS49-PEO55-Bz	10300[c]	1.1	6200	1.03	52.9	39.4	>0.90

[a] Numbers indicate average degree of polymerization P_n, calculated using *b* and *f*. [b] Solvent THF, PS-Standards, calibration factor of 0.717.[26] [c] THF, PS-Standards. [d] Calculated using P_n. [e] Calculated using M_n of homoblock (*b* and *f*). [g] Determined from ^{1}H NMR, using M_n from GPC and MALDI.

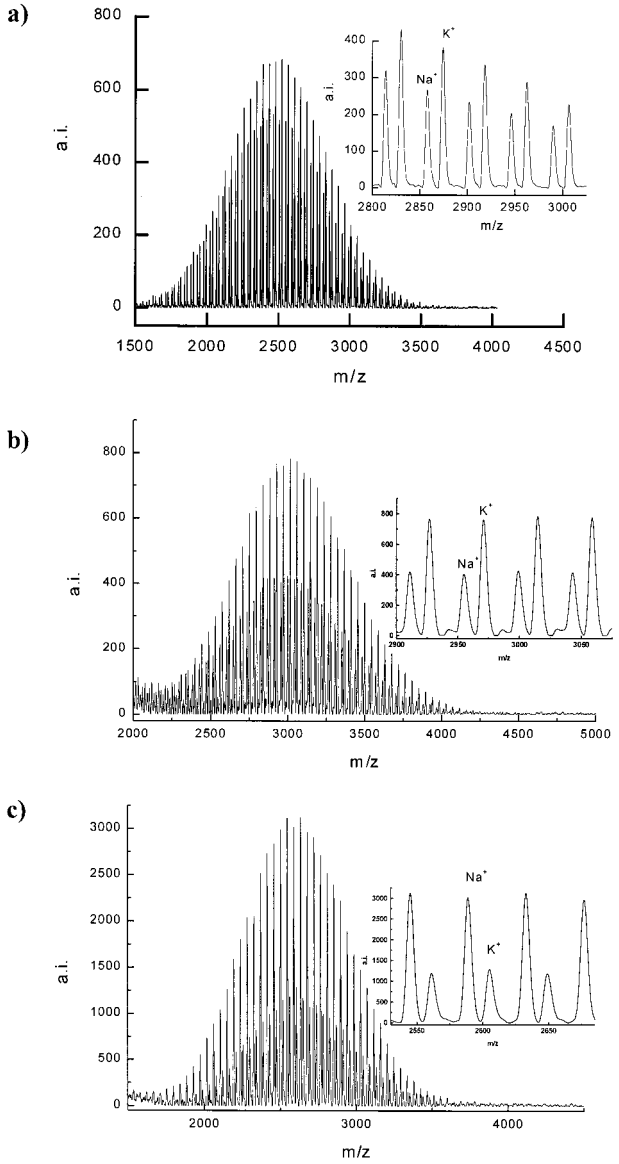

Figure 4. MALDI-TOF mass spectrometry of PEO56-H (a), PEO64-COOK (b), and PEO55-Bz (c); the insets show the two different ionized species, one with sodium and the other potassium as added cation.

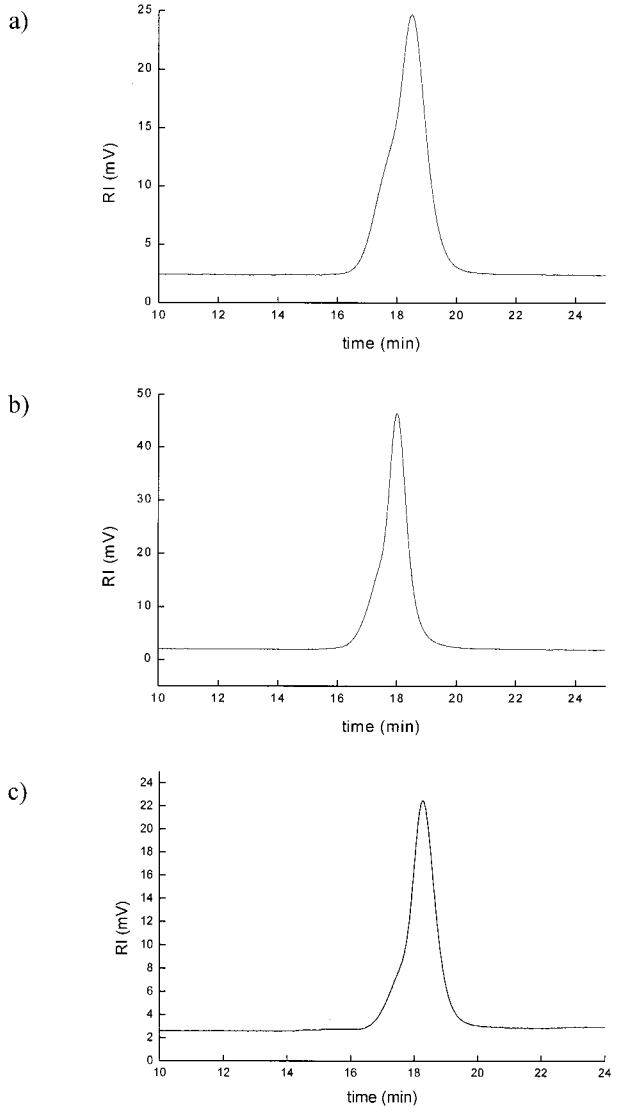

Figure 5. GPC in THF of MA-PDMS59-PEO56-H (a), MA-PDMS65-PEO64-COOK (b), and MA-PDMS49-PEO55-Bz (c).

are even more flat. This favors the interpretation that the diblock copolymers have the tendency to interact strongly with the graphite surface. Since the PDMS is far above its glass transition temperature, the micellar structures are somewhat fluidlike, and the main parameter of stabilization is the interfacial energy. The breakdown of these forces during sample preparation might be the reason for the wetting behavior of the material. Nevertheless, the diameter of a cylindrical structure is comparable to the circular objects. On the other hand, it is known that uranyl acetate is a helpful tool for negative staining in the preparation of TEM specimen.[30] To check any possible influence on the morphology, the AFM substrate containing the prepara-

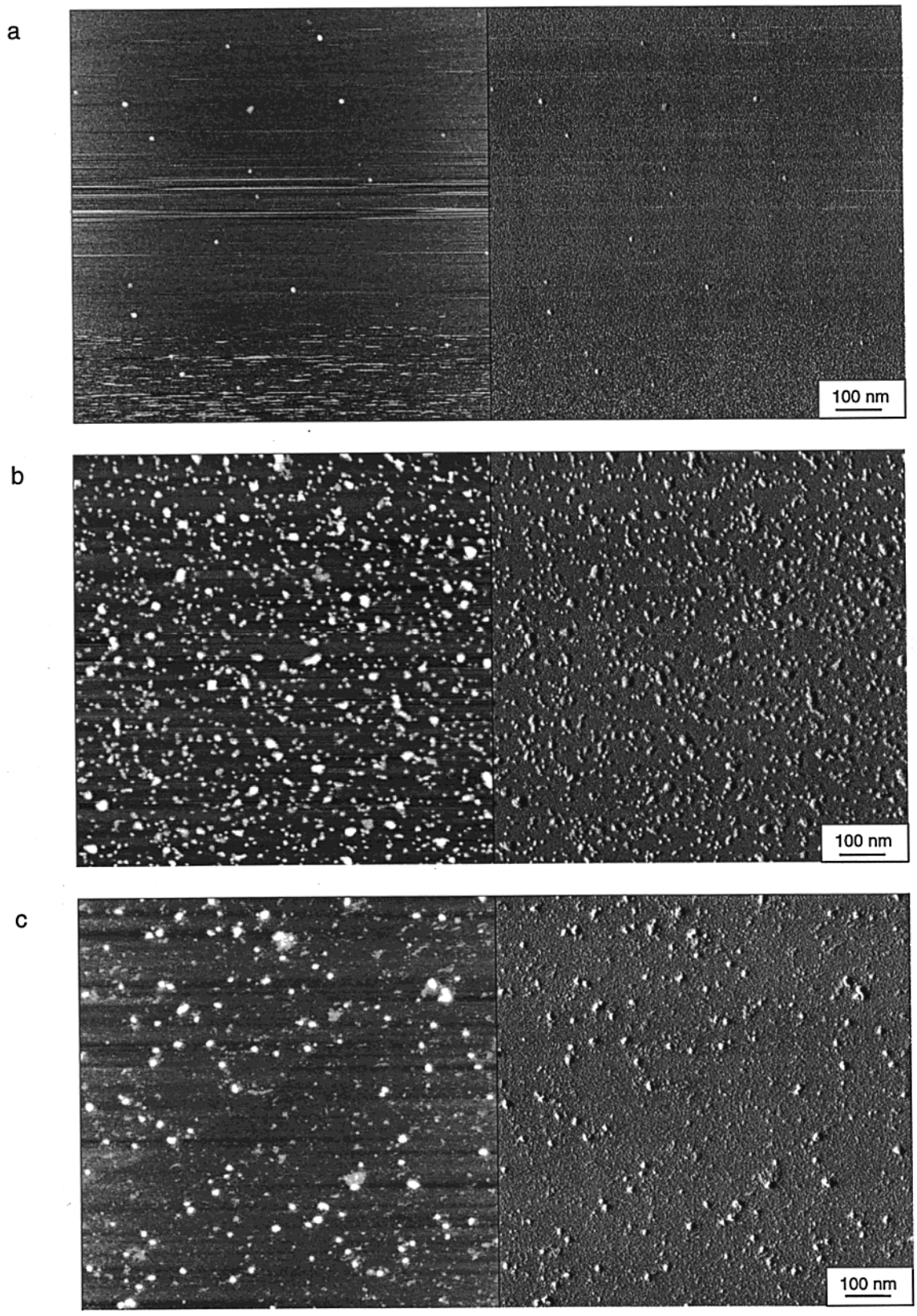

Figure 6. AFM of MA-PDMS59-PEO56-H (left, height; right, amplitude): (a) spin-cast on mica from aqueous solution ($c = 0.4$ g/L) without initiator and cross-linker; (b) after photo-cross-linking with initiator and cross-linker (120 min UV); (c) cross-linked particles (after 5 h UV in aqueous solution) transferred into tetrahydrofuran ($c = 0.8$ g/L).

tion of MA-PDMS49-PEO55-Bz is treated with an aqueous solution of uranyl acetate and again examined by AFM. The result can be found in Figure 8b. It is clearly seen that the observed spherical and cylindrical structures are preserved. Besides this, the "staining" seems to work also for the AFM in this case, because the contrast has been improved and the cylindrical structures are easier to identify. To check the morphology and structure of the aggregates, transmission electron microscopy (TEM) has also been used. Aqueous

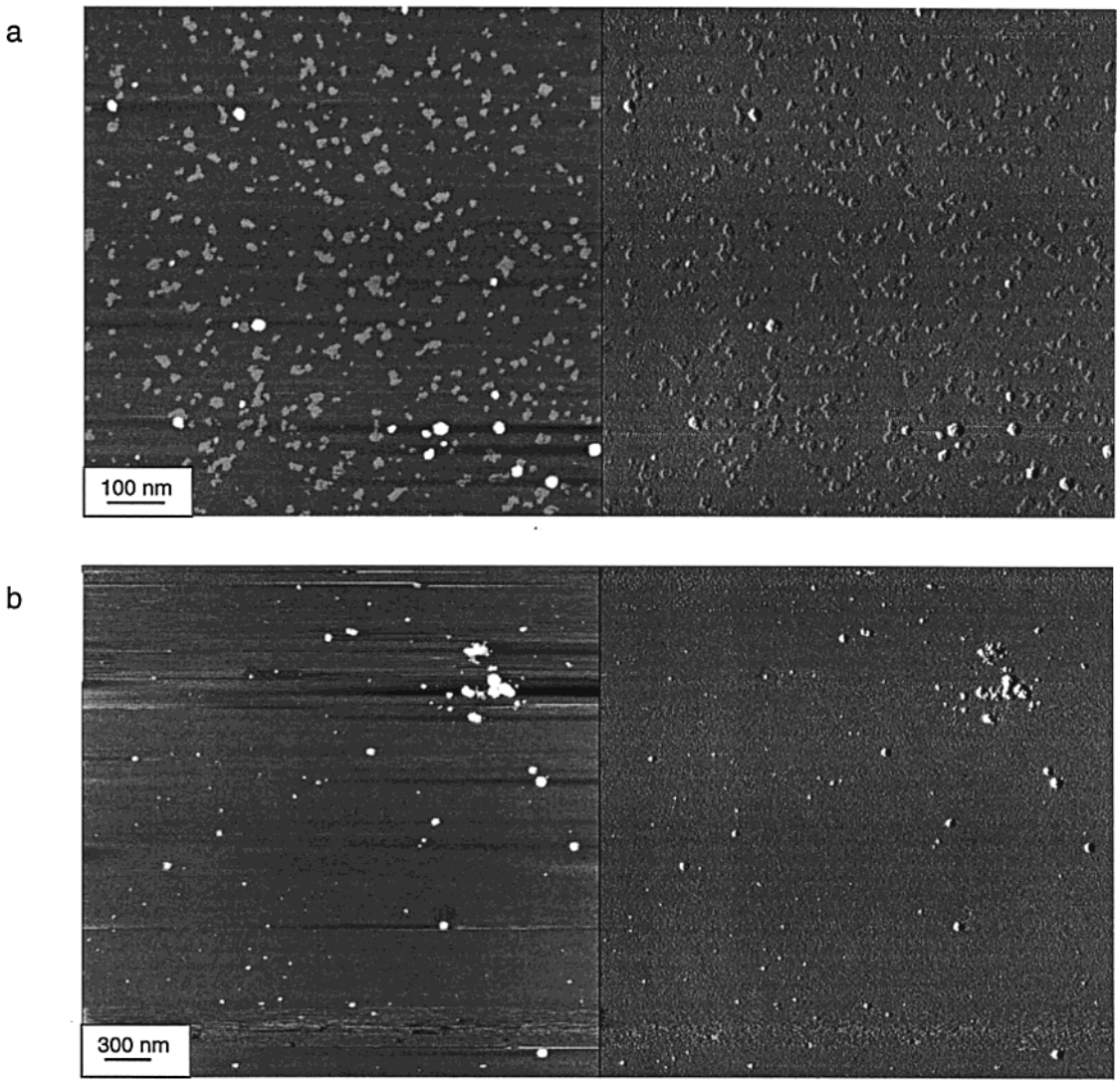

Figure 7. AFM of MA-PDMS65-PEO64-COOK (left, height; right, amplitude): (a) spin-cast on mica from aqueous solution (c = 1.55 g/L) after photo-cross-linking with initiator and cross-linker (120 min UV); (b) cross-linked particles transferred into tetrahydrofuran (c = 7.76 g/L).

solutions have been dropped onto carbon-coated copper grids and subsequently stained with an aqueous solution of uranyl acetate.[30] The results are given in Figure 9.

Figure 9a shows a TEM of a solution of MA-PDMS59-PEO56-H. This spot of the sample shows very drastically the existence and presence of cylindrical objects. The ensemble is formed upon drying of the solvent. The diameter of the cylinders is approximately 25 nm, which is comparable to the dimensions found with AFM. Besides the cylinders, spherical micelles with comparable dimensions are also visible. The situation is the same for MA-PDMS65-PEO64-COOK (Figure 9b). The cylinders and spherical micelles have diameters of approximately 25 nm. The cylinders are of different lengths, up to several microns. Even more interesting is the situation in the case of MA-PDMS49-PEO55-Bz (Figure 9c). Here the cylinders again have diameters of approximately 25 nm, but the spherical micelles show diameters of approximately 10−25 nm. The formation of smaller micelles is thought to be caused by the fact that the hydrophobic benzylic end groups do not want to stay in close contact with the water, and one possible way of avoiding this situation in dilute concentration is the "hiding" of the benzyl groups by backfolding into the hydrophobic core of the micelle. This would decrease the association number of diblocks per micelle and thus decrease the diameter of the micelles. This has to be analyzed in more detail and can only be treated as speculation so far. Nevertheless, these results favor the theses that the sample preparation for TEM seems to be more suitable to examine the nonfixed structures compared to the method of sample preparation used for AFM. A possible influence of the substrate on the structure as well as the corresponding characterization in solution with light scattering techniques is currently in progress and will be discussed separately in the future.

Fixed Micelles. To fix the structures inside the hydrophobic core, the aqueous solutions of the micelles are slightly swollen with small amounts of hydrophobic cross-linker (1,3-bis(3-methacryloxypropyl)tetramethyldisiloxane) and UV initiator (2,2-dimethoxy-2-phenylacetophenone).

Subsequent photopolymerization of the aqueous diblock copolymer solution by UV irradiation at 366 nm for 2 h results in the structural fixation of the micelles. The irradiated solutions are again spin-cast onto mica. The corresponding AFM micrographs are shown in Figure 6b for MA-PDMS59-PEO56-H and in Figure 7a for MA-

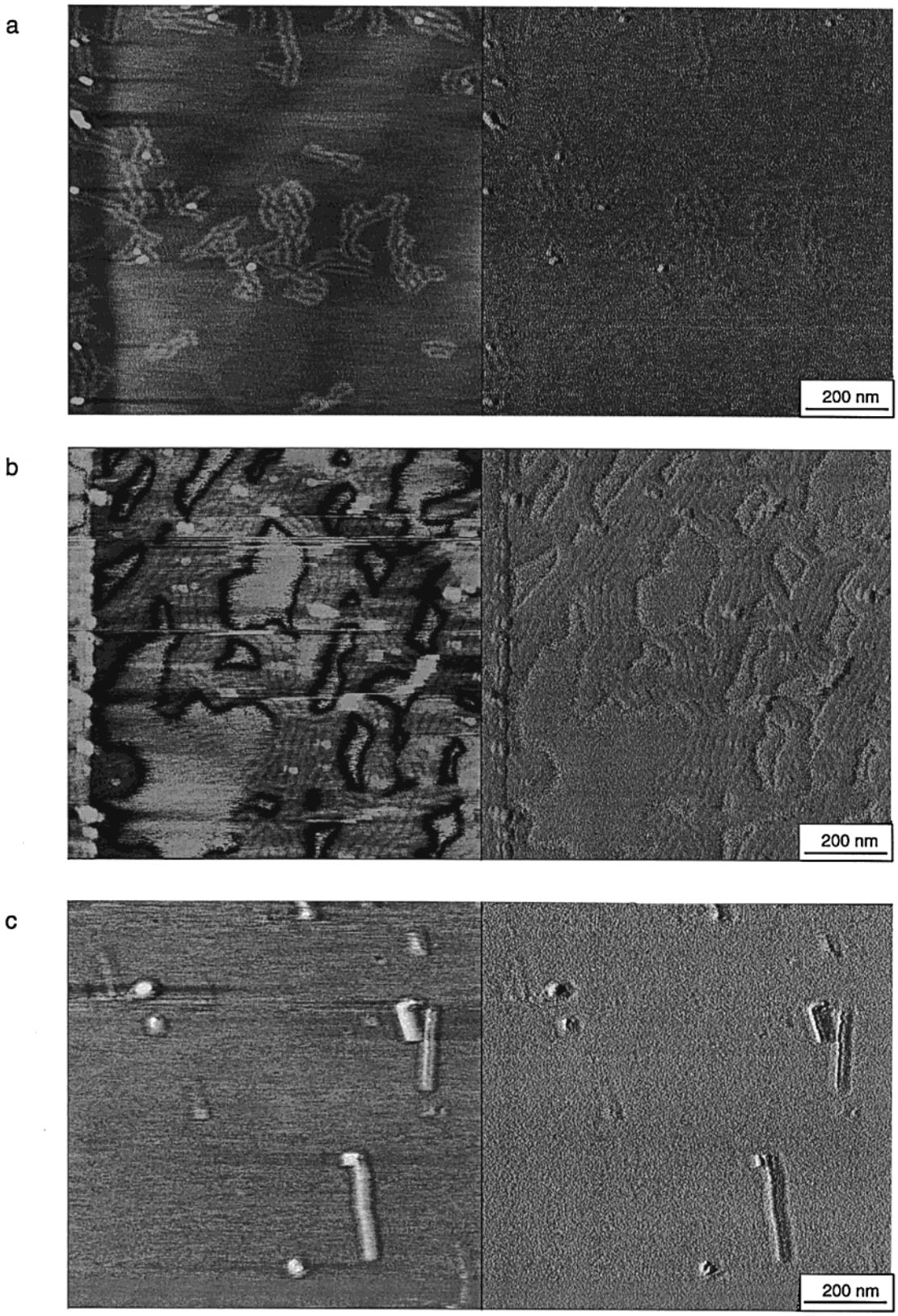

Figure 8. AFM of MA-PDMS49-PEO55-Bz (left, height; right, amplitude): (a) spin-cast on graphite from aqueous solution (c = 0.55 g/L); (b) same as (a), but additionally treated with 2 wt % aqueous uranyl acetate solution; (c) cross-linked sample transferred into tetrahydrofuran (c = 1.14 g/L).

PDMS65-PEO64-COOK. No significant change in size is observed. In the case of MA-PDMS59-PEO56-H circular particles are observed. The particles show diameter between 6 and 18 nm ($\langle D \rangle$ = 12.0 nm, average of 110 particles, standard deviation 2.0 nm, height 2−3 nm). The increase in the height of the particles is a first indication that the cross-linking leads to a fixation. Nevertheless, the appearance of smaller objects can only be explained if the cross-linking is below 100%, which in fact is a reasonable assumption since the amount of

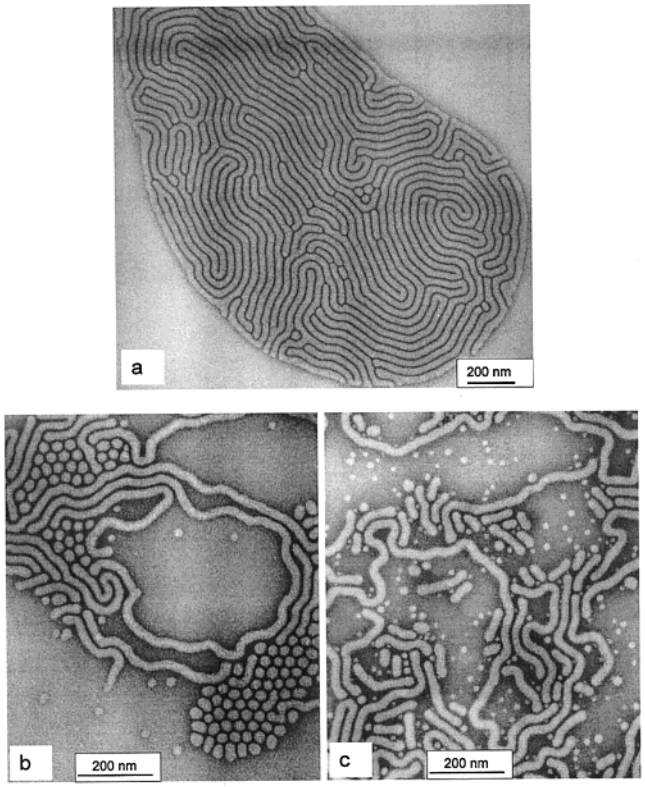

Figure 9. TEM of aqueous solutions ($c = 1$ g/L) dropped onto carbon-coated copper grids, negatively stained with aqueous uranyl acetate: (a) MA-PDMS59-PEO56-H; (b) MA-PDMS65-PEO64-COOK; (c) MA-PDMS49-PEO55-Bz.

cross-linker and initiator is kept small to avoid any possible influence on the morphology. To prove the fixation, the aqueous solution of cross-linked micelles has been dried in vacuo and the solute has been redissolved in THF. This solution is again characterized by AFM, and the resulting picture is presented in Figure 6c. The structured AFM is already a direct proof for the successful cross-linking. The diameter of the particles varies between 8 and 24 nm and the height between 2 and 4 nm. The mean diameter increased slightly to 13.0 nm (average of 114 particles, standard deviation 4.0 nm). This can be explained by the fact that THF is a good solvent for both blocks and the PDMS does no longer collapse in solution. The expanded core in solution yields a slight increase of the particle diameter observed on the substrate. These results also show that the cross-linking has to be improved in order to decrease the amount of incomplete fixation.

For MA-PDMS65-PEO64-COOK the circular structures and particles consisting of larger aggregates of these structures are visualized. The AFM picture (Figure 7a) of the cross-linked micelles of MA-PDMS65-PEO64-COOK in dilute aqueous solution ($c = 1.55$ g/L) shows micelles comparable in size to the ones consisting of MA-PDMS59-PEO56-H and in addition to this islands of unreacted diblock copolymer. The diameter of the particular objects range from 6 to 24 nm, with a mean diameter of 17.0 nm (average of 21 particles, standard deviation 5.0 nm, height 2.5 nm). The polydispersity compared to that of MA-PDMS59-PEO56-H is increased, which is again dedicated to the influence of the method of sample preparation used, i.e., spin-casting and subsequent drying of the substrate. After transfer into tetrahydrofuran, the AFM picture (Figure 7b) shows an increase in the diameter ($15.0 < D < 39.0$ nm, $\langle D \rangle = 26.0$ nm, average of 13 particles, standard deviation 8.0 nm, height between 3 and 5 nm) and larger aggregates due to the relative high concentration of $c = 7.76$ g/L used. Again, the increase can be explained by a swelling of the cross-linked PDMS core of the fixed structures in THF. Figure 8c shows the AFM picture of cross-linked micelles of MA-PDMS49-PEO55-Bz transferred from aqueous solution into THF. In this case it has been also possible to visualize cross-linked cylindrical particles. Both spherical and cylindrical particles show diameters of about 25−30 nm, again a slight increase compared to the results obtained from aqueous solution. The heights of the particles determined from the AFM range from 3 to 8 nm, an indication that the structural fixation through the cross-linking reaction has been successful.

Finally, the AFM micrographs of all three cross-linked samples of MA-PDMS59-PEO56-H (Figure 6c), MA-PDMS65-PEO64-COOK (Figure 7b), and MA-PDMS49-PEO55-Bz (Figure 8c) show particles with mean characteristic dimensions between 13 and 25 nm after transfer into tetrahydrofuran, which is a direct evidence for the structural fixation.

From GPC in THF as eluent, the yield of cross-linked micelles is determined indirectly by the decrease of the intensity of the diblock copolymer peak recorded with a refractive index detector. For this purpose, the intensity of the detector signal has been calibrated using different concentrations of each diblock copolymer, neglecting a possible influence of the small amount of cross-linker and initiator. Besides this, only a small signal is obtained by UV detection for the unreacted diblock copolymer. For MA-PDMS59-PEO56-H the yield of unreacted diblock copolymer is 62%, which corresponds to a yield of 38% of cross-linked product. Besides this result, the GPC trace shows a small peak of the cross-linked product in the refractive index signal and no response for the UV detection. Compared to the results obtained by AFM, the cross-linked particles seem to have additional interactions with the column material which leads to a poor recovery and enhanced adsorption of the cross-linked product compared to the unreacted diblock.

The same holds true for MA-PDMS65-PEO64-COOK and MA-PDMS49-PEO55-Bz. In these cases the yield of cross-linked particles is determined to be 49% and 45%.

The obtained yields might be influenced by the fact that the irradiation times have been chosen to 2 h. On the other hand, irradiation times of 18 h and more result in macroscopic cross-linking and the loss of single particle properties. This still has to be clarified and improved. Nevertheless, it is possible to generate functional nanoparticles by cross-linking of micelles formed by amphiphilic poly(dimethylsiloxane)-*b*-poly(ethylene oxide) diblock copolymers in a selective solvent.

Conclusion and Outlook

It has been shown that heterotelechelic, amphiphilic diblock copolymers of the type α-poly(dimethylsiloxane)-*b*-poly(ethylene oxide)-*ω* with α- = methacrylic end group can be successfully used to construct new nanoparticles. The formation of micellar structures through self-association of the diblock copolymers in water as solvent selective for PEO combined with the addition of small amounts of cross-linker and initiator and subsequent photopolymerization results in the fixation

of the micellar structures. The cross-linked particles have been transferred into a nonselective solvent and identified by AFM. Both spherical and cylindrical structures have been visualized. From the TEM pictures obtained from the micellar aggregates in aqueous solution it can be concluded that the diblock copolymers synthesized with different ω-end groups show spherical and cylindrical structures of comparable size. The only exception is found for MA-PDMS49-PEO55-Bz, the diblock copolymer carrying a hydrophobic ω-end group. Here, in addition to the structures observed also for the other diblock copolymers, smaller spherical objects are found, too.

Following this synthetic route, it should be possible to prepare cross-linked micelles with different degrees of functionality. This can be achieved by mixing diblock copolymers with different PEO-sided end groups prior to cross-linking. After cross-linking, this "mixture" of end groups should be found quantitatively in the fixed nanostructures. Also, besides spherical and cylindrical structures, other micellar architectures can be realized.[7,12,23,24]

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