Organization of Hybrid Dendrimer−Inorganic Nanoparticles on Amphiphilic Surfaces

Franziska Gröhn,[‡] Xiaohong Gu,[†] Holger Grüll,[§] J. Carson Meredith,[⊥] Giovanni Nisato,[§] Barry J. Bauer, Alamgir Karim,* and Eric J. Amis*

Polymers Division and Building Materials Division,
National Institute of Standards and Technology,
Gaithersburg, Maryland 20899

Received October 16, 2001

Introduction. Multiple length scale structuring of organic−inorganic composites is a powerful technique for the creation of materials and devices. Because of quantum size effects, nanoscale inorganic structures can show special electronic, optical, optoelectronic, and magnetic behavior.[1,2] To take advantage of these unique properties, one has to be able to design such nanostructures in a controlled manner and to organize the nanoparticles on larger length scales. The design of materials structured on multiple length scales from the molecular to the macroscopic level has recently come into focus as modular chemistry. As with the development of any new materials, a parallel requirement is the need for appropriate measurement methods to characterize the properties of these materials.

One approach that can lead to defined nanoscale architectures is the method of "polymer nanotemplating" in which an inorganic crystal is nucleated within a polymeric matrix that controls the growth of the nanocrystal.[3,4] Recently, it has been shown that poly(amidoamine) (PAMAM) dendrimers represent an interesting model system for stabilizing and templating inorganic nanocrystals.[5−16] Dendrimers are stepwise synthesized and well-characterized molecules of narrow polydispersity in the size range from 2 to 15 nm, covering the mesoscopic size range between typical organic molecules and polymers or colloids. In the nanoparticle synthesis, we found a transition in the behavior from that of a classical low-molecular-mass stabilizing agent at low dendrimer generation to an efficient polymer template at higher dendrimer generation.[16] Thus, the higher generation dendrimers might be considered the "smallest polymeric templates". Hybrid particles have been fully characterized showing that nanoclusters are formed in individual dendrimer molecules, that they consist of a defined number of atoms determined by the dendrimer, and that they are located off-center within the dendrimer (Figure 1) (for all details see ref 16). Thus, we have small and precisely characterized *hybrid building blocks* that can contain nanoclusters of differing chemistry and in addition provide a high functionality by virtue of their amine terminal groups.

In this communication, we investigate the ability of the dendrimer−inorganic hybrid particles to self-organize on amphiphilic patterned surfaces with micrometer length scale features. In addition to the potential for building mesoscale materials, we also address the application of these stable nanoparticle components as markers for chemical and physical labeling of other mesostructures.

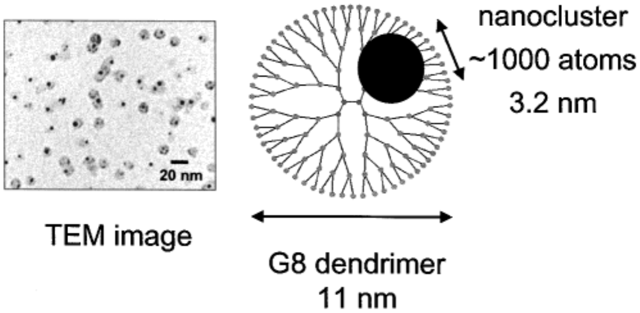

Figure 1. Dendrimer−nanocluster building block: the G8 PAMAM dendrimers of 11 nm diameter include gold colloids of 3.2 nm diameter. Shown is a TEM micrograph in which the (stained) dendrimer appears gray and the gold appears black as well as a cartoon of the structure derived from TEM, SAXS, and SANS. For details see ref 16.

Self-Assembly on Self-Assembled Monolayer Substrates. We study the deposition of gold-containing dendrimers on stripe-patterned self-assembled monolayer (SAM) substrates. The patterned substrates were prepared using the microcontact printing method, i.e., printing of an "inking solution" of one thiol ($HS(CH_2)_{15}$-COOH in hexadecane) on a gold-coated silicon wafer using a PDMS stamp and subsequent "filling" of the nonstamped regions with a second thiol ($HS(CH_2)_{15}CH_3$ in ethanol).[17] The pattern consists of alternating stripes of $-CH_3$- and $-COOH$-terminated alkanethiols that cover a 1 cm^2 area. Atomic force microscopy (AFM) was performed with a Digital Nanoscope Dimension 3100 instrument[18] operating in Tapping Mode, using integrated silicon tips with a nominal curvature radius of 10 nm and cantilevers with a nominal spring constant of 30 N m^{-1}. AFM characterization of the initial gold substrate shows a roughness of less than 3 nm. The patterned SAM substrates are topologically uniform.[17] When exposed to a certain humidity, the stripe pattern can be measured in the phase mode, showing a homogeneous pattern of $-COOH$ stripes of 2 μm width and $-CH_3$ stripes of 3 μm width in correspondence with the expectation based on the AFM characterization of the stamp itself.

SAM-covered substrates were exposed to aqueous solutions of PAMAM dendrimers or nanocluster-containing PAMAM dendrimers (for synthesis see ref 16) at varying concentration for $^1/_2$ h, rinsed by dipping in deionized water, and dried using a slow nitrogen stream. The pH of the solution was chosen so that the dendrimer amine groups partly carry a positive charge while the acid groups of the substrate are negatively charged. This electrostatic attraction is in addition to the "hydrophilic−hydrophobic" discrimination also present. Figure 2 shows an AFM height image after exposure to a solution of a gold-containing G8 dendrimer (mass fraction of 0.1% dendrimer in solution). The image shows that the PAMAM dendrimers are selectively deposited on hydrophilic $-COOH$ stripes of the patterned substrates but not on the hydrophobic $-CH_3$ stripes (nor on the hydrophobic $-CH_3$ SAM region surrounding the

---

[†] Building Materials Division.

[‡] Current address: Max Planck Institute for Polymers, Ackermannweg 10, 55128 Mainz, Germany.

[§] Current address: Philips Research Laboratories, 5656 AA Eindhoven, The Netherlands.

[⊥] Current address: School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA.

10.1021/ma011800c CCC: $22.00

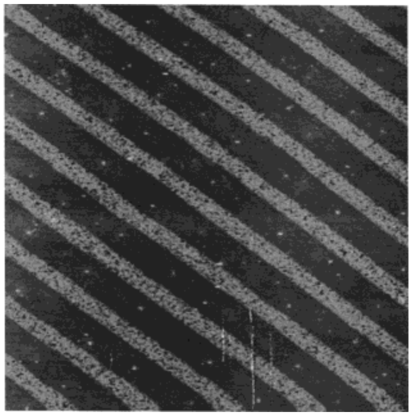

Figure 2. AFM height scan of dendrimer−hybrid particles deposited on SAMs of alternating −COOH- and $-CH_3$-terminated stripes. The image width is 50 μm.

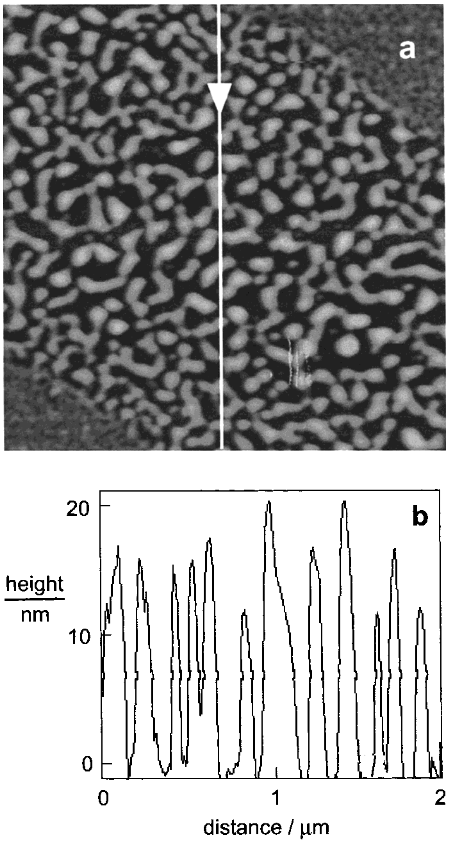

Figure 3. AFM height scan of the same sample as in Figure 2. Shown is a smaller scan with (a) an image width of 2 μm and (b) the corresponding line height profile.

pattern). The fine pattern on the hydrophobic stripes might be water droplets or excess thiol, which are self-organized as is known for confined dewetting on stripe pattern substrates. Since they are already observed on the SAM prior to exposure to the dendrimer solution, the possibility that the fine pattern on the hydrophobic stripes consist of dendrimers can be excluded. Figure 3 displays a smaller scan of the hydrophilic region together with a line height profile across the image. The maximum height corresponds to a thickness of 20 ± 2 nm, and in some regions of deposited dendrimer the maximum height is 11 ± 2 nm. The diameter of the initial gold-containing G8 dendrimer is 11 nm, in agreement with the diameter of an unmodified G8 dendrimer, as previously determined by small-angle X-ray scattering, small-angle neutron scattering, and transmission electron microscopy.[16] Thus, the dendrimers are deposited in monolayer to bilayer thickness on the stripes. The reason for dendrimers being deposited as bilayers is not obvious; excess dendrimers from solution that were not washed off may play a role. Furthermore, a phase-separation-like almost bicontinuous structuring within the hydrophilic stripes is seen in Figure 3. We have investigated how this structure can be influenced and find that the dendrimer concentration of the initial solution is the important controlling factor. If the concentration is lowered, the continuity of dendrimer-covered region within the hydrophilic stripes decreases, and only “droplets” of dendrimers are seen. No influence of the exposure time of the stamped substrate to the solution has been observed. It might be that these patterns are formed during the relatively slow solvent evaporation by solution phase separation in the late stages of drying. The same results are obtained for the dendrimer itself and the nanocluster-containing dendrimer.

In total, the surface structure can be controlled on three levels: the hybrid particle on a few-nanometer scale by dendrimer templating, the structure within the hydrophilic stripes on a hundred-nanometer scale via the dendrimer concentration, and the surface pattern on a micron scale via microcontact printing. We have not focused on resolving the structure of the deposited dendrimers on a single-molecule level. Recent literature investigates dendrimers by AFM.[19−22]

Self-Assembly on Polymer Blend Substrates. A different kind of potential substrate for selective dendrimer deposition/labeling is phase-separated polymer blends consisting of a more hydrophilic and a less hydrophilic component. Here, we use a poly(DL-lactide)/poly(ϵ-caprolactone) (PDLA/PCL) blend, a biodegradable polymer blend for which the phase behavior has recently been reported by Meredith and Amis.[23] As compared to the SAM substrates, a slight difference in hydrophilicity rather than electrostatic attraction represents the potential driving force in this system. In addition, the features of the phase-separated blend are a magnitude larger than in the SAM pattern. In these experiments, we use dendrimers that contain “quantum dots”, cadmium sulfide nanocrystals which show a strong fluorescence in the visible range upon excitation with UV light.[16,24]

The PDLA/PCL polymer blends were prepared by spin-coating on silicon wafers from a chloroform solution containing both polymers and dried under vacuum.[23] Samples were exposed to aqueous solutions of PAMAM dendrimers or nanocluster-containing PAMAM dendrimers at varying concentrations for $^1/_2$ h, rinsed with water, and dried using nitrogen. Fluorescence microscopy was performed using an Olympus-BH_2 microscope equipped with a Photometrix-Quantix 12-bit cooled CCD camera[18] at a magnification of 312.5. The available filters (excitation wavelength 320−400 nm, emission 410−510 nm) led us to use nanocrystals with a blue emission.

We detected no fluorescence for the control sample of pure PCL, while fluorescence is observed for the PDLA control sample, indicating that the nanocluster−dendrimers only adsorbed to the PDLA surface. Figure 4 shows fluorescence microscopy of a sample with a critical 36% PCL/64% PDLA composition blend substrate that had been prepared by a temperature jump

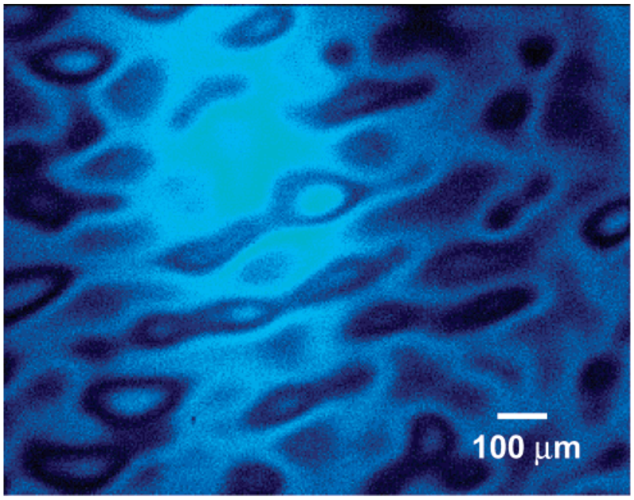

Figure 4. Fluorescence microscopy image of a phase-separated PL/PCL blend after deposition of CdS-containing dendrimers.

into the two-phase region. The fluorescent (blue) spinodal-like microstructure corresponds to the phase-separated morphology observed by optical microscopy (Figure 3c, ref 23), indicating that the CdS−nanocluster−dendrimer is selectively deposited on the PDLA-rich domains of the blend. The preparation conditions could not produce full coverage of the PDLA domains, perhaps due to some PCL in the PDLA-rich domains. Even without uniform coverage, the principle of selective deposition on a PCL/PDLA blend and the preferential interaction between PAMAM dendrimer and the PDLA rich phase is demonstrated.

Such selective deposition on polymer blends represents a promising route to designing hybrid structures, since methods are now well established for the preparation of polymer blend and block copolymer microstructures that are tunable via temperature, composition, and substrate.[23] We note here that a different type of (bulk) hybrid material containing the same components (cadmium sulfide and PCL) was obtained by using PCL for the stabilization of CdS nanoclusters.[25] On the other hand, dendrimer templating within a different polymer matrix also allowed the formation of solid bulk composites.[26] The selective deposition described here is also a valuable method for *characterizing* polymer blend morphologies and identifying the phase composition, particularly for blend systems that do not show strong optical or electron contrast. Further, we have recently demonstrated that quantum dots formed inside dendrimers can show emissions of differing colors and with photostability compared to conventional organic fluorophores. This can open the way to surface structure fabrication with multicolor labeling in polymeric systems on the first level for characterization and for potentially optical and optoelectronic applications. In this context we would like to mention an interesting study in which cadmium selenide particles have been patterned on SAMs.[27]

Conclusions. Nanosize dendrimer−inorganic hybrid particles have been selectively deposited on micron-scale hydrophilic domains of amphiphilic surfaces, both on SAMs of alternating stripes of acid- and methyl-terminated thiols and on a PDLA−PCL polymer blend film surface. Characterization by AFM shows a monolayer to bilayer deposition in the topography of the dendrimer stripes on the SAM hydrophilic region. Dendrimers containing CdS were also selectively deposited on the blend film surface. They retain their fluorescence, demonstrating the feasibility of dendrimer−quantum dot hybrids as probe molecules for characterizing self-organized systems and their potential for optoelectronic applications.

Acknowledgment. We thank Dr. Peter Barker (Biotechnology Division, NIST) for the use of his fluorescence microscopy equipment, Drs. Vitalii Silin and John Woodward for preparation of gold-coated silicon wafers, and Dr. Donald Tomalia of MMI for donation of the dendrimers used in this study. H.G. thanks the Alexander von Humboldt Foundation for financial support. This material is based upon work supported in part by the U.S. Army Research Office under Contract 35109-CH.

References and Notes

(1) Nirmal, M.; Brus, L. *Acc. Chem. Res.* **1999**, *32*, 407.
(2) Eychmüller, A. *J. Phys. Chem. B* **2000**, *104*, 6514.
(3) Antonietti, M.; Göltner, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 910.
(4) Antonietti, M.; Gröhn, F.; Hartmann, J.; Bronstein, L. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2080.
(5) Balogh, L.; Tomalia, D. A. *J. Am. Chem. Soc.* **1998**, *120*, 7355.
(6) Zhao, M.; Sun, L.; Crooks, R. M. *J. Am. Chem. Soc.* **1998**, *120*, 4877.
(7) Esumi, K.; Suzuki, A.; Aihara, N.; Usui, K.; Torigoe, K. *Langmuir* **1998**, *14*, 3157.
(8) Sooklal, K.; Hanus, L. H.; Ploehn, H. J.; Murphy, C. J. *Adv. Mater.* **1998**, *10*, 1083.
(9) Zhao, M. Q.; Crooks, R. M. *Angew. Chem., Int. Ed.* **1999**, *38*, 364.
(10) Beck Tan, N. C.; Balogh, L.; Trevino, S. F.; Tomalia, D. A.; Lin, J. S. *Polymer* **1999**, *40*, 2537.
(11) Zhao, M.; Crooks, R. M. *Adv. Mater.* **1999**, *11*, 217.
(12) Garcia, M. E.; Baker, L. A.; Crooks, R. M. *Anal. Chem.* **1999**, *71*, 256.
(13) Zhao, M.; Crooks, R. M. *Chem. Mater.* **1999**, *11*, 3379.
(14) Esumi, K.; Suzuki, A.; Yamahira, A.; Torigoe, K. *Langmuir* **2000**, *16*, 2604.
(15) Esumi, K.; Hosoya, T.; Suzuki, A.; Yamahira, A.; Torigoe, K. *Langmuir* **2000**, *16*, 2978.
(16) Gröhn, F.; Bauer, B. J.; Akpalu, Y. A.; Jackson, C. L.; Amis, E. J. *Macromolecules* **2000**, *33*, 6042.
(17) Kumar, A.; Biebuyck, H. A.; Whitesides, G. M. *Langmiur* **1994**, *10*, 1498.
(18) Certain commercial materials and equipment are identified in this article in order to specify adequately the experimental procedure. In no case does such identification imply recommendation by the National Institute of Standards and Technology, nor does it imply that the material or equipment identified is necessarily the best available for this purpose.
(19) Hierlemann, A.; Campbell, J. K.; Baker, L. A.; Crooks, R. M.; Ricco, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 5323.
(20) Bliznyuk, V. N.; Rinderspacher, F.; Tsukruk, V. V. *Polymer* **1998**, *39*, 5249.
(21) Imae, T.; Funayama, K.; Aoi, K.; Tsutsumiuchi, K.; Okada, M.; Furusaka, M. *Langmuir* **1999**, *15*, 4076.
(22) Li, J.; Piehler, L. T.; Qin, D.; Baker, J. R.; Tomalia, D. A.; Meier, D. J. *Langmuir* **2000**, *16*, 5613.
(23) Meredith, J. C.; Amis, E. J. *Macromol. Chem. Phys.* **2000**, *201*, 733.
(24) Gröhn, F.; Bauer, B. J.; Amis, E. J. *ACS Polym. Prepr.* **2000**, *41*, 560.
(25) Carrot, G.; Scholz, S. M.; Plummer, C. J. G.; Hilborn, J. G.; Hedrick, J. L. *Chem. Mater.* **1999**, *11*, 3571.
(26) Gröhn, F.; Bauer, B. J.; Amis, E. J. *Macromolecules* **2001**, *34*, 2179.
(27) Chen, C. C.; Yet, C. P.; Wang, H. N.; Chao, C. Y. *Langmuir* **1999**, *15*, 6845.

MA011800C