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Self-Assembly of Uracil−PAMAM Dendrimer Systems into Domains of Micrometer Length Scale

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Molecular self-assembly has over the past decades attracted significant attention due to its novel structural organizations and potential applications in advanced nanotechnology. Studies have in particular concerned block copolymer systems of various architectures which have been shown to form highly ordered nanometer scaled structures in the bulk,[1,2] in solution,[3] or in thin films.[4]

Block copolymer lithography has drawn special attention due to the wide range of potential applications within the microelectronics industry.[4−6] The characteristic length scale of these polymeric systems is in the range 1−10 nm as determined by the overall size of the polymer coil. Even though this nanometer length scale is attractive for a variety of future developments, many applications will remain restricted domain structures approaching the scale of visible light wavelengths, e.g., memory devices addressed by laser light and photonic band-gap materials. As a result, it remains a challenge to control molecular self-assembly on an even larger scale to create micrometer patterning. Some success in this area has been achieved by synthesizing molecules of extreme molar masses,[7] by swelling the nanoscale structures into microscale,[8] and by the assembly of shell cross-linked nanoparticles.[9] Another approach has been to utilize the selective wetting of thin-film block copolymers to a surface where mismatch between thickness and domain size may lead to the formation of micrometer scaled islands or holes.[10−12] A more recent approach has been to utilize self-organization from a receding meniscus in dewetting processes, leading to aligned micrometer-scale lamellae.[13]

Recently, there have been reports on molecular assemblies of dendrimers and other highly branched molecules. Tsukruk et al., for example, reported self-association into nanometer thick, macroscopically long molecular fibers, where the driving forces were speculated being related to hydrogen bonding, π-bonding, crystallization, or combinations of these.[13,14] Thayumanavan et al. showed amphiphilic dendrimers, which on substrates associate into superhydrophobic films, given by disklike assemblies of roughly 200 nm diameter.[15]

We show in this Communication that a new dendrimer-based system spontaneously self-assembles into a thin film of highly ordered micrometer-scale domain structure. The system used is based on a series of uracil−PAMAM dendrimers from generation 0 (tetrafunctional) to generation 4 (64 chain end-functional groups) mixed with the organosilane coupling agent (3-(methylamino)propyl)trimethoxysilane (MAP). The uracil−PAMAM dendrimers were synthesized by coupling the synthesized uracil−1-acetic acid with the free primary amino groups at the chain ends of commercially available PAMAM dendrimers (Aldrich).[17] MAP reactant was obtained from Aldrich and used without further purification. Films were made by mixing 2 mg of the uracil−PAMAM dendrimer into a 1 mL solution of 1 wt % MAP in Milli-Q water. The mixture was filtered through a 0.22 μm Millex-GS to ensure that no large aggregates were present before film casting. Finally, the mixture was drop-cast onto a cleaned (using piranha solution) quartz plate and inserted into an oven for 1 h at 100 °C. We will in this Communication focus on the first-generation dendrimer uracil-G1-PAMAM with eight chain-end uracil groups (shown in Figure 1), but preliminary studies of higher-generation uracil−PAMAM dendrimers (up to $G = 4$ with 64 uracil groups) has demonstrated equivalent micrometer-scaled ordered aggregates.

The resulting domain structure of the uracil-G1-PAMAM/MAP composite is according to the AFM pattern in Figure 2 on the order of 2 μm in width while the length ranges from 5 to at least 50 μm. On the basis of the AFM scans, we further conclude an ellipsoidal cross section with an aspect ratio of the order of 5−10. With a film thickness of the order of 5−10 μm, the film thereby consists of a few layers of densely packed worm- or ribbonlike aggregates. Figure 2 moreover strongly indicates that some of the aggregates are not restricted to the top layer but continue in layers below.

The observed micrometer-scale ordered structure of the dendrimer−MAP composite is highly reproducible and can be achieved homogeneously over macroscopic dimensions. Figure 3 demonstrates the homogeneous pattern within a 1.5 × 1.7 mm quartz plate viewed in an optical microscope. With the dimension of first-generation uracil−PAMAM and MAP molecules being of the order of respectively 5 and 1 nm, i.e., 3 orders of magnitude smaller than the domain dimension, the cross-sectional area of the wormlike aggregates clearly consists of an assembly of a large number of molecules. No corresponding large-scale domain structure was observed in equivalent films made from respectively pure uracil−PAMAM dendrimers and pure MAP dispersions. Furthermore, attempts to obtain similar highly ordered structures in films using a second series of uracil-functionalized dendrimers, uracil−2,2-bis(hydroxymethylpropionic acid) (bis-MPA), again from the first to fourth generation failed. The formation of aggregates in the PAMAM case alone is therefore most likely due to a specific interaction between both the chain ends of the dendrimer as well as the backbone with the silicate MAP precursor. Significantly, no covalent bonding could be detected between MAP and the dendrimers, as measured by Raman spectroscopy.

A variety of experimental conditions were varied to reveal which parameters determine the domain size. With the given quartz substrate used, 2 mg/mL solutions with 1% v/v MAP

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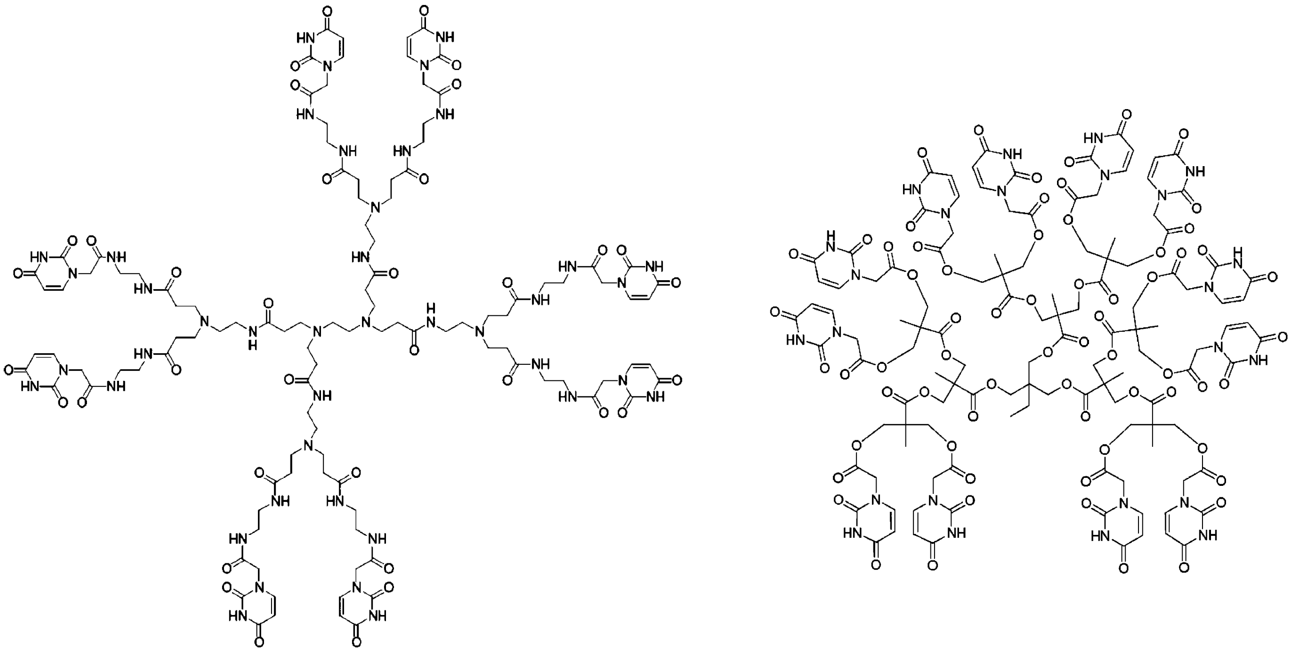

a) 1st generation uracil-PAMAM .

b) Uracil-G2-bis-MPA.

Figure 1. Chemical structures of (a) first generation uracil−PAMAM and (b) second-generation uracil−bis-MPA.

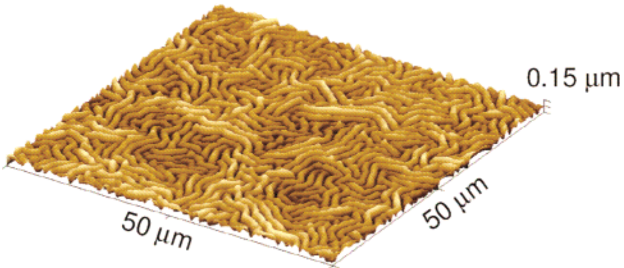

Figure 2. AFM picture of a self-assembled uracil-G1-PAMAM/MAP structured film.

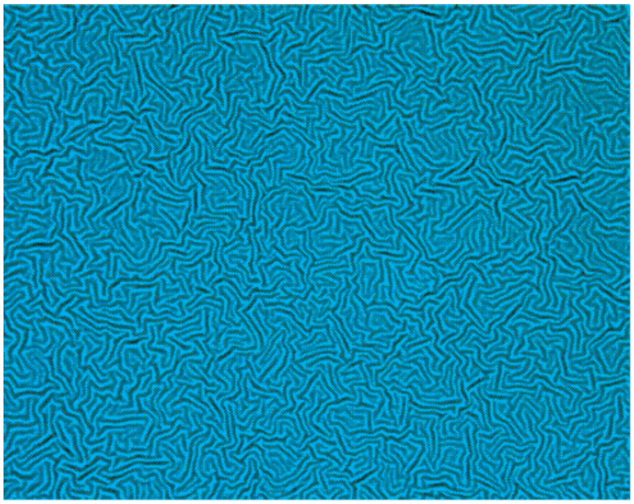

Figure 3. Optical microscope picture of a large area (1.7 × 1.5 mm) self-assembled uracil-G1-PAMAM/MAP system.

seems close to optimum for creating the homogeneous ∼2 μm structured films. For concentrations below 2 mg/mL, incomplete domains are observed, while for concentrations above ∼10 mg/mL, no domain structure was observed. The domain size remained constant within the 2−10 mg/mL concentration range. Increasing the MAP concentrations had also a negative effect on the structuring. No domains were observed using MAP solutions 5−50% v/v.

Substrates alternative to quartz were also investigated, showing significant substrate specificity. In films made on aluminum substrates pattern formation was also observed. These patterns, however, appear only after a few months and continue changing in time, creating major noncovered Al regimes. On aluminum dewetting seems therefore to be the driving force for patterning. The micrometer-scale structure on quartz, on the contrary, forms abruptly and remains stable for more than a year.

Previously, MAP has been used successfully to orient nematic liquid crystals parallel to the surface of a substrate.[18,19] One may speculate on a corresponding effect in the uracil−PAMAM/MAP interaction. To investigate this question, both wide-angle and small-angle X-ray scattering were performed on the structured dendrimer/MAP films using grazing incidence geometry. The small-angle scattering results were all totally dominated by scattering from the reflected beam. No structural features related to the molecular order could be resolved. In contrast, wide-angle X-ray scattering showed two relative broad, azimuthally isotropic, correlation peaks corresponding to real-space distances, $d = 2\pi/q$, of 13.4 and 3.4 Å, q being the scattering momentum transfer (Figure 4). Both of these correlation peaks are observed in reference samples of pure MAP and are accordingly ascribed to this. No additional structural features, which could be related to the dendrimer molecules, were resolved. The isotropic diffraction pattern corresponds to randomly oriented ordered domains within the cm^2-large probed area. With the random domain orientation shown in Figures 2 and 3, we cannot conclude on possible randomness or alignment within the individual domain. These studies strongly suggest that the self-assembled micrometer-scale structure is made up of both uracil−PAMAM dendrimers and MAP reactant, but with domains of MAP molecules organized in structures similar to that of pure MAP.

To supplement the solid-phase structural studies, dynamic light scattering (DLS) was used to investigate possible aggregation in the solution prior to densification and film formation.

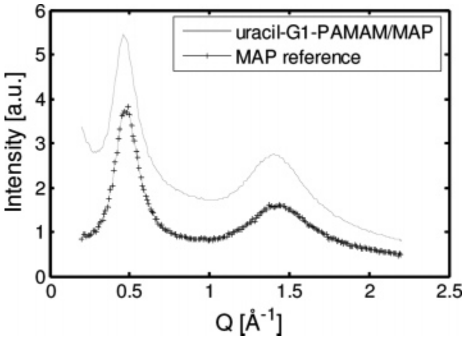

Figure 4. Wide-angle X-ray scattering data, $I(Q)$, vs scattering momentum Q as obtained on (i) a film of self-assembled uracil-G1-PAMAM/MAP composite and (ii) on the pure MAP the matrix component.

Aqueous samples with a consistent concentration of 8 mg/mL of the dendrimer were used for these studies. The DLS results showed no aggregation in the pure dispersions. When 1 wt % MAP was introduced, the dispersions indicate the formation of some aggregates, thus confirming that MAP has a crucial role in the formation of aggregates. The first-generation uracil−PAMAM/MAP system stabilizes after few minutes in aggregates of the order of 1−200 nm, however, with rather poor reproducibility. These aggregates are still significantly smaller than the characteristic $\sim$2 μm lateral domain size observed in films, indicating higher order hieratical assembling after formation of these initial aggregates.

A range of studies have been made in parallel on related mixtures of polymers/oligomers and MAP. As described above for the bis-MPA dendrimers, the vast majority of these studies did not result in any visible structured films, and only in a single case was micrometer-sized domains observed, namely for a small oligopeptide (L-ornithine(N^{α}-uracil-1-ylacetyl))$_6$-NH$_2$/MAP.[20] Again here one may speculate on the crucial role of MAP, but also on a common denominator: the peptide bond. A significant difference between these studies is that in the oligopeptide system structural changes clearly were observed over time (weeks to months) and did not occur evenly over the whole substrate. In contrast, the uracil−PAMAM/MAP films were stable and no change in the micrometer-sized domain structure or dewetting was observed.

In conclusion, we have shown results demonstrating the hieratical formation of a highly reproducible worm- or ribbonlike ordered dendritic structure on the micron length scale from uracil-functionalized PAMAM dendrimers and 3-(methylamino)propyltrimethoxysilane. To the best of our knowledge, our results are the first successful examples of highly ordered dendrimer structures of this length scale, and the versatility of the dendrimer architecture and the high degree of structural control may provide an exciting novel materials platform for formation of multifunctional hieratically structured thin films.

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References and Notes

(1) Bates, F. S.; Fredrickson, G. H. *Phys. Today* **1999**, *52*, 32.
(2) Fasolka, M. J.; Mayes, A. M. *Annu. Rev. Mater. Res.* **2001**, *31*, 323.
(3) Pochan, D. J.; Chen, Z. Y.; Cui, H. G.; Hales, K.; Qi, K.; Wooley, K. L. *Science* **2004**, *306*, 5693.
(4) Thurn-Albrecht, T.; Schotter, J.; Kastle, G. A.; Emley, N.; Schibauchi, T.; Krusin-Elbaum, L.; Guarini, K.; Black, C. T.; Tuominen, M. T.; Russell, T. P. *Science* **2000**, *290*, 2126.
(5) Mark, M.; Harrison, C.; Chaikin, P. M.; Register, R. A.; Adamson, D. H. *Science* **1997**, *276*, 1401.
(6) Edwards, E. W.; Montague, M. F.; Solak, H. H.; Hawker, C. J.; Nealey, P. F. *Adv. Mater.* **2004**, *16*, 1315.
(7) Hadjichristidis, N.; Pispas, S. *Adv. Polym. Sci.* **2006**, *200*, 37.
(8) Bates, F. S.; Maurer, W.; Lodge, T. P.; Schulz, M. F.; Matsen, M. W.; Almdal, K.; Mortensen, K. *Phys. Rev. Lett.* **1995**, *75*, 4429.
(9) Germack, D. S.; Harrisson, S.; Brown, G. O.; Wooley, K. L. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 5218.
(10) Coulon, G.; Ausserre, D.; Russell, T. P. *J. Phys. (Paris)* **1990**, *51*, 777.
(11) Liu, Y.; Zhao, W.; Zheng, X.; King, A.; Singh, A.; Rafailovich, M. H.; Sokolov, J.; Dai, K. H.; Kramer, E. J.; Schwarz, S. A.; Gebizlioglu, O.; Sinha, S. K. *Macromolecules* **1994**, *27*, 4000.
(12) van Dijk, M. A.; van den Berg, R. *Macromolecules* **1995**, *28*, 6773.
(13) Yabu, H.; Shimomura, M. *Adv. Funct. Mater.* **2005**, *15*, 575.
(14) Ornatska, M.; Peleshanko, S.; Genson, K. L.; Rybak, B.; Bergman, K. N.; Tsukruk, V. V. *J. Am. Chem. Soc.* **2004**, *126*, 9675.
(15) Ornatska, M.; Peleshanko, S.; Rybak, B.; Holxmueller, J.; Tsukruk, V. V. *Adv. Mater.* **2004**, *16*, 2206.
(16) Chen, Y.; Ambade, A. V.; Vutukuri, D. R.; Thayumanavan, S. *J. Am. Chem. Soc.* **2006**, *128*, 14760.
(17) Lohse, B.; Vestberg, R.; Ivanov, M. T.; Hvilsted, S.; Berg, R. H.; Ramanujam, P. S.; Hawker, C. J., submitted for publication.
(18) Arkles, B. *CHEMTECH* **1977**, *7*, 766.
(19) Arkles, B.; Steinmetz, J. R.; Zazyczny, J.; Mehta, P. *Silicon Compounds. Registry and Review*, 5th ed.; United Chemical Technologies: Bristol, 1991.
(20) Lohse, B.; Berg, R. H.; Hvilsted, S.; Ramanujam; P. S. *Jpn. J. Appl. Phys.* **2006**, *45*, 488.

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