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A Statically Oleophilic but Dynamically Oleophobic Smooth Nonperfluorinated Surface**

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Extensive research on the preparation of superhydrophobic surfaces has been reported in the past decade, ranging from basic research to practical applications. Such surfaces usually exhibit water contact angles (CAs) larger than 150°. However, studies on superoleophobic surfaces, on which nonpolar (NP) liquid droplets (in particular, small volumes ca. 3–5 μL) that have appreciably low surface tensions (LSTs) can easily roll across and off, and which have a minimum tilt angle (TA) for droplet motion of less than 10°,[1–3] are rare, despite of the practical advantages they offer. It is very challenging to fabricate surfaces that strongly promote dewetting of NP liquids, such as *n*-hexadecane and *n*-dodecane, because of their LSTs ($\gamma_{lv} = 27.5$ and $25.4\,\mathrm{dyn\,cm^{-1}}$ at 20 °C, respectively[4]). When most superhydrophobic surfaces encounter such NP-LST liquids, they exhibit Wenzel wetting behavior: the liquid droplet sticks to the surface and does not roll off or dewet at any TA (poor dynamic oleophobicity).[5] Although textured surfaces with low surface energy usually maintain high advancing CAs (θ_A), when the high-surface-tension (HST) liquid is replaced with a NP-LST one, receding CAs (θ_R) are greatly decreased, which results in marked increases in CA hysteresis values ($\Delta\theta = \theta_A - \theta_R$). However, a few reports have described the formation of superoleophobic surfaces that are capable of preserving the excellent mobility of NP-LST liquid droplets.[2,3] Tuteja et al.[2] successfully fabricated perfluorinated patterned surfaces with a θ_A value of more than 150° and TA = 15° for a 10 μL drop of *n*-octane ($\gamma_{lv} = 21.8\,\mathrm{dyn\,cm^{-1}}$ at 20 °C[4]). Zhang and Seeger[3] also prepared a superoleophobic surface consisting of CF_3-terminated oxidized-silicone nanofilaments with topographical features similar to the "perfectly hydrophobic surface" reported by Gao and McCarthy.[6a] In that case, the minimum TAs needed for movement of 5 μL droplets of NP-LST liquids, such as *n*-decane ($\gamma_{lv} = 23.8\,\mathrm{dyn\,cm^{-1}}$ at 20 °C[4]) and *n*-hexadecane, was only approximately 2–5°.[3] For the preparation of surfaces with such excellent dynamic oleophobicity, Zhang and Seeger[3] emphasized the necessity of producing weak interactions between the NP-LST droplets and the substrate surfaces.

In contrast to such topographically modified surfaces, there have only been a few reports of flat or smooth surfaces with a low CA hysteresis value for both HST and NP-LST liquids. Proper control of both the molecular architecture (branched or ring-shaped molecules) and the physical nature of the modified surface (liquid-like surface that results from high mobility of functional groups in the surface-tethered molecules) are required to realize excellent dynamic dewetting behavior and to allow HST/NP-LST liquid droplets to easily dewet from the surface at low TAs, independent of the magnitude of the CA (this is a practical definition of "ultralyophobic").[6b] Fadeev and McCarthy[7] and several other groups[8] have previously reported ultralyophobic smooth surfaces that have only approximately 1° CA hysteresis for water and approximately 2° for *n*-hexadecane. Another unique smooth surface that is based on a similar concept has also been reported very recently by Wong et al.[9] They employed nano/microstructured substrates infused with thick noncovalently bound liquid films of lubricating perfluorinated fluids, and successfully demonstrated excellent dynamic dewetting behavior with various probe liquids that are not miscible with the entrapped liquids. Regardless of surface topography, the surface tension of the probe liquid, and the magnitude of the CA, liquid drops on surfaces that have low CA hysteresis values can move easily and need only low TAs to roll off ultralyophobic surfaces in all cases.

Herein, we report an approach, not only to achieve excellent dynamic dewettability for both HST/NP-LST liquids, but also to realize thermoresponsive control of the ease of droplet motion for typical probe liquids. Our principle is simple and effective, and is based on the chemical, rheological, and physical properties of smooth, polymer-melt brush films of linear, low molecular weight (MW) poly(dimethylsiloxane) (PDMS). In contrast to previous reports, our technique offers several clear practical advantages: first, neither surface roughening nor perfluorination is necessary; second, adhesion between the brush films and the substrates is covalent and stable; third, HST and NP-LST as well as immiscible and miscible probe liquids can be applied; fourth, our technique is applicable to a wide variety of substrates (as well as Si); and finally, simply heating the substrate can induce pronounced transitions in the dynamic dewetting behavior. The distinguishing aspect of this method is that the properties of PDMS that are utilized to control surface dewettability are physical, not chemical. By taking advantage of these merits, we can achieve excellent dynamic dewettability for NP-LST

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liquids on PDMS brush films, despite the polymer surfaces being statically oleophilic as a result of the methyl groups on the siloxane backbone. Such nonperfluorinated surfaces have also been in demand recently because the chemical and physical effects of perfluorinated compounds on human health as well as the environment have been viewed with suspicion lately.[10] Until now, reports of surfaces that are designed for stimuli-responsive (solvent,[11] UV-light,[12] heat,[13] electric fields,[14] and so on) wettability or dewettability have been confined to water and only to static situations (a liquid droplet is fixed to a horizontal surface) without consideration for altering the dynamic dewettability (tailoring the ease of droplet motion or minimum tilt angle that is required for droplet movement). Such surface modifications have focused on the changes in surface energy through molecular conformational rearrangements by a specific stimulus to alter only static CAs on the surfaces. Furthermore, neither control of the dynamic dewetting behavior of NP-LST liquids or surfaces which have thermoresponsive dynamic behavior for any liquid has been well established. Better understanding and control of such dynamic and thermoresponsive behaviors of liquids with LSTs and HSTs is greatly desirable for the design and preparation of potentially useful functional surfaces.

In this study, vinyl-terminated PDMS (MW = 6000) was grafted to the Si-H moieties of a 1,3,5,7-tetramethylcyclotetrasiloxane (D_4^H)-derived monomeric layer on oxidized Si (Si^{SiO_2}) surfaces[8b] through Pt-catalyzed hydrosilylation.[15] After the formation of the 0.5 nm-thick D_4^H-monomeric layer covalently bound to the Si^{SiO_2} surfaces, the hydrophilic Si^{SiO_2} surface became ultralyophobic, with a low CA hysteresis value for water ($\theta_A/\theta_R = 106°/105°$ and $\Delta\theta = 1°$) and n-hexadecane ($\theta_A/\theta_R = 33°/31°$ and $\Delta\theta = 2°$).[8b] Without the Pt catalyst, PDMS was not grafted to the D_4^H-monomeric layer, as confirmed by CA analysis and ellipsometry (data not shown). As shown by X-ray photoelectron spectroscopy (XPS) and infrared reflection absorption spectroscopy (IRRAS), the PDMS brush film undoubtedly formed in the presence of the Pt catalyst (see Section S1 in the Supporting Information). The grafting of the PDMS to the Si-H surface moieties produced extremely smooth, defect-free, 3.0 nm-thick brush films with a root mean square roughness (R_{rms}) of only 0.374 nm (Figure S2 in the Supporting Information,). Thus, the dynamic dewettability of the PDMS surface is not influenced by surface morphology and is determined only by the chemical and physical properties of the surface. According to the estimated grafting and reduced tethering density (Σ) values of 0.292 chains nm^{-2} and $\Sigma = 1.798$, respectively, the PDMS brush film is considered to be in the "mushroom-to-brush" transition regime.[16a]

Table 1 shows that our PDMS brush surface has a low CA hysteresis value for both HST (water and diiodomethane) and NP-LST (n-hexadecane and n-dodecane) probe liquids at room temperature (25 °C). Although it has been previously reported that PDMS brush films consisting of low-MW PDMS (MW < 2000) have a low CA hysteresis value for water,[16b] the reason for this unique dynamic behavior has not yet been clearly identified, especially for NP-LST liquids. It has been noted that the "lenses" that water drops form on thicker films of silicone oils contribute to the CA hysteresis of those surfaces.[16b] The unique droplet dewetting behavior for all liquids in this study is considered to be related to the high mobility of the chains in the polymer-melt brush film, which results in a film with an excellent liquid-like nature. Our brush film has such rheological properties because PDMS is a liquid polymer melt at room temperature (the glass transition temperature (T_g) of PDMS is −127 °C[17c,d]). In fact, the low-MW PDMS polymer used in this study has a bulk viscosity of 100 cSt at 25 °C as reported by the manufacturer, which is similar to that of olive oil. By placing a water/diidomethane droplet on the liquid polymer-brush surface, the surface–probe liquid interface can be described as a "discrete liquid–liquid interface" (Figure 1 a), which is similar to that between bulk oil and water phases. As a result of this unique interface, our surface has highly-desirable low CA hysteresis values for HST liquids ($\Delta\theta = 4.6°$ and 4.8° for water and diiodomethane, respectively). This is in significant contrast with the typical "solid–liquid interface" and the resulting higher CA hyste-

Table 1: Variation of dynamic CAs (θ_A/θ_R), CA hysteresis ($\Delta\theta$), and TAs of probe liquids (3 μL) with different surface tensions (γ) on the PDMS brush surface before and after heating.

Probe liquid	γ [dyn cm^{-1}][a]	T [°C]	θ_A/θ_R [°]	$\Delta\theta$ [°]	$\Delta(\Delta\theta)$ [°]	TA [°]
Water	72.8	25	108.8/104.2	4.6	−2.5	18.7
		70	112.8/110.7	2.1		—[b]
CH_2I_2	50.8	25	72.7/67.9	4.8	−4.1	9.7
		70	69.2/68.5	0.7		5.0
$C_{16}H_{34}$	27.5	25	34.5/32.5	2.0	−1.7	5.0
		70	27.8/27.5	0.3		2.2
$C_{12}H_{26}$	25.4	25	21.4/19.3	2.1	−1.3	3.8
		70	16.6/15.8	0.8		1.8

[a] At 20 °C (from reference [4]). [b] TA could not be accurately measured as a result of fast evaporation of the small droplet upon heating the substrate.

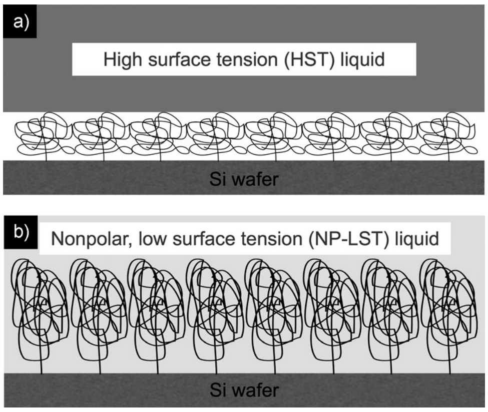

Figure 1. Illustration of two different types of "liquid–liquid interfaces" between the probe liquids and the PDMS brush-film surfaces. a) PDMS is insoluble in HST liquids, therefore, a "discrete liquid–liquid interface" is likely to form when such a liquid droplet is placed on the polymer brush film. b) As NP-LST liquids can dissolve PDMS, the polymer brush film is likely to be swollen by such a probe liquid, and a "blended liquid–liquid interface" is likely to be formed.

resis values that result from conventional surface-modification methods.[1–3,5–7,11–14,18,19]

Our surface also has statically oleophilic properties ($\theta_S = 33°$), which indicates strong interactions between the NP-LST liquids and the sample surface. However, both CA hysteresis values ($\Delta\theta = 2.0°$ and 2.1° for *n*-hexadecane and *n*-dodecane, respectively) and TAs (5.0° and 3.8° for 3 μL droplets of *n*-hexadecane and *n*-dodecane, respectively) were very small, which is in marked contrast with previous results.[5] The dynamic dewetting behavior of NP-LST liquid droplets (both CA hysteresis and TA) on conventional oleophilic surfaces is generally worse.[5] As highlighted by Zhang and Seeger,[3] there are only a limited number of surfaces on which droplets of NP-LST liquids can easily dewet and roll off. Such a phenomenon generally appears only when the surface has superoleophobic properties and has CAs larger than 150°. The unique dynamic dewetting behavior of NP-LST liquid droplets on our surface is believed to originate in the affinity between the probe liquids and PDMS brush surface, as both NP-LST liquids are good solvents of bulk PDMS. We confirmed the solubility of PDMS in these NP-LST probe liquids and easily prepared transparent 25 wt% solutions of PDMS. Thus, we believe that the *n*-hexadecane and *n*-dodecane droplets most likely swelled and plasticized the PDMS brush film,[20] thereby significantly increasing the mobility of the polymer chain. This swelling results in the enhancement of the liquid-like properties of the film and suppresses the terminal relaxation time.[17] In contrast to the HST probe liquids and their formation of a discrete liquid–liquid interface on the PDMS brush surface (see above), the NP-LST probe liquids are considered to interact preferentially with PDMS by taking advantage of their mutual miscibility to form a "blended liquid–liquid interface" (Figure 1b). The resulting dynamic dewettability of PDMS brush films undoubtedly originates from the miscibility or solubility of the polymer with the NP-LST liquids. Therefore, the CA hysteresis values of *n*-hexadecane and *n*-dodecane were lower than those of water and diiodomethane. Furthermore, despite good mutual miscibility between the probe liquid and PDMS, the probe liquid did not leave any tracks as it moved across the surface. In most cases, NP-LST liquids tend to stick to surfaces and have relatively high TAs (15°), even when drops with a larger volume (10 μL) are employed.[2] The ease of the movement of NP-LST liquid droplets on our smooth PDMS brush surface seems to be the same as that of the specially-roughened surface reported by Zhang and Seeger,[3] despite the obvious differences in surface morphology and chemistry.

Finally, the chemistry and physical nature of our polymer brush-film surface allowed for enhancement of the mobility of HST/NP-LST liquid droplets by moderate heating of the surface. At 70 °C, significant decreases in the CA hysteresis values were detected for all four probe liquids (Table 1). This clearly demonstrates that our PDMS surface exhibits thermoresponsive dynamic dewettability for all liquid droplets. As a liquid polymer, PDMS exhibits lower viscosity with increasing temperature.[17] This physical property is shared by other molten polymer melts above their respective T_g.[17c,d] By increasing the temperature from 25 °C to 70 °C, the liquidity of the bulk molten polymer is visibly altered to more closely resemble water. The viscosity-temperature coefficient (VTC) of PDMS is approximately 0.6 (as reported by the manufacturer), which indicates a 60% decrease in the viscosity of the polymer between 38 °C and 99 °C.[17b] As Laup and Goedel[21] reported that the rheological properties of liquid polymer melts extend from the bulk to the brush film, we expect that the mobility of PDMS chains in the brush film also increases with increasing temperature. This assumption is indirectly confirmed by the decrease in CA hysteresis values for all four probe liquids (Table 1). Decreases in the CA hysteresis values for the PDMS brush-film surface ranged from 1.3° for *n*-dodecane and 1.7° for *n*-hexadecane to 2.5° for water and 4.1° for diiodomethane. This represents declines of 62%, 85%, 54%, and 85% in CA hysteresis values, respectively. For HST liquids, the motion of such droplets was improved because of the significant increase in the PDMS chain mobility at higher temperatures. It has been argued that the origin of CA hysteresis is pinning of the contact line of the liquid droplet on the surface, which hinders its motion and results in a lower θ_R value.[19] It seems that by increasing the mobility of the polymer chains by heating the brush film, the pinning of the receding contact line by the molten polymer brush film was significantly reduced, which allows the simultaneous increase in the θ_R values and a decrease in the CA hysteresis values. On the other hand, for the NP-LST liquids, slight decreases in θ_A/θ_R values were detected upon heating (Table 1). This indicates a greater interaction between the probe liquids and the polymer brush film, most likely through increased solubility or miscibility of PDMS in the probe liquids.[17c,d,20] Nonetheless, as the CA hysteresis values decrease overall as a result of heating the substrate, the TAs for 3 μL drops of *n*-hexadecane and *n*-dodecane also decrease considerably, from 5.0° and 3.8° at 25 °C, to 2.2° and 1.8°, respectively, at 70 °C, despite the surface exhibiting a statically oleophilic property! IR-RAS spectra of the PDMS brush film that were acquired at 25 °C and 70 °C displayed near-perfect overlap, which confirms that heating did not cause changes in the chemical conformational of PDMS (Figure S1 in the Supporting Information). Whereas the NP-LST probe liquids might interact with the D_4^H-derived monolayer beneath the PDMS film, the monolayer itself does not have any thermoresponsive dynamic dewetting properties. Furthermore, although there are obvious changes in the viscosity and surface tension of the probe liquids upon heating from 25 °C to 70 °C, such effects on the dynamic dewettability were deemed negligibly small (see Section S2 in the Supporting Information). We thus conclude that the liquid-like nature of polymer melt PDMS brush films and the rheological properties that accompany its molten state are the key factors in the preparation of smooth, nonperfluorinated surfaces with tunable thermoresponsive dynamic dewetting behavior of liquid droplets, regardless of the liquid surface tension.

In summary, by employing PDMS brush films that consist of low-MW polymer chains, we have successfully demonstrated a controllable, dynamic dewetting behavior (CA hysteresis and TAs) of both HST and NP-LST liquid droplets. Our results offer clear evidence that the chemical, physical, and rheological properties of smooth PDMS brush films play key roles in the dynamic behavior of various probe liquids; in particular, the thermal effect on increasing the ease of motion of liquid droplets on the surface is truly remarkable. The principles we have demonstrated in this study are simple and effective, and provide a new technique for further fundamental scientific studies on the dynamic dewettability of a wide range of liquids, and the industrial applications thereof.

Experimental Section

Materials: 1,3,5,7-tetramethylcyclotetrasiloxane (D_4^H), Karstedt's catalyst (2.1–2.4 % Pt in xylene) and vinyl-terminated poly(dimethylsiloxane) (PDMS) polymer were purchased from Gelest Inc. and used as received. The PDMS polymer had a number-averaged MW of 6000 and viscosity of 100 cSt, as reported by the manufacturer. Hexane (96 + %, GC) and acetone (99.5 + %, GC) were purchased from Wako Inc. and used as received. Silicon (Si) wafer substrates ($10 \times 10 \times 0.5$ mm^3) were cut from n-type Si(1,0,0) wafers, and cleaned by UV/ozone treatment.

Grafting PDMS to the Si wafer: The cleaned Si wafer samples were exposed to D_4^H vapor in closed, 60 cm^3 PFA block digestion vessels (Savillex) in a N_2 atmosphere with less than 10 % relative humidity for 3 days at 80 °C.[8b] Each sample was rinsed with hexane, acetone, and water, in that order, to remove physisorbed D_4^H. The D_4^H-covered samples were immediately placed in glass scintillation vials and submerged in solutions of 20 vol % vinyl-terminated PDMS in hexane, with Karstedt's catalyst (ten parts per million Pt). Pt-catalyzed hydrosilylation was generally carried out for 3 days at 50 °C. The samples were then rinsed with copious amounts of hexane, acetone, and water, in that order, to remove unreacted bulk PDMS.

Characterization: CA measurements were performed with a CA goniometer (Kyowa Interface Science, CA-X). The θ_A and θ_R values were collected in Milli-Q water (10^{-18} Ω cm^{-1}) at room temperature (ca. 25 °C) as the probe liquid (ca. 3 μL) was added and withdrawn from the drop, respectively. The CA data (θ_A and θ_R values) were determined by averaging the values measured at three different locations on each surface. All values for each sample were in the range of ± 2°. Minimum TAs that were needed to set probe-liquid droplets (3 μL) in motion on the substrate were measured by using a tilt-angle meter (Kyowa Interface Science) at three different locations on each surface. All values for each sample were in the range of ± 0.2°. The substrates were heated by using a custom-made ceramic sample stage connected to a programmable temperature controller. The thermocouple was attached to the corner of the sample surface. Film thicknesses were determined by ellipsometry (Philips, PZ2000 equipped with a He-Ne laser (632.8 nm) with its incident angle fixed at 70°). The morphology of the samples was observed by atomic force microscope (AFM, XE-100, Park Systems) with a Si probe (Park Systems, 910M-NCHR; spring constant = 42 N m^{-1} and response frequency of 330 kHz) in tapping mode.

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[1] X. M. Li, D. Reinhoudt, M. Crego-Calama, *Chem. Soc. Rev.* **2007**, *36*, 1350 – 1368.

[2] a) A. Tuteja, W. Choi, M. L. Ma, J. M. Mabry, S. A. Mazzella, G. C. Rutledge, G. H. McKinley, R. E. Cohen, *Science* **2007**, *318*, 1618 – 1622; b) A. Tuteja, W. Choi, J. M. Mabry, G. H. McKinley, R. E. Cohen, *Proc. Natl. Acad. Sci. USA* **2008**, *105*, 18200 – 18205.

[3] J. P. Zhang, S. Seeger, *Angew. Chem.* **2011**, *123*, 6782 – 6786; *Angew. Chem. Int. Ed.* **2011**, *50*, 6652 – 6656.

[4] Surface tensions were obtained from the Landolt-Börnstein Database.

[5] a) H. J. Li, X. B. Wang, Y. L. Song, Y. Q. Liu, Q. S. Li, L. Jiang, D. B. Zhu, *Angew. Chem.* **2001**, *113*, 1793 – 1796; *Angew. Chem. Int. Ed.* **2001**, *40*, 1743 – 1796; b) Q. D. Xie, J. Xu, L. Feng, L. Jiang, W. H. Tang, X. D. Luo, C. C. Han, *Adv. Mater.* **2004**, *16*, 302 – 305; c) J. Zimmermann, M. Rabe, G. J. R. Artus, S. Seeger, *Soft Matter* **2008**, *4*, 450 – 452.

[6] a) L. C. Gao, T. J. McCarthy, *J. Am. Chem. Soc.* **2006**, *128*, 9052 – 9053; b) W. Chen, A. Y. Fadeev, M. C. Hsieh, D. Oner, J. Youngblood, T. J. McCarthy, *Langmuir* **1999**, *15*, 3395 – 3399; c) L. C. Gao, T. J. McCarthy, *Langmuir* **2006**, *22*, 2966 – 2967.

[7] A. Y. Fadeev, T. J. McCarthy, *Langmuir* **1999**, *15*, 3759 – 3766; A. Y. Fadeev, T. J. McCarthy, *Langmuir* **1999**, *15*, 7238 – 7243; A. Y. Fadeev, T. J. McCarthy, *Langmuir* **2000**, *16*, 7268 – 7274.

[8] a) A. Hozumi, T. J. McCarthy, *Langmuir* **2010**, *26*, 2567 – 2573; b) A. Hozumi, D. F. Cheng, M. Yagihashi, *J. Colloid Interface Sci.* **2011**, *353*, 582 – 587.

[9] T. S. Wong, S. H. Kang, S. K. Y. Tang, E. J. Smythe, B. D. Hatton, A. Grinthal, J. Aizenberg, *Nature* **2011**, *477*, 443 – 447.

[10] a) Y. Zushi, J. N. Hogarh, S. Masunaga, *Clean Technol. Environ. Policy* **2012**, *14*, 9 – 20; b) A. B. Lindstrom, M. J. Strynar, E. L. Libelo, *Environ. Sci. Technol.* **2011**, *45*, 7954 – 7961.

[11] S. Minko, M. Muller, M. Motornov, M. Nitschke, K. Grundke, M. Stamm, *J. Am. Chem. Soc.* **2003**, *125*, 3896 – 3900.

[12] a) X. Feng, J. Zhai, L. Jiang, *Angew. Chem.* **2005**, *117*, 5245 – 5248; *Angew. Chem. Int. Ed.* **2005**, *44*, 5115 – 5118; b) H. S. Lim, W. H. Lee, S. G. Lee, D. Lee, S. Jeon, K. Cho, *Chem. Commun.* **2010**, *46*, 4336 – 4338; c) R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe, *Nature* **1997**, *388*, 431 – 432.

[13] a) H. W. Xia, F. Xia, Y. C. Tang, W. Guo, X. Hou, L. Chen, Y. Hou, G. Z. Zhang, L. Jiang, *Soft Matter* **2011**, *7*, 1638 – 1640; b) T. L. Sun, G. J. Wang, L. Feng, B. Q. Liu, Y. M. Ma, L. Jiang, D. B. Zhu, *Angew. Chem.* **2004**, *116*, 361 – 364; *Angew. Chem. Int. Ed.* **2004**, *43*, 357 – 360.

[14] a) J. Lahann, S. Mitragotri, T. N. Tran, H. Kaido, J. Sundaram, I. S. Choi, S. Hoffer, G. A. Somorjai, R. Langer, *Science* **2003**, *299*, 371 – 374; b) B. Kakade, R. Mehta, A. Durge, S. Kulkarni, V. Pillai, *Nano Lett.* **2008**, *8*, 2693 – 2696; c) D. Tian, Q. Chen, F. Nie, J. Xu, Y. Song, L. Jiang, *Adv. Mater.* **2009**, *21*, 3744 – 3749.

[15] a) J. Stein, L. N. Lewis, Y. Gao, R. A. Scott, *J. Am. Chem. Soc.* **1999**, *121*, 3693 – 3703; b) P. W. Zheng, T. J. McCarthy, *Langmuir* **2010**, *26*, 18585 – 18590.

[16] a) W. J. Brittain, S. Minko, *J. Polym. Sci. Part A* **2007**, *45*, 3505 – 3512; b) J. W. Krumpfer, T. J. McCarthy, *Faraday Discuss.* **2010**, *146*, 103 – 111; J. W. Krumpfer, T. J. McCarthy, *Langmuir* **2011**, *27*, 11514 – 11519.

[17] a) A. J. Barlow, G. Harrison, J. Lamb, *Proc. R. Soc. London Ser. A* **1964**, *282*, 228 – 251; b) B. Arkles, G. Larson, *Silicon Compounds: Silanes & Silicones*, Gelest, Morrisville, PA, **2008**, pp. 462 – 487; c) L. H. Sperling, *Introduction to Physical Polymer Science*, 4th ed., Wiley, Hoboken, **2006**, pp. 71 – 196, 358 – 365, 507 – 556; d) J. E. Mark, *Polymer Data Handbook*, Oxford University Press, New York, **1999**, pp. 411 – 435.

[18] K. A. Wier, L. C. Gao, T. J. McCarthy, *Langmuir* **2006**, *22*, 4914 – 4916.

[19] L. C. Gao, T. J. McCarthy, *Langmuir* **2006**, *22*, 6234 – 6237; L. C. Gao, T. J. McCarthy, *Langmuir* **2009**, *25*, 14105 – 14115.

[20] a) H. Huang, J. Y. Chung, A. J. Nolte, C. M. Stafford, *Chem. Mater.* **2007**, *19*, 6555 – 6560; b) U. Raviv, S. Glasson, N. Kamph, J. F. Gohy, R. Jérôme, J. Klein, *Nature* **2003**, *425*, 163 – 165; c) R. C. Advincula, W. J. Brittain, K. C. Caster, J. Rühe, *Polymer Brushes*, Wiley-VCH, Weinheim, **2004**, p. 55.

[21] C. Luap, W. A. Goedel, *Macromolecules* **2001**, *34*, 1343 – 1351.