

Hyperbranched Polymer Layers as Multifunctional Interfaces

A. Sidorenko, X. W. Zhai, A. Greco, and V. V. Tsukruk*

Materials Science & Engineering Department, Iowa State University, Ames, Iowa 50011

Received October 9, 2001. In Final Form: December 17, 2001

We suggest a simple, one-step procedure to prepare a homogeneous functional polymer layer grafted to a silicon oxide substrate. We demonstrate that robust and uniform nanoscale layers can be fabricated from the functionalized hyperbranched polymer with dual nature of terminal branches: alkyl chains combined with epoxy-functionalized chains. A branched chemical architecture with multiple epoxy groups provides the grafting capability inducing surface functionality along with simultaneous hydrophobization of the surface. We suggest the monolayer structure of these grafted films. These hyperbranched monolayers are thicker than conventional alkyl-chain self-assembling monolayers (SAMs) and demonstrate elastic properties typical for cross-linked polymer layers. The surface is composed of epoxy groups randomly distributed within alkyl peripheral branches. Grafted hyperbranched polymer layers are homogeneous on a nanoscale without signs of the microphase separation and heterogeneous domain surface structures usually observed for two-component SAMs.

Introduction

An introduction of surface chemical functional groups in the form of the molecular interfacial layers is considered an effective approach in alternating the surface properties of solid materials. This approach allows fine tailoring of the surface properties on a molecular scale without affecting the bulk properties of materials. It offers new routes to tuning surface adsorption of biological species,^{1–3} grafting of multilayered films and ultrathin polymer films,^{4–7} variation/patterning of surface amphiphilicity,^{8,9} modification of surface friction and nanomechanical properties,^{10–13} introduction of variable adhesive properties,¹⁴ and changing flow-governing surface properties.¹⁵ The major approach, which is widely used to date, is the fabrication of surface layers with different terminal groups

in the form of self-assembled monolayers (SAMs) composed of bifunctional organic molecules.^{9,16,17} Typically, short-chain molecules such as alkoxy-silanes and alkanethiols are used for the fabrication of functional SAMs with carboxyl, hydroxyl, amine, sulfate, and epoxy terminal groups on silicon, glass, mica, and gold surfaces.^{9,14,16}

Despite significant progress in the controlled modification of the surface properties and chemical surface reactivity, the functional SAMs showed some limitations, which cannot be easily overcome within the traditional approach. The most important drawback of this approach is its inability to provide surfaces with widely variable surface concentration of the functional groups. Dense, one-component SAMs give high surface concentration of the functional groups with the surface area close to 0.2 nm² per group. The attempt to change the surface concentration of the functional groups via their “dilution” with an additional component and the fabrication of multicomponent SAMs usually results in their nonuniform molecular structures caused by the microphase separation of different components.^{12,16} Another important circumstance is that the vast majority of SAMs are very thin layers with thickness, usually, within 1–2 nm. Under certain conditions, such layers do not screen completely solid substrates and do not prevent their direct interaction with environment. The attempts to increase the surface layer thickness by using longer chain molecules were not successful due to the fact that such SAMs become more disordered. Alternative usage of long-chain molecules lead to effective screening of the functional groups buried within random-coiled chains.

In our attempt to overcome these limitations and introduce a new type of anchoring interfacial layers with widely variable surface functionalities, we turned atten-

* To whom correspondence should be addressed: phone, 515-2946904; fax, 515-295444; e-mail: vladimir@iastate.edu.

(1) Wilbur, J. L.; Biebuyck, H. A.; MacDonald, J. C.; Whitesides, G. M. *Langmuir* **1995**, *11*, 825.

(2) Garrison, M. D.; McDevitt, T. C.; Luginbühl, R.; Giachelli, C. M.; Stayton, P.; Ratner, B. D. *Ultramicroscopy* **2000**, *82*, 193. Sheller, N. B.; Petrash, S.; Foster, M. D.; Tsukruk, V. V. *Langmuir* **1998**, *14*, 4535.

(3) Kenausis, G. L.; Vörös, J.; Elbert, D. L.; Huang, N.; Hofer, R.; Ruiz-Taylor, L.; Textor, M.; Hubbell, J. A.; Spencer, N. D. *J. Phys. Chem. B* **2000**, *104*, 3298. Feldman, K.; Hähner, G.; Spencer, N. D.; Harder, P.; Grunze, M. *J. Am. Chem. Soc.* **1999**, *121*, 10134.

(4) Zhao, M.; Zhou, Y.; Bruening, M. L.; Bergbreiter, D. E.; Crooks, R. M. *Langmuir* **1997**, *13*, 1388.

(5) Sidorenko, A.; Minko, S.; Schenk-Meuser, K.; Duschner, H.; Stamm, M. *Langmuir* **1999**, *15*, 8349.

(6) Tokuhisa, K.; Zhao, M.; Baker, L. A.; Phan, V. T.; Dermody, D. L.; Garcia, M. E.; Peez, R. F.; Crooks, R. M.; Mayer, T. M. *J. Am. Chem. Soc.* **1998**, *120*, 4492. Zgao, M.; Liu, Y.; Crooks, R. M.; Bergbreiter, D. E. *J. Am. Chem. Soc.* **1999**, *121*, 923.

(7) Luzinov, I.; Julthongpipit, D.; Tsukruk, V. V. *Macromolecules* **2000**, *33*, 7629. Luzinov, I.; Julthongpipit, D.; Tsukruk, V. V. *Polymer*, **2001**, *42*, 2267.

(8) Folkers, J. P.; Laibinis, P. E.; Whitesides, G. M. *Langmuir* **1992**, *8*, 1330. Maoz, R.; Netzer, L.; Gun, J.; Sagiv, J. *J. Chem. Phys.* **1988**, *85*, 1059.

(9) Noy, A.; Vezenov, D. V.; Lieber, C. M. *Annu. Rev. Mater. Sci.* **1997**, *27*, 381.

(10) Noy, A.; Frisbie, C. D.; Rozsnyai, L. F.; Wrighton, M. S.; Lieber, C. M. *J. Am. Chem. Soc.* **1995**, *117*, 7943. Vezenov, D. V.; Noy, A.; Rozsnyai, L. F.; Lieber, C. M. *J. Am. Chem. Soc.* **1997**, *119*, 2006.

(11) Green, J. B.; McDermott, M. T.; Porter, M. D.; Siperko, L. M. *J. Phys. Chem.* **1995**, *99*, 10960. McDermott, M. T.; Green, J. B.; Porter, M. D. *Langmuir* **1997**, *13*, 2504.

(12) Marti, A.; Hähner, G.; Spencer, N. D. *Langmuir* **1995**, *11*, 4632. van der Vegte, E. W.; Hadziioannou, G. *Langmuir* **1997**, *13*, 4357. Beake, B. D.; Leggett, G. J. *Langmuir* **2000**, *16*, 735.

(13) Tsukruk, V. V.; Bliznyuk, V. N. *Langmuir* **1998**, *14*, 446. Tsukruk, V. V.; Nguyen, T.; Lemieux, M.; Hazel, J.; Weber, W. H.; Shevchenko, V. V.; Klimenko, N.; Sheludko, E. In *Tribology Issues and Opportunities in MEMS*; Bhushan, B., Ed.; Kluwer Academic Publishers: Dordrecht, 1998; p 608.

(14) Tsukruk, V. V. *Adv. Mater.* **2001**, *13*, 95.

(15) Xia, Y.; Whitesides, G. M. *Angew. Chem.* **1998**, *37*, 550.

(16) Ulman, A. *Introduction to Ultrathin Organic Films*; Academic Press: San Diego, CA, 1991. Tsukruk, V. V. *Prog. Polym. Sci.* **1997**, *22*, 247.

(17) Barness, Y.; Gershevit, O.; Sekar, M.; Sukenik, C. N. *Langmuir* **2000**, *16* (1), 247.

tion to functional dendrimers and hyperbranched polymers with highly branched, treelike chemical microstructure of macromolecules.^{18–21} These polymers, if grafted properly to a surface, form well-ordered and uniform layers with the majority of terminal functional groups located at the layer surface and with molecules being in either globular or compressed globular conformation.²⁰ This property has been used to fabricate grafted monolayers and multilayered self-assembled films, composite layers from dendrimers and alkyl SAMs.^{4,6,21} The presence of multiple anchoring groups in the terminal branches chemically attached to one core makes these molecules unique in their multiple grafting ability. One can expect the formation of the uniform surface layer with suppressed tendency toward microphase separation of dissimilar multifunctional arms due to chemical constraints imposed by the branched microstructure. Variation of chemical functionalities of the different branches can be an effective route to tailor surface properties of such layers without a risk of having heterogeneous surfaces. On the other hand, having molecules with higher molecular weight as a single building block, we can fabricate “thick” (3–10 nm) layers, which can possess enhanced micromechanical properties characteristic of macromolecular materials rather than low molar mass organics.

In this Letter, we report results on the fabrication of such an anchoring layer from a hyperbranched polyester (EHBP) with 32 terminal branches including 11 epoxy-functionalized arms (Figure 1). The polymer is based on tetrafunctional ethoxylated pentaerythritol extended with the third generation hyperbranched polyester of dimethylolpropionic acid.^{22,23} The hyperbranched core (G3) is functionalized by long alkyl chains (from C₁₂ to C₂₄) with secondary epoxy groups embedded in the fraction of branches of the hyperbranched shell (see an idealized chemical formula in Figure 1). The ratio of epoxy-containing branches and alkyl branches is approximately 1:2. The dual nature of the terminal branches was considered critical for one-step hydrophobization and functionalization of a silicon oxide surface. On the other hand, it was expected that chemical constraints imposed by their chemical attachment to a single core would prevent microphase separation of dissimilar constituents and, thus, suppress the fabrication of highly heterogeneous

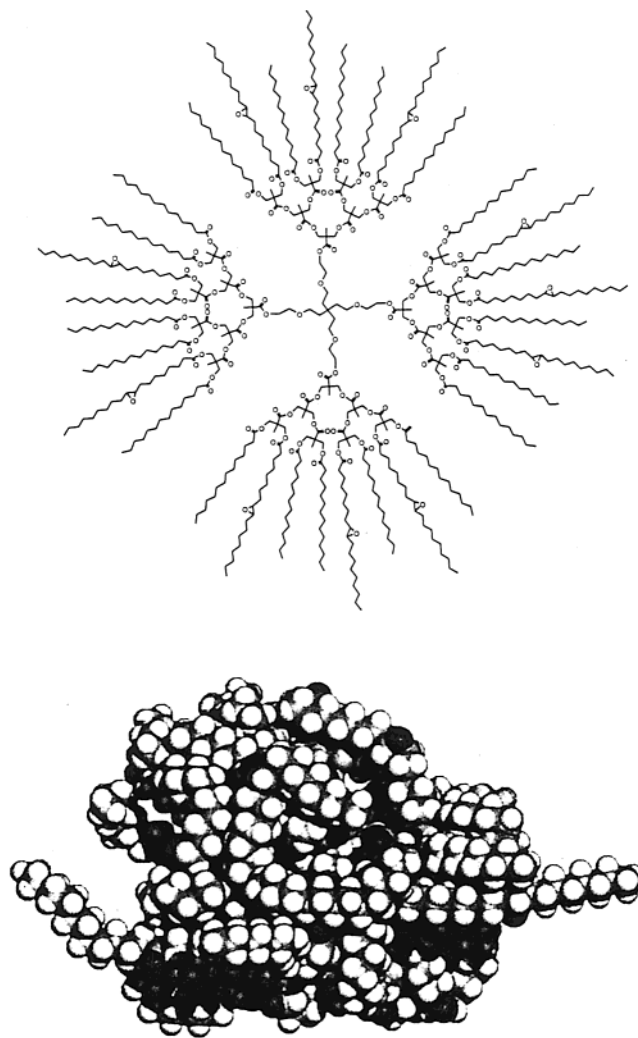


Figure 1. Idealized chemical structures of the hyperbranched polyester with epoxy groups in terminal branches (EHBP) (top). The molecular model of a dense packed randomized conformation of the EHBP molecule (bottom).

surface structures usually observed for multicomponent SAMs, including recently introduced dendrimers/alkyl SAMs.^{6,16}

It is worth noting that the chemical structure presented in Figure 1 reflects the idealized structure of hyperbranched molecules. As is well-known, in hyperbranched materials internal cyclization and other irregular branching can occur, hence, resulting in internal defects such as random branching, variable chemical composition, and wide molecular weight distribution.²¹ However, our recent direct measurements of the molecular volume demonstrated that, overall, theoretical models are a reasonable approximation of hyperbranched polyesters with defects playing a noticeable but not critical role in overall shape and behavior of molecules.²⁴

Experimental Section

The substrates were atomically smooth silicon wafers of the {100} orientation with one side polished (Semiconductor Processing Co.). Silicon wafers were treated in an ultrasonic bath for 10 min followed by a “piranha” solution (30% concentrated hydrogen peroxide, 70% concentrated sulfuric acid) bath for 1 h. After the “piranha” bath, the samples were rinsed several times

(18) Newkome, G. R.; Moorefield, C. N.; Vogtle, F. *Dendritic Molecules*; Wiley-VCH: Weinheim, 1996. Frechet, J. M. J.; Hawker, G. J.; Gitsov, I.; Leon, J. W. *J. Macromol. Sci., Pure Appl. Chem.* **1996**, *A33* (10), 1399. Jansen, J. F.; de Brabander-van den Berg, E. M.; Meijer, E. W. *Science* **1994**, *266*, 1226. Tomalia, D. A. *Adv. Mater.* **1994**, *6*, 529. Percec, V.; Kawasumi, M. *Macromolecules* **1994**, *27*, 4441. Tomalia, D. A.; Naylor, A. M.; Goddard, W. A., III *Angew. Chem.* **1990**, *29*, 138. Hawker, C. J.; Lee, R.; Frechet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, 4583. Hawker, C. J.; Frechet, J. M. J. *Macromolecules* **1990**, *23*, 4726. Frechet, J. M. J. *Science* **1994**, *263*, 1711. Tomalia, D. A. *Adv. Mater.* **1994**, *6*, 529. Tokuhisa, H.; Crooks, R. M. *Langmuir* **1997**, *13*, 2172.

(19) Hierlemann, A.; Campbell, J. K.; Baker, L. A.; Crooks, R. M.; Ricco, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 5323. Wells, M.; Crooks, R. M. *J. Am. Chem. Soc.* **1996**, *118*, 3988. Mackay, M. E.; Carmezini, G.; Sauer, B. B.; Kampert, W. *Langmuir* **2001**, *17*, 1708.

(20) Tsukruk, V. V.; Rinderspacher, F.; Bliznyuk, V. N. *Langmuir* **1997**, *13*, 2171. Bliznyuk, V. N.; Rinderspacher, F.; Tsukruk, V. V. *Polymer* **1998**, *39*, 5249.

(21) Hult, A.; Johansson, M.; Malmstrom, E. *Adv. Polym. Sci.* **1999**, *143*, 1. Ihre, H.; Johansson, M.; Malmstrom, E.; Hult, A. *Adv. Dendritic Macromol.* **1996**, *3*, 1. Benthem, R. A.; Meijerink, N.; de Koster, E.; Muscat, D.; Froehling, P. E.; Hendricks, P. H.; Vermeulen, C. J.; Zwartkruis, T. J. *Macromolecules* **2001**, *34*, 3559. Kim, Y. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 1685. Voit, B. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2505. Zhang, X.; Klein, J.; Sheiko, S.; Muzafarov, A. M. *Langmuir* **2000**, *16*, 3893.

(22) Mezzenga, R.; Boogh, L.; Manson, J.-A. E.; Pettersson, B. *Macromolecules* **2000**, *33*, 4373.

(23) Pettersson, B. WO Patent 9723538, 1997.

(24) Sidorenko, A.; Zhai, X. W.; Peleshanko, S.; Greco, A.; Shevchenko, V. V.; Tsukruk, V. V. *Langmuir* **2001**, *17*, 5924.

Table 1. Characteristics of the Hyperbranched Polyesters

	theoretical M_n	experimental M_n	polydispersity index	contact angle, deg	thickness, nm	theoretical length/diameter
EHBP	11290 ^b	11500	2.6	82	4.0–4.8	3.4–4.2
G3	3604 ^b	3400	1.9	42	3.0 ^c	1.7–1.9
EpoxySAM ^a	236	NA	NA	52	0.6–0.9	0.9

^a Data from ref 35. ^b Calculated for chemical formulas presented in Figure 1. ^c Bilayer thickness (ref 24).

Table 2. XPS Data on the Chemical Composition of EHBP Layer (for detail discussion see ref 28)

conditions	chemical composition for different carbon atoms shown in boldface		
	alkyl chains, %	oxygen-containing core fragments, %	
	C–H₂	C–O–C	O–C=O and C–O–C
idealized chemical structure (Figure 1)	68.2	9.1	22.7
composition, topmost 2 nm	66.6	9.2	24.2
composition, whole film	60.0	10.9	29.3

with “Nanopure” water (resistivity of 18 M Ω cm) and dried under the stream of dry nitrogen. All sample preparations were performed inside a Cleanroom 100 facility (Contamination Control Products, Supply King, Inc.). The commercially available epoxy-functional hyperbranched polyester and hydroxyl-terminated hyperbranched polyester of third generation (Figure 1) were donated by Perstorp Polyols Inc. The EHBP materials were treated to remove traces of unreacted alkyl chains observed in preliminary gel permeation chromatography (GPC) measurements as follows. The solution of EHBP in 1-butanol (1:3) was poured in a 3-fold excess of methanol and shaken intensely for several minutes. The emulsion obtained was allowed to separate overnight in two layers. The bottom layer was taken out and placed in a vacuum at 50 °C for 24 h to remove the alcohols. Grafting on the silicon substrate was carried out from both solution and melt. For the solution grafting, the substrate was kept in dilute solutions for different times and rinsed thoroughly followed by drying before characterization. For the melt grafting, the 10% THF solution was deposited on the substrate by spin-coating to form a film of 300 nm thickness. Specimens were immediately placed in an oven in Ar atmosphere within a temperature range from 40 to 150 °C for different times. The residual ungrafted polymer was removed by multiple washing with THF in an ultrasonic bath at 50 °C.

Initially, GPC measurements of the polymer samples were carried out to test molecular weight distribution. These measurements were conducted in THF solutions using a Waters GPC. The thickness of grafted layers was measured with a Compel ellipsometer (InOmTech, Inc.) according to the usual procedure.²⁴ Surfaces were also examined by static contact angle (sessile droplet) measurements using a custom-built instrument combining a microscope and a digital camera. Imaging of the grafted layers was performed with an atomic force microscope (AFM) Dimension-3000 (Digital Instrument, Inc.) in the “light” tapping mode according to an experimental procedure described in detail elsewhere.^{25,26} The volume/dimension calculations of molecules in the conformation with minimum energy were completed after a dynamic mechanics execution of the initially fully extended conformation at an elevated temperature followed by annealing. Molecular simulations were performed on a SGI workstation with Cerius² 3.9 program.²⁷ Multiple repetitions of the molecular simulations with different initial conditions showed similar densely packed states with close parameters.

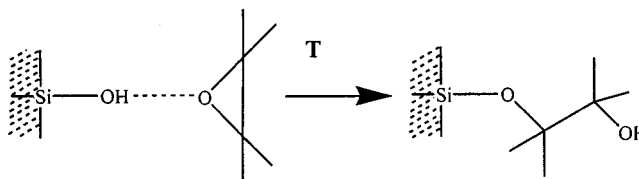
Results and Discussion

GPC analysis of the G3 and EHBP compounds showed a number average molecular weight of 3400 and 11500 g/mol, respectively (Table 1). Although GPC data should be treated with care, the experimentally measured molecular weights of both compounds were fairly close to the

values evaluated from the idealized models presented in Figure 1. Even more important is that X-ray photoelectron spectroscopy (XPS) results showed a good agreement of the experimental chemical composition within the grafted polymer layer with the element ratio calculated from the idealized chemical structure (Table 2) (detail discussion of XPS data will be published elsewhere²⁸). Alkyl chain content was lower than one expected for the idealized structure indicating that a vast majority of branches bears peripheral alkyl chains. Respectively, the measured amount of oxygen-containing segments was proportionally higher reflecting modest internal cyclization. Therefore, we concluded that in the real chemical structure, three to four terminal alkyl chains were missing due to internal cyclization and defects.

The solution adsorption of both compounds on the silicon substrate was studied according to the procedure applied earlier to higher generation hyperbranched polyesters.²⁴ For the hyperbranched core, G3, we observed the formation of a uniform layer with the thickness of 3.0 nm. As we discussed earlier for analogous hyperbranched polyesters, these layers are stabilized by a network of hydrogen bonding between surface SiOH groups and terminal hydroxyl groups of the multiple branches.²⁴ Unlike G3, epoxy-functional hyperbranched molecules of the EHBP compound showed no signs of the formation of the adsorbed monolayers from solution. Weak interactions between hydrophobic alkyl chains and the hydrophilic silicon surface were, obviously, not sufficient for the formation of the monolayer that strongly adhered to the substrate.

Therefore, we exploited chemical grafting from melt to fabricate the EHBP monolayer by using the known reaction between silanol and epoxy groups at elevated temperatures.^{29–31}



In the course of this study, we varied grafting conditions, such as solvent nature, concentration of the solution, spin-

(28) Sidorenko, A.; Zhai, X. W.; Simon, F.; Pleul, D.; Tsukruk, V. V. Submitted for publication in *Macromolecules*.

(29) Kalal, J.; Tlustakova, M. *Acta Polym.* **1979**, *30*, 40.

(30) Xue, G.; Ishida, H.; Koenig, J. E. *Angew. Makromol. Chem.* **1986**, *140*, 127.

(31) Hortschansky, P.; Heublein, G. *Makromol. Chem.* **1991**, *192*, 1535.

(25) Tsukruk, V. V. *Rubber Chem. Technol.* **1997**, *70* (3), 430.

(26) Ratner, B.; Tsukruk, V. V., Eds. *Scanning Probe Microscopy in Polymers*; ACS Symposium Series 694; American Chemical Society: Washington, DC, 1998.

(27) Cerius² 3.9, San Diego: Molecular Simulations Inc., 1999.

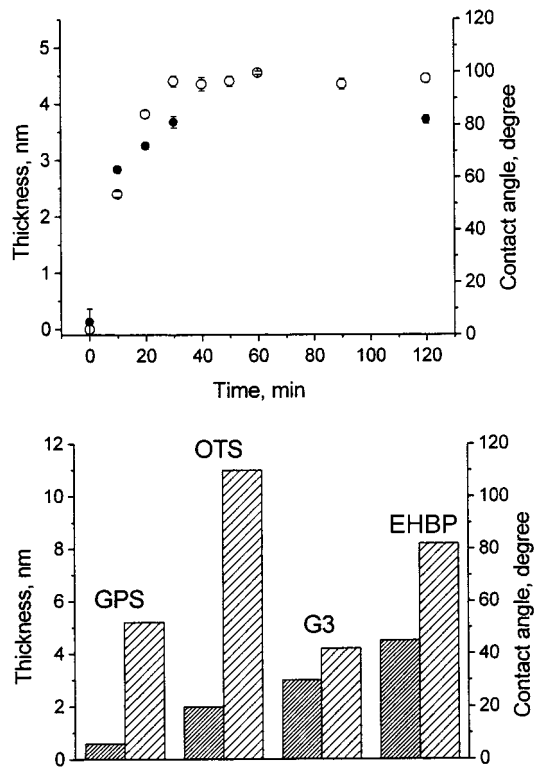


Figure 2. (top) Kinetics of grafting of the EHPB polymer from melt to a silicon surface at 120 °C as monitored with ellipsometry (open circles) and contact angle measurements (filled circles). (bottom) Comparison of contact angles and thicknesses (diagonal columns) of the monolayers obtained in this work with epoxy-terminated SAM (GPS, ref 35) and alkyl-terminated SAM (OTS, ref 32).

coating conditions for initial film, and grafting time and temperature, to avoid frequently occurring dewetting phenomena and to ensure the formation of a uniform layer. As we observed, initial film preparation from THF solution followed by chemical grafting at 120 °C resulted in steady growth of the grafted film with its thickness reaching the ultimate value of 4.3 nm (Figure 2). This value is reached after 30 min of reaction and stays unchanged for a longer time up to several hours. The contact angle also reached the constant value of 82° within the same time interval (Figure 2).

An AFM image of the EHPB film grafted this way showed very smooth and homogeneous surface coverage with the microroughness of 0.2 nm within a $1 \times 1 \mu\text{m}$ surface area, which was comparable to the atomically flat surface of the silicon substrate (Figure 3). Uniform phase images indicated homogeneous chemical composition of polymer layers without any traces of domain structures usually observed in two-component polymer nanofilms. This, indeed, suggested that chemical constraints imposed by the dendritic-type architecture on spatial distribution of epoxy-containing branches and alkyl chains in fact suppressed a natural tendency to the microphase separation of dissimilar fragments. This observation is in sharp contrast with the highly heterogeneous surface structure proposed for composite layers from dendrimers and alkyl-chain SAMs.⁶

The grafted hyperbranched layer was very stable and sustained high shear force, which could easily damage physically adsorbed layers of hyperbranched polymers without epoxy functionalities. Only very high normal forces, close to 1 μN , damaged the grafted layer by scrapping the material within the surface area scanned in the contact mode as demonstrated in Figure 3. This

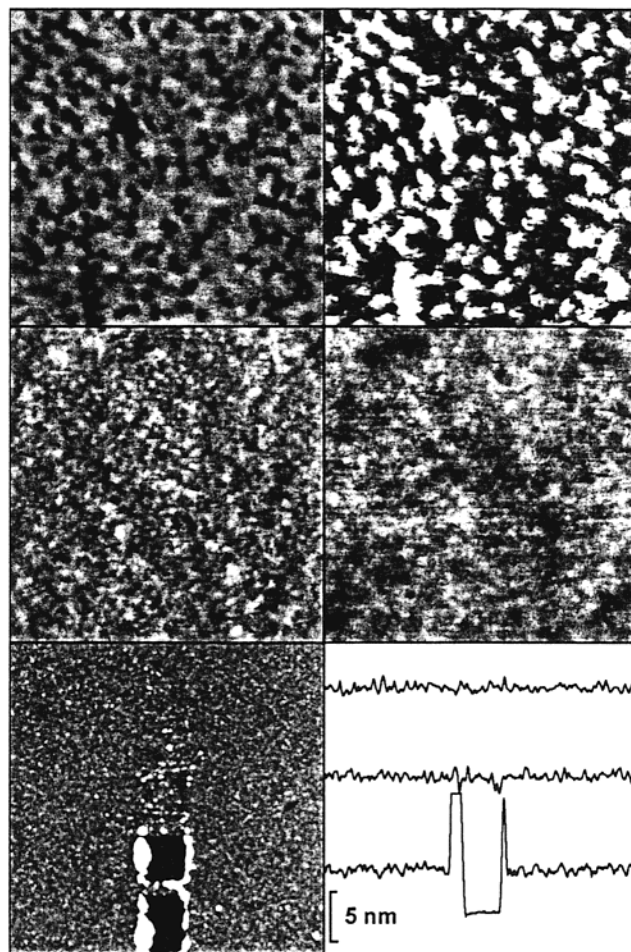


Figure 3. AFM images of grafted monolayers of EHPB with commonly occurring dewetting pattern (top) and uniform monolayer obtained under optimal grafting conditions (middle): right is topography, left is a phase image; scan size $1 \times 1 \mu\text{m}$; height scale is 3 nm; phase scale is 30°. (bottom) Wearing test showing sequential scanings with increasing forces from top to bottom (left, topographical image, see $1 \times 1 \mu\text{m}$ tracks in the center of the image), scan size is $6 \times 6 \mu\text{m}$. (bottom right) A cross section of the worn areas.

level of the anchoring strength to the substrate is typical for chemically grafted polymer and organic layers.^{7,32} The thickness of the layer, measured from the depth of the through hole, was 4.5 nm, which is in good agreement with the 4.3 nm value obtained from ellipsometry measurements. The thickness of the layer was close to the diameter of the molecules with densely packed segments (Table 1, Figure 1).

Several arguments support the suggestion that these films are, indeed, monolayers composed of a single layer of densely packed molecules. First, the values for the layer thickness obtained from two independent techniques, AFM (direct measurement) and ellipsometry (calculated based on assumption that refractive index and, thus, density of the layer, are identical to the bulk state), coincide within experimental accuracy. This indicates dense packing of molecular branches within the layer and excludes loose packing, significant porosity, or exceeding cross-linking. Second, the thickness measured is very close to the average molecular dimension of densely packed molecules estimated from molecular modeling. As known, direct correlation between molecular dimensions and the thickness

(32) Luzinov, I.; Julthongpipit, D.; Gorbunov, V.; Tsukruk, V. V. *Tribol. Int.* **2001**, *35*, 335.

of grafted polymer films is observed for both monodisperse and polydisperse functionalized macromolecules and serves as an indication of the monolayer formation (see results and review of data for molecular weight dependence of grafted polymer in ref 33). We did not test here a range of hyperbranched polymers with different molecular dimensions but we do not believe that the correlation observed is a mere coincidence. Third, XPS data on surface distribution of chemical composition (for detail description see ref 28) indicated slightly preferred localization of alkyl tails within the topmost surface layer with the oxygen-enriched core to be located closer to the surface (Table 2). Such preferential distribution confirms slightly stretched conformation of the molecules and rules out a random cross-linked network of multiple hyperbranched molecules with their cores and terminal chains randomly distributed across the film.

Indeed, the only alternative suggestion to the monolayer can be the formation of disordered films composed of significantly flattened hyperbranched molecules cross-linked with each other. Considering constraints imposed by the treelike architecture of this polymer, these molecules will possess a thickness of 1–2 nm even in a highly compressed state. Therefore, two–four highly flattened molecules with average molecular weight would be required to compose a layer of a total thickness of 4.5 nm. This model, however does not explain why the value of the saturated thickness of 4.5 nm (see Figure 1 for variable conditions) is close to the average dimension of molecular chains. Within this model, this should be treated as a pure coincidence. Indeed, saturation at this thickness cannot be explained easily because it suggests that the thickness is controlled by continuous cross-linking of neighboring molecules in melt. It cannot be explained why the cross-linking process stops at two–four molecules and is not propagating further in melt if reaction time increases manifold (Figure 2). Moreover, the major suggestion of this model about the flattened state of hyperbranched polymers contradicts a general trend observed for compliant dendritic molecules at interfaces.¹⁴ Strong interfacial interactions between peripheral groups and the surface are required for significant flattening of dendritic molecules (e.g., hydroxyl-terminated dendrimers on silicon oxide surfaces). In our case, interactions between hydrophobic alkyl tails (about 70% of total volume) and the hydrophilic, hydroxyl-terminated silicon oxide surface is so weak that it is not sufficient even for the formation of a physically adsorbed layer from solution. A very low level of interfacial interactions cannot be considered a significant driving force for the flattening of hyperbranched polymers.

From this consideration, it became clear that the epoxy functional groups should be partially “used” for the surface grafting with some fraction to be excluded from the interaction with the surface due to significant steric constraints for complete flattening of the molecules. The measured value of the contact angle for the monolayer was below the 110° expected for fully alkyl-terminated surface that indicated significant surface presence of the epoxy groups (Table 1, Figure 2). To evaluate the fraction of the epoxy groups on the layer surface, we used the Cassie equation for the estimation of the surface chemical

composition.³⁴ We excluded the silicon surface and the hyperbranched core from the consideration due to the fact of the complete surface coverage should screen these constituents. Therefore, we considered epoxy groups and alkyl chains as two major components affecting the surface properties.

Under these assumptions, we applied the Cassie equation to the two-component surface using the contact angle values of 110° and 52° for the alkyl and epoxy-terminated surfaces, respectively. These values were obtained earlier for alkyl and epoxy-terminated SAMs (Table 1).^{33,35} As a result of this estimation, we obtained a surface fraction of the epoxy group of about 40% and the surface area per epoxy group is close to 0.5 nm². Taking into account that the ratio of the epoxy-containing branches to the alkyl branches is closer to 1:2 and assuming that half of the terminal branches are located on the surface, we can estimate that more than approximately one-third of epoxy groups is not exposed on the surface. These groups, obviously, can participate in grafting of the hyperbranched layer to the silicon substrate.

Conclusion

In conclusion, we suggested a simple, one-step grafting procedure to prepare functionalized uniform polymer monolayers firmly tethered to the silicon oxide surface. We demonstrated that robust, complete, and uniform layers grafted to the silicon surfaces can be fabricated from the epoxy-functionalized hyperbranched polymer containing both alkyl chains and epoxy-containing terminal branches. We suggested that these layers are, indeed, monolayers composed of densely packed molecules in close to globular conformation. These monolayers were thicker than alkyl-based SAMs (4.5 nm versus 1–2 nm) and demonstrated enhanced micromechanical elastic properties typical for cross-linked and grafted polymer layers. We estimated that about 40% of surface area was occupied by epoxy groups distributed within alkyl branches without any signs of microphase separation usually observed for two-component SAMs. A further study of microstructure and properties of these functional layers including detailed XPS and micromechanical analyses will be published elsewhere.²⁸ We can speculate that expansion of this approach toward application of dendrimers and hyperbranched polymers with different types of functional terminal groups will allow fabrication of a new family of robust nanoscale coatings with widely variable surface functionality.

Acknowledgment. This study is funded by the National Science Foundation, DMR-0074241 Grant. The authors are grateful to P. D. Bloom and V. Sheares for GPC analysis, S. Minko and S. Peleshanko for useful discussions and technical assistance, and F. Simon and D. Pleul for providing XPS data. The authors also thank Jeffrey Jones (Perstorp Polyols, Toledo, Ohio) and Birger Midelf (Perstorp Specialty Chemicals AB, Sweden) for sample donation and useful technical discussion on chemical composition of these compounds.

LA011526F

(34) Adamson, A. W. *Physical Chemistry of Surfaces*; John Wiley & Sons: New York, 1990.

(35) Tsukruk, V. V.; Luzinov, I.; Julthongpipit, D. *Langmuir* **1999**, *15*, 3029. Luzinov, I.; Julthongpipit, D.; Liebmann-Vinson, A.; Cregger, T.; Foster, M. D.; Tsukruk, V. V. *Langmuir* **2000**, *16*, 504.

(33) Luzinov, I.; Julthongpipit, D.; Malz, H.; Pionteck, J.; Tsukruk, V. V. *Macromolecules* **2000**, *33*, 1043.