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Amphiphilic and Hydrophobic Surface Patterns Generated from Hyperbranched Fluoropolymer/Linear Polymer Networks: Minimally Adhesive Coatings via the Crosslinking of Hyperbranched Fluoropolymers

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ABSTRACT: Hyperbranched fluoropolymers (HBFPs), based on benzyl ether linkages and having a large number of pentafluorophenyl chain ends, were crosslinked by a reaction with diamino-terminated poly(ethylene glycol) (PEG) or diamino-terminated poly(dimethyl siloxane) (PDMS) to form hyperbranched-linear copolymer networks of different compositions, structures, and properties. The crosslinking reactions involved the nucleophilic aromatic substitution of the pentafluorophenyl *para*-fluorines of HBFP by the amine functionalities of the respective telechelic linear segments. The contact angles, differential scanning calorimetry, thermogravimetric analysis, tensile measurements, and atomic force microscopy (AFM) were used to characterize the resulting network film samples. The surface wettability of the crosslinked materials was affected by the nature and amount of the linear polymer crosslinking agent employed. Amphiphilic polymer networks were formed by the incorporation of diamino-terminated PEG as a crosslinker, whereas diamino-terminated PDMS produced polymer networks of a hydrophobic character. The mechanical properties improved upon crosslinking, as measured by tensile testing. The mechanical integrity of the films was also found to improve upon crosslinking, as measured by AFM machining protocols. The AFM images revealed topographical morphologies that appeared to be the result of phase segregation of HBFP from PEG or PDMS; the dimensions of the phase-segregated domains were dependent on the stoichiometry of HBFP to the linear polymer and the thickness of the coating. As the content of PEG increased, fouling by human fibrinogen, used as a model protein, decreased. Further studies are in progress to determine the effects of the surface composition, morphology, and topography on the biofouling characteristics.

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Keywords: amphiphiles; coatings; crosslinking; hyperbranched; phase separation; protein adsorption

INTRODUCTION

The global objectives of the work reported herein include the development of synthetic methodolo-

gies that allow for the preparation of polymer coatings that inhibit the settlement of marine organisms. Because the primary mode of attachment of marine organisms to a surface involves the secretion of glycoprotein adhesives,^{1,2} our design of minimally adhesive materials, capable of preventing the attachment and promoting the release of a broad range of organisms, is based on the creation of a complex surface profile on the size scale of the proteins themselves, the

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nanoscale regime. It is hypothesized that surfaces that exhibit nanoscopically resolved morphological and topographical surface domains will be capable of inhibiting protein adsorption. The surface complexity is designed to include the composition, morphology, and topography, and it is supported by a large number of studies that indicate that the surface charge,^{3,4} wettability (hydrophobicity/hydrophilicity),^{5,6} and other surface chemistries⁷ that influence nonspecific molecular interactions (e.g., the presence of hydrogen-bonding donors or acceptors)⁸ affect the adsorption of proteins.^{9,10}

The synthetic methodology that is described for the preparation of robust materials that present a complex surface profile relies on the phase segregation of polymer blends. This strategy has been applied to impart (partial) surface hydrophilicity to hydrophobic membranes, and resistance toward protein adsorption has been realized for self-organizing blends of amphiphilic comb polymers with poly(vinylidene fluoride).^{11,12} However, the key difference in the current approach is the application of covalent crosslinking reactions to reinforce the materials. Given our interest in the generation of highly complex nanoscale surface features, composite crosslinked networks were prepared from combinations of polymers with different molecular architectures, physical properties, and chemical compositions, the phase segregation being driven by compositional and topological differences. Therefore, blends of hyperbranched fluoropolymers (HBFPs)¹³ and linear poly(ethylene glycol) (PEG) or poly(dimethyl siloxane) (PDMS), each with reactive chain-end functionalities, were studied. HBFPs offer the high solubility and low viscosity associated with highly branched polymer materials^{14–16} and also incorporate fluorocarbon character for low coefficients of friction (μ) and low adhesive forces (F_a).¹⁷ The selection of the linear polymers was based on the fact that surface coverage by PEG is well known to inhibit protein adsorption and PDMS has been commercialized as an antifouling and nontoxic coating.

The concept of crosslinked networks of hyperbranched polymers and linear polymers can be considered from two different perspectives, that is, the hyperbranched component serving as a highly functionalized crosslinking agent or the linear polymer serving to link together the hyperbranched globular macromolecules. Either perspective retains the commonality that the low-viscosity hyperbranched material is transformed

into a robust three-dimensional network. Such crosslinking schemes have been used in the study and application of hyperbranched polymers as components in coatings.^{18–22} The preparation of crosslinked composite coatings as hybrid hyperbranched–linear polymer networks is reported here, the surface features of which are controlled by the coating composition and the coating thickness. The initial results from protein adsorption studies are also described.

EXPERIMENTAL

Measurements

IR spectra were obtained with a Mattson Polaris spectrometer for samples in the form of thin films on NaCl or KBr disks. For the characterization of the soluble precursors, solution-state NMR spectroscopy was employed: ¹H NMR spectra were recorded on solutions in CDCl₃ on a Varian Unity 300-MHz spectrometer with the solvent proton signal as a reference, ¹³C NMR spectra were recorded at 75.4 MHz on solutions in CDCl₃ on a Varian Unity 300 spectrometer with the solvent carbon signal as a reference, and ¹⁹F NMR spectra were recorded at 282.2 MHz on solutions in CDCl₃ on a Varian Unity 300 spectrometer with external CFC₃ as a standard. Size exclusion chromatography (SEC) was conducted on a Hewlett–Packard series 1050 HPLC instrument with a Viscotek model 110 differential viscometer, a Wyatt MiniDawn low-angle laser light scattering detector, and a Hewlett–Packard 1047A refractive-index detector connected in series. SEC data analysis was performed with Viscotek (Houston, TX) Trisec software (version 2.70) and Trisec gel permeation chromatography/light scattering/viscometry (SEC) software (version 3.0). Two 5- μ m Polymer Laboratories PL gel columns (300 mm \times 7.7 mm) connected in series in order of increasing pore size (500 Å, mixed-bed C) were used with tetrahydrofuran (THF) distilled from CaH₂ as a solvent.

The sol–gel analysis was conducted on crosslinked samples prepared according to method I or II and retained on glass microscope slides after drying *in vacuo* for 2 days; the initial dry weight (W_0) was obtained. For the extraction of the soluble components, the samples were heated at reflux in THF for 20 h, placed into a thimble in a Soxhlet extractor, extracted with THF for 2 days, and then dried *in vacuo* until no

further reduction in their mass was observed (W_t). The molecular weight of the soluble component in THF was measured by SEC. The gel percentage was calculated as follows: gel percentage = $(W_t/W_0) \times 100\%$.

Contact angles were measured as static contact angles with the sessile drop technique²³ with a TanteC CAM micro-contact-angle meter and the half-angle measuring method. The contact angles of water (4 μ L) and hexadecane (4 μ L) were measured on the films at 30 s and 4 min after the drop application.

Differential scanning calorimetry (DSC) was conducted on a PerkinElmer DSC-4. The heating rate was 10 °C/min. Glass-transition temperatures (T_g 's) were measured as the midpoint of the inflection tangent during the third or subsequent heating scans. Melting temperatures (T_m 's) were measured as the onset of the melting endotherms. Thermogravimetric analyses (TGAs) were conducted on a PerkinElmer TGS-2 at a heating rate of 10 °C/min under nitrogen. The onset temperature for weight loss was the point at which two tangential lines in the TGA curves intersected. For both DSC and TGA, the PerkinElmer instruments were upgraded with the Instrument Specialists (Antioch, IL) PE temperature program interface, and data were acquired and analyzed with TA-PC software (version 2.11, Instrument Specialists).

Tensile tests were measured with an Instron 5583 machine (Instron, Inc., Canton, MA) with a video-monitored optical extensometer under ambient conditions. The crosshead rate was 0.1 in/min. Six specimens were tested for each sample. The tensile modulus was calculated from the initial slope of the stress-strain curve. The tensile strength and elongation were the values at the break point. Each of the sample films that was subjected to tensile testing was prepared according to method II.

Atomic force microscopy (AFM) experiments were performed with a Nanoscope III scanning probe microscope (Digital Instruments, Santa Barbara, CA). The polymer morphologies were examined in the tapping mode with a DI Multi-mode instrument under ambient conditions. The sample preparation was analogous to method I, except that the deposition of the reaction mixture of diisopropylethylamine (DIEA), HBFP, and PEG or PDMS was accomplished by the spin coating of a THF solution (15 μ L, 0.01 g/mL) onto freshly cleaved mica (New York Mica Co.). The samples were heated to effect crosslinking by the

same method used for the preparation of the crosslinked materials on glass slides (100 °C, 1 h) and were then stored *in vacuo* for 24 h. The AFM machining protocol was performed under nitrogen by a procedure reported previously.¹³ In brief, a silicon nitride tip was scanned in a 5 μ m \times 5 μ m area across the polymer surface, with the fast scan direction perpendicular to the long axis of the cantilever. The set point was increased by a constant value to achieve a 50 nN external normal force (F_{ne}) applied on the surface in stepwise increments of eight equal time intervals. The lateral force signal was plotted as a function of F_{ne} , in which the slope was directly proportional to μ and the extrapolated x intercept gave F_a . A silicon wafer with a μ value of 0.06, as reported in the literature,²⁴ was used for calibration. A spring constant of 0.58 N/m for the cantilever, as specified by the manufacturer, was used in the calculations.

Materials

DIEA, bis(3-aminopropyl)-terminated PEG [number-average molecular weight (M_n) = 1600 Da, number-average degree of polymerization (DP_n) = 34], and bis(3-aminopropyl)-terminated PDMS (M_n = 2700 Da, DP_n = 33) were purchased from Aldrich Chemical Co. and were used as received. THF was distilled from Na/benzophenone. HBFP [**1**; weight-average molecular weight (M_w) = 8100 Da, M_n = 4700 Da, DP_n = 10] was synthesized as described previously.¹³

General Procedure for the Preparation of HBFP Crosslinked with Bis(3-aminopropyl)-Terminated PEG (**2**)

A mixture of **1** (0.10 g, 0.021 mmol, 0.21 mmol of pentafluorophenyl groups), bis(3-aminopropyl)-terminated PEG (0.17 g, 0.11 mmol, 0.22 mmol amino groups for **2e**; 0.085 g, 0.053 mmol, 0.11 mmol amino groups for **2d**; 0.034 g, 0.021 mmol, 0.042 mmol amino groups for **2c**, 0.017 g, 0.011 mmol, 0.022 mmol amino groups for **2b**; and 0.0085 g, 0.0053 mmol, 0.011 mmol amino groups for **2a**), and DIEA (0.27 g, 0.21 mmol) was dissolved in THF (2 mL). The solution was drawn onto a microscope slide, the solvent was allowed to evaporate under ambient conditions, and the slide was then heated at 100 °C for 1 h to afford **2** according to method I. Alternatively, heating the reaction mixture at reflux for 20 h, followed by the drawing of the solution onto a microscope slide (or

spin coating onto freshly cleaved mica for AFM studies), allowing the solvent to evaporate under ambient conditions, and then heating the slide at 100 °C for 1 h gave **2** according to method II. In each case, the coating possessed a slightly hazy yellow color.

IR: 2887, 1657, 1598, 1507, 1467, 1344, 1280, 1242, 1148, 1114, 1060, 964, 942, 842, 690 cm^{-1} .

General Procedure for the Preparation of HBFP Crosslinked with Bis(3-aminopropyl)-Terminated PDMS (**3**)

A mixture of **1** (0.10 g, 0.021 mmol, 0.21 mmol of pentafluorophenyl groups), bis(3-aminopropyl)-terminated PDMS (0.30 g, 0.11 mmol, 0.22 mmol amino groups for **3e**; 0.15 g, 0.056 mmol, 0.11 mmol amino groups for **3d**; 0.061 g, 0.022 mmol, 0.044 mmol amino groups for **3c**, 0.030 g, 0.011 mmol, 0.022 mmol amino groups for **3b**; and 0.015 g, 0.0056 mmol, 0.011 mmol amino groups for **3a**), and DIEA (0.27 g, 0.21 mmol) was dissolved in THF (2 mL). The solution was drawn onto a microscope slide, the solvent was allowed to evaporate under ambient conditions, and the slide was then heated at 100 °C for 1 h to afford **3** according to method I. Alternatively, heating the reaction mixture at reflux for 20 h, followed by the drawing of the solution onto a microscope slide (or spin coating onto freshly cleaved mica for AFM studies), allowing the solvent to evaporate under ambient conditions, and then heating the slide at 100 °C for 1 h gave **3** according to method II. In each case, the coating was slightly opaque.

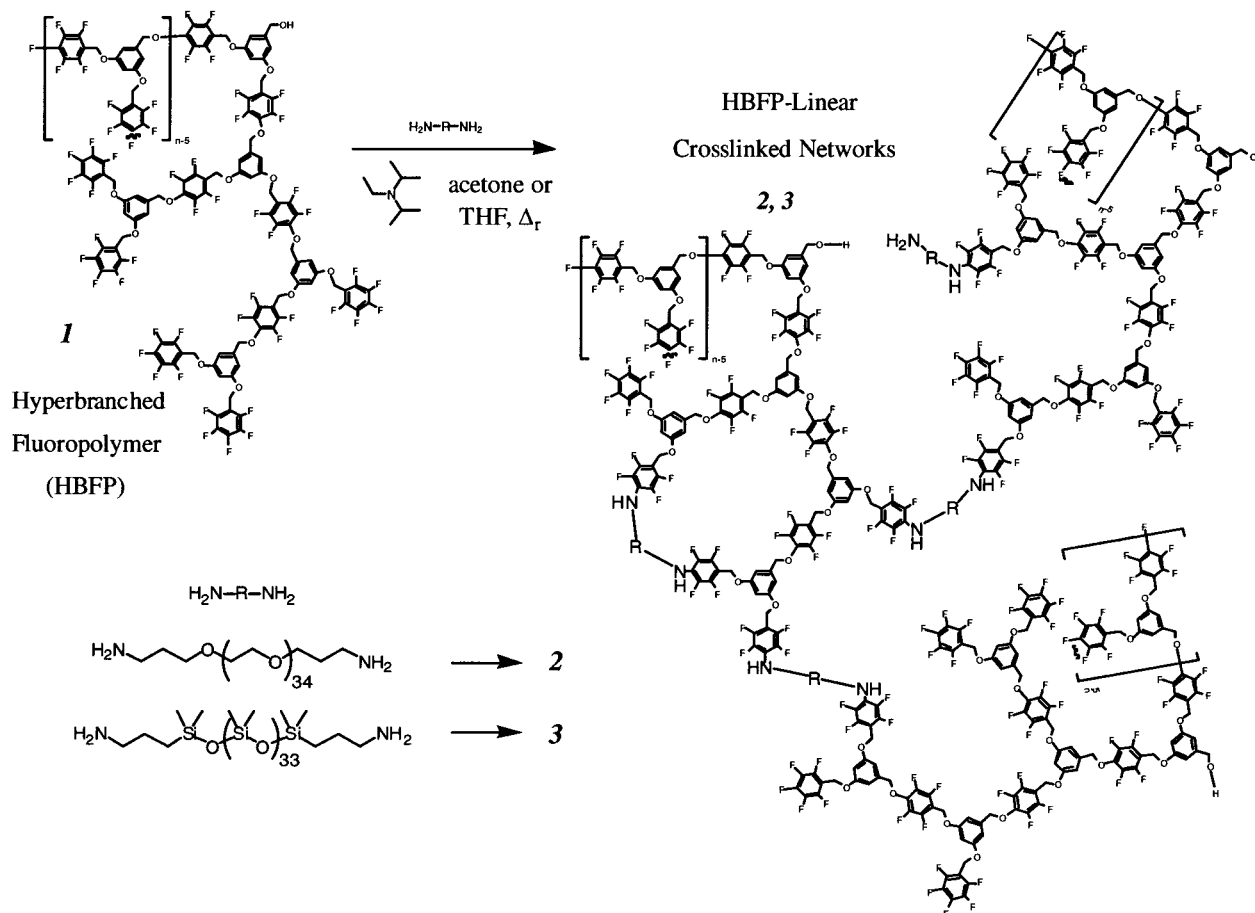
IR: 2963, 2908, 1653, 1599, 1507, 1457, 1380, 1262, 1094, 1022, 941, 800, 690 cm^{-1} .

RESULTS AND DISCUSSION

HBFPs, constructed from benzyl ether linkages and containing an average of one pentafluorophenyl chain-end group per repeat unit (**1**), were used as fluorocarbon-based, multifunctional crosslinking agents along with bifunctional linear polymers of hydrophilic or hydrophobic character to create crosslinked networks that presented morphologically and topographically complex surfaces. The effects of the composition of the telechelic linear chain segments on the properties of the resulting coatings were probed by the use of hydrophilic PEG and hydrophobic PDMS to create the hyperbranched-linear networks **2** and **3**, respectively (Scheme 1). Crosslinking was afforded

by the nucleophilic aromatic substitution of the *para*-fluorines of the pentafluorophenyl groups present within the HBFP by the amino termini of PEG or PDMS chains. The HBFP ($M_w = 8100$ Da, $M_n = 4700$) had a number average of 10 repeat units, or 10 pentafluorophenyl groups per HBFP macromolecule, whereas PEG and PDMS each contained two amines per chain. As illustrated in Scheme 1, the bifunctional linear polymer chains can establish bridging crosslinks between the hyperbranched macromolecules, but intramolecular loops can also be formed by the reaction of the two chain ends of the linear polymer with pentafluorophenyl chain ends within the same HBFP molecule, and dangling ends can remain from the reaction of only one of the two amino termini of the linear polymer chain. Variations in the relative amounts of HBFP and PEG or PDMS theoretically could result in differences in the crosslinking densities and also in the overall compositions of the network composite materials. The stoichiometry of the dissimilar components is an important parameter for tuning the bulk and surface features, by which the thermodynamically driven phase segregation of HBFP from PEG or PDMS is kinetically trapped by the crosslinking reactions. As demonstrated throughout this article, this process of thermodynamic assembly and kinetic crosslinking serves as a general methodology for modifying the surface properties of the coatings.

Two methods were investigated for the crosslinking reaction conditions; each employed THF as the solvent and DIEA as a tertiary amine to scavenge the HF byproduct upon nucleophilic aromatic substitution by the amino chain ends of the linear polymer with the pentafluorophenyl groups of HBFP, which was facilitated at elevated temperatures. For method I, a solution of HBFP, the respective diamino-terminated linear polymer, and DIEA in THF was drawn onto a glass slide and heated at 100 °C for 1 h. For method II, a solution of HBFP, the diamino-terminated linear polymer, and DIEA was heated at reflux in THF for 20 h (macroscopic insoluble gel particles appeared when heating was continued beyond 24 h) and then transferred onto a glass slide and heated at 100 °C for 1 h. The stoichiometric ratio of amino groups to pentafluorophenyl groups was altered from 5 to 100% (Table 1) to control the degree of crosslinking, the composition of the coating, and the resulting surface features. Traditional measurements, such as swelling and me-



Scheme 1

chanical properties, were performed to evaluate the effects of network formation.

Sol-Gel Studies

Each of the crosslinked films contained some fraction of a THF-soluble material, which was identified by ^1H and ^{19}F NMR spectroscopy and SEC to be mostly **1** and some soluble starlike or partially crosslinked products from the condensation of **1** with diamino-PEG or diamino-PDMS. Sol-gel analyses of **2** and **3** were performed with THF as a solvent, and the gel percentage was reported as a proportion of the insoluble material (Fig. 1). The gel percentage was consistently higher for the samples prepared by method II, which underwent the preliminary crosslinking condensation reactions in the THF solution to a pregel point state. This may have been due to the preparation of preassembled HBFP-linear copolymer stars or networks, which increased the homogeneity of the

system and thereby reduced the degree to which phase segregation could occur upon subsequent deposition onto the glass substrate and limited the formation of isolated polymer domains. In support of this argument, it was also found that simply increasing the curing time did not lead to significantly higher values of the gel percentage. For both methods, the gel percentage increased as the stoichiometric balance of amine groups to pentafluorophenyl groups was approached.

Contact-Angle Measurements

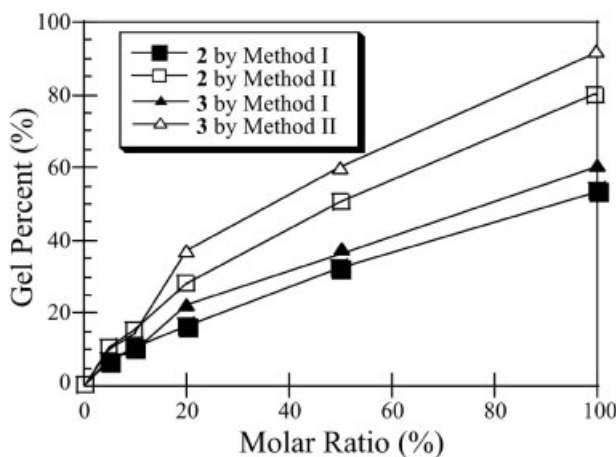
The static contact angles of all films with water and hexadecane were measured (Table 1). As expected, the contact angles of water upon films of **2** decreased with increasing amounts of the hydrophilic diamino-PEG crosslinking agent. A significant decrease in the contact-angle value occurred over time, likely because of sample reorganization and presentation of PEG to a higher proportion of

Table 1. Sample Listing for the Parent HBFP (**1**) and Crosslinked Materials Prepared from HBFP with Diamino-Terminated PEG (**2a–2e**) or Diamino-Terminated PDMS (**3a–3e**) and Static Contact-Angle Values for Water or Hexadecane Measured by the Sessile Drop Method

Sample	Molar Ratio (%) ^a	θ_{water} (°)		$\theta_{\text{hexadecane}}$ (°)	
		30 s	4 min	30 s	4 min
1	0	89 ± 2	81 ± 2	25 ± 2	18 ± 3
2a	5	87 ± 4	68 ± 2	25 ± 2	19 ± 1
2b	10	69 ± 3	40 ± 3	21 ± 1	16 ± 2
2c	20	61 ± 3	26 ± 2	26 ± 2	17 ± 1
2d	50	57 ± 2	17 ± 1	29 ± 2	24 ± 2
2e	100	54 ± 3	10 ± 1	23 ± 2	20 ± 2
3a	5	84 ± 2	79 ± 4	13 ± 2	11 ± 3
3b	10	82 ± 3	75 ± 2	13 ± 2	11 ± 2
3c	20	79 ± 3	73 ± 2	14 ± 2	9 ± 1
3d	50	78 ± 2	74 ± 3	13 ± 2	10 ± 1
3e	100	83 ± 2	78 ± 2	15 ± 2	10 ± 1

^a Based on the molar ratio of amino groups to pentafluorophenyl functionalities.

the film surface.^{25–27} High contact angles with little change over time were observed consistently for samples of **3** at all ratios of PDMS to HBFP; this is representative of the hydrophobic nature of

**Figure 1.** Plot of the gel percentage of HBFP–linear copolymer networks **2** and **3** versus the molar ratio of amine groups to pentafluorophenyl groups, illustrating the increase in insoluble materials as the stoichiometric balance of functionality is approached. In method I, the reaction mixture was drawn onto a glass slide and heated at 100 °C for 1 h; in method II, the reaction mixture was heated at reflux in THF for 20 h, deposited onto a glass slide, and heated at 100 °C for 1 h.**Table 2.** Mechanical Properties of Crosslinked Networks **2d** and **3d**^a

Sample	Tensile Modulus (MPa)	Strength at Break (MPa)	Elongation at Break (%)
2d	858 (Sd 58)	4.58 (Sd 0.44)	13.0 (Sd 2.3)
3d	947 (Sd 37)	3.59 (Sd 0.49)	11.7 (Sd 3.1)

^a The mechanical properties were determined with an Instron, at 23 ± 2 °C, with a crosshead speed of 0.1 in./min. Sd is the standard deviation.

each of these components. The contact angles of hexadecane differed between the series **2** or and series **3** materials, but within each series, there was no correlation to the network composition.

Thermal Analyses

The thermal transition temperatures were measured by DSC. Phase segregation was observed by the presence of T_m for the PEG-containing crosslinked networks prepared at molar ratios of 20% amine/pentafluorophenyl functionality or greater (**2c–2e**). T_g of **1** was observed at 55 °C, but this was obscured by the PEG T_m and was not discernable for any of the crosslinked materials. The thermal stabilities of the materials were examined by TGA under nitrogen. Each of the samples investigated was thermally stable up to 300 °C. For noncrosslinked HBFP (**1**) as well as **2** and **3**, having various amounts of PEG or PDMS incorporated, the decomposition onset temperatures and the temperatures at which 10% mass loss occurred were consistently between 330 and 350 °C.

Mechanical Properties

The mechanical properties of crosslinked polymer networks **2** and **3** were measured by tensile tests with an Instron instrument under ambient conditions. No measured mechanical data for the hyperbranched and linear polymer precursors were obtained because of an inability to produce free-standing films. In contrast, when **1** was crosslinked by either PEG or PDMS linear segments, uniform films were obtained. Films of hyperbranched–linear networks (**2d** and **3d**), each with a 50% molar ratio of amine functionalities to pentafluorophenyl functionalities, were subjected to mechanical property testing with an Instron

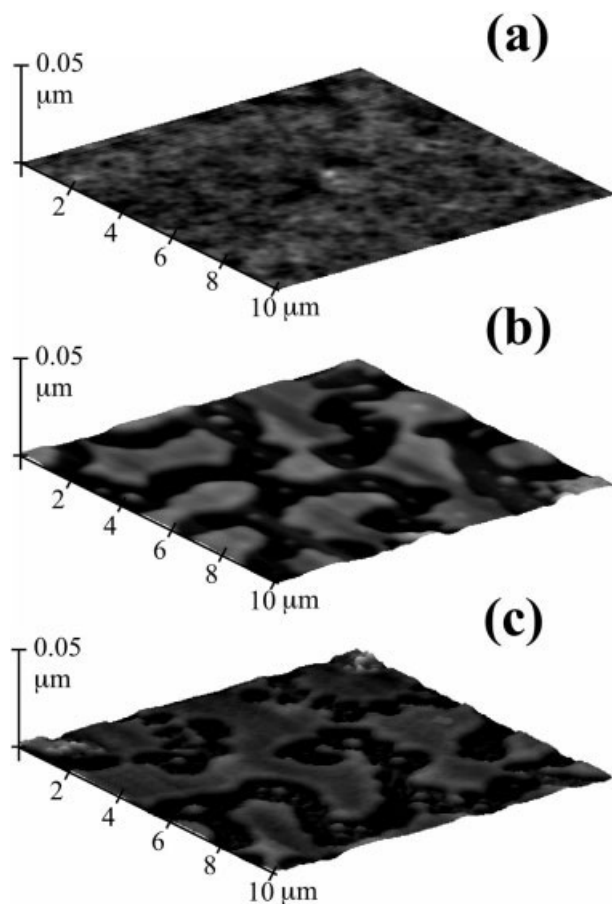


Figure 2. AFM images of (a) **1**, (b) **2d**, and (c) **3d**.

instrument; samples with 100 or 10% crosslinker had insufficient mechanical integrity to be manipulated as freestanding films.

Table 2 summarizes the mechanical properties of **2d** and **3d**. Method II was used to prepare the samples, for which the gel percentages of these two HBFP–linear networks were similar (Fig. 1). In addition, the chain lengths of PDMS and PEG were similar. No distinguishable difference in the mechanical properties of polymer **2d** and **3d** was observed, as shown in Table 2. Despite the increase in the mechanical properties in comparison with those of noncrosslinked HBFP, possibilities remain for further improvements because many other crosslinkers can be used and the chain length of the crosslinker can be varied.

AFM Studies

AFM proved to be an invaluable tool for evaluating the surface features of the crosslinked materials and for probing the roles of the preparation

conditions and coating compositions in the surface topography. Films produced by the spin coating of a solution of **1** onto a mica substrate possessed surface roughness that was characteristic for glassy polymers [Fig. 2(a) and Table 3]. The surface roughness increased with the incorporation of the linear polymers (Fig. 2 and Table 3). As noted previously, these films were indeed crosslinked networks, as demonstrated by their levels of insolubility after curing. Moreover, the mechanical integrity of the films improved after curing, as evidenced by the AFM images shown in Figure 3, in which the AFM machining protocol resulted in less material buildup at the ends of the micromachining scan runs (from mechanical removal, that is, scratching, by the AFM probe tip) and instead produced a roughening of the surfaces. μ increased with the incorporation of the linear polymers. The material containing HBFP crosslinked with linear PEG diamine gave the lowest value for F_a , and this caused us to our focus efforts on the further investigation of these HBFP–PEG network materials.

The height variations and rougher topographies exhibited across surfaces of **2** and **3** were believed to be the result of the phase separation of HBFP from the linear polymers, as observed for many other crosslinking systems and polymer blends.^{28–30} Therefore, the dimensions of the phase-segregated surface domains and overall surface compositions could be conveniently modified by the variation of the composition of the prenetwork polymer mixture. With increasing relative amounts of PEG, the relative surface coverage appeared to transition from predominantly HBFP to a majority of PEG, as the weight percentage of HBFP was varied from 92 to 85 to 75 to 54 to 37% for **2a**, **2b**, **2c**, **2d**, and **2e**, respectively [Fig. 4(b–f), respectively].

It was also observed that decreasing the film thickness yielded smaller phase-segregated sur-

Table 3. Surface Properties of HBFP and HBFP–Linear Copolymer Networks as Measured by AFM

Sample	Root-Mean-Square Roughness (nm) ^a	μ ($\times 10^{-2}$) ^b	F_a (N) ^b
1	0.27 ± 0.06	6.2 ± 0.5	81 ± 15
2d	0.45 ± 0.06	15.3 ± 0.8	72 ± 15
3d	0.40 ± 0.07	9.8 ± 1.5	97 ± 18

^a Measured over a $1 \mu\text{m} \times 1 \mu\text{m}$ scanning area.

^b Measured by the AFM machining protocol.

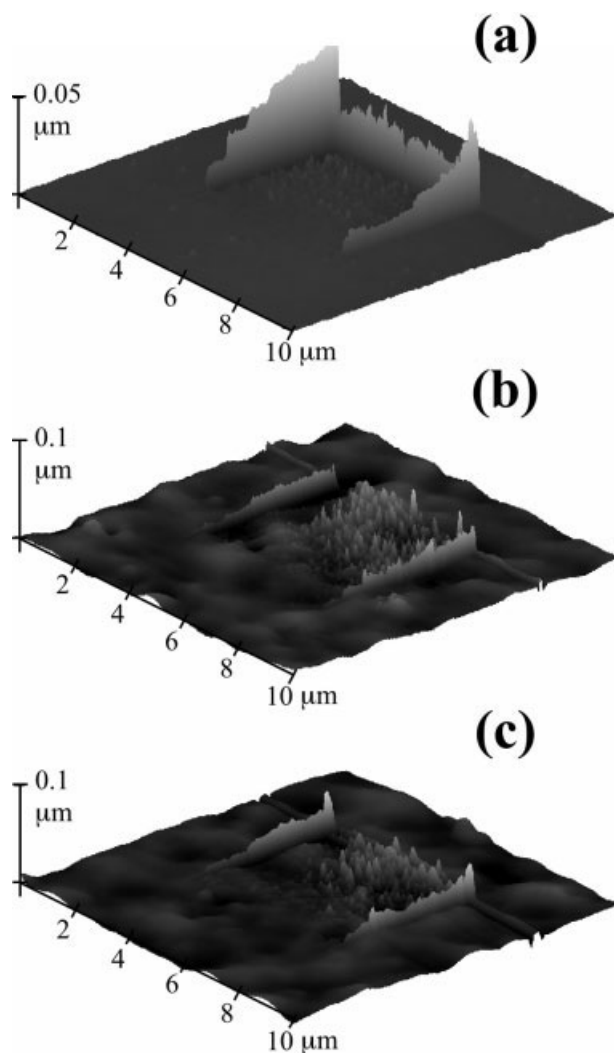


Figure 3. AFM images of (a) **1**, (b) **2d**, and (c) **3d** after eight stepwise machining scans by a silicon nitride tip over $5\ \mu\text{m} \times 5\ \mu\text{m}$ scanning areas.

face domains and increasing surface texture, ultimately leading to nanoscale resolution over the surface features (Fig. 5). This behavior suggests that the substrate influenced the phase segregation, pinning³¹ smaller domain sizes as the coating thickness decreased, and follows a trend previously observed for polymer blends.^{32–36}

Studies of the adsorption of a protein (human fibrinogen) onto the polymer surfaces, as a function of the composition of the crosslinked film (and, therefore, as a function of the surface topography and morphology, as previously illustrated), revealed that the extent of protein fouling diminished as the PEG content increased. AFM was used to evaluate qualitatively the extent of protein coverage across surfaces that had been im-

mersed in a solution of human fibrinogen. As shown in Figure 6, HBFP, although a low-surface-energy material, experienced the greatest relative degree of protein adsorption. As the PEG content increased from 25 to 46 to 63 wt % for **2c**, **2d**, and **2e**, respectively, the relative amount of protein adsorption appeared to decrease. Of course, it is well known that the surface presentation of oligo(ethylene glycol) or PEG units improves protein resistance,³⁷ and the inhibition of settlement by marine fouling organisms has also been demonstrated recently.³⁸ However, we are

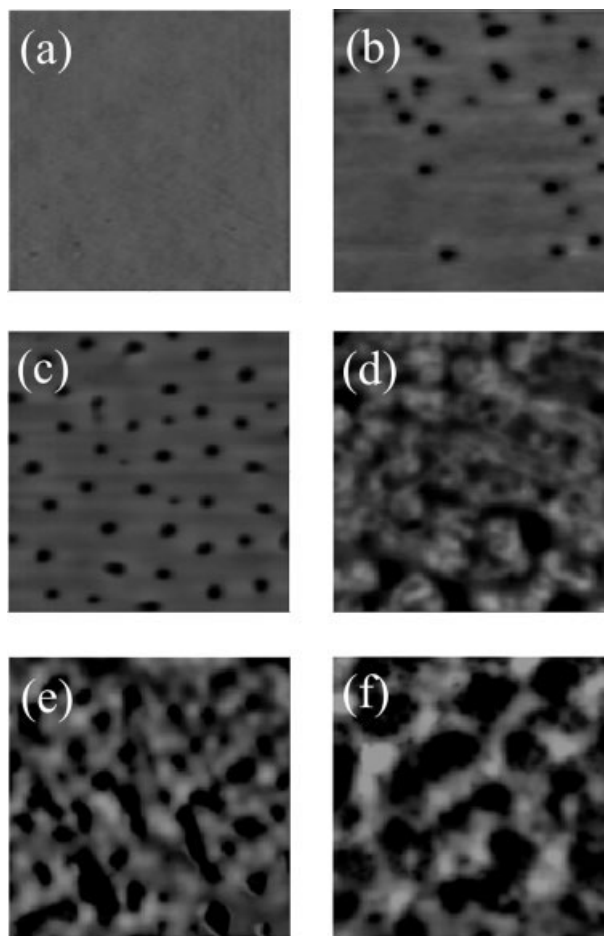


Figure 4. AFM images revealing differences in the phase-segregated surface patterns as a function of the coating composition. Tapping-mode AFM images are shown for $5\ \mu\text{m} \times 5\ \mu\text{m}$ scans acquired for (a) HBFP **1** and (b–f) crosslinked networks with diamino-PEG molar ratios of amine at 5% [(b) **2a**], 10% [(c) **2b**], 20% [(d) **2c**], 50% [(e) **2d**], and 100% [(f) **2e**], with respect to the HBFP pentafluorophenyl functionalities. The AFM images are shaded according to the height (z axis); the higher surfaces are lighter, and so the darker areas are lower surfaces.

currently studying to what extent the antifouling properties are dependent on the surface composition versus the surface topography and morphology, and we are also developing quantitative measures of the protein fouling behaviors.

CONCLUSIONS

The thermodynamically driven phase segregation of (co)polymers, combined with kinetic trapping by intermolecular covalent crosslinking reactions, has been extended from the stabilization of nanoscopic objects in solution³⁹ to the formation of macroscopic objects possessing nanoscopically resolved features. Having demonstrated control over the surface features of these unique crosslinked network films, we will investigate in detail the parameters of surface topography and morphology, and the size scale at which they are produced, to determine their importance in regu-

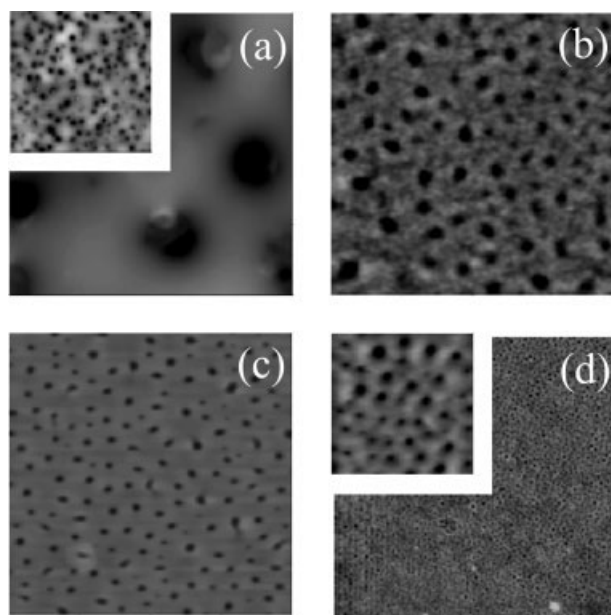


Figure 5. AFM images illustrating the surface-segregated patterns resulting from differences in the coating thicknesses for **2b**, an HBFP crosslinked by diamino-terminated PEG, at a stoichiometry of 10% amino/pentafluorophenyl groups and coating thicknesses of (a) 120, (b) 60, (c) 32, and (d) 10 nm. Each of the images represents a $10\ \mu\text{m} \times 10\ \mu\text{m}$ area, with the inset for part a being $50\ \mu\text{m} \times 50\ \mu\text{m}$ and that for part d being $1\ \mu\text{m} \times 1\ \mu\text{m}$. The AFM images are shaded according to the height (z axis); the higher surfaces are lighter, and so the darker areas are lower surfaces.

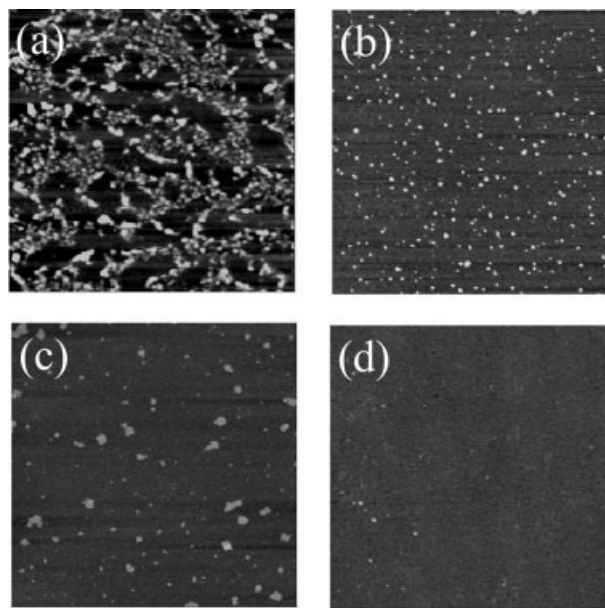


Figure 6. Tapping-mode AFM images, collected after a 10-min immersion of the coatings in a human fibrinogen solution (0.5 mg/mL), showing that the extent of protein biofouling of the surfaces decreased with increasing PEG content: (a) **1**, (b) **2c**, (c) **2d**, and (d) **2e**. The height scale is 40 nm, represented by a gray scale, with lighter features being at a greater height. The coating thicknesses were about 10 nm, so that the polymer height undulations were less than those of the protein aggregates.

lating the adsorption of biological entities. The properties and utility of the subsurface microscopic and nanoscopic domains will also be studied, with the intention of those domains being used as reservoirs or channels.^{9,10,40} We also intend to explore further the synthetic methodologies by which, for example, well-defined star structures are being employed as precursors to control the sizes of phase-segregated domains and surface features.

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