Polyvalent Hydrogen-Bonding Functionalization of Ultrathin Hyperbranched Films on Polyethylene and Gold

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ABSTRACT: Hyperbranched poly(acrylic acid) and poly(*N*-isopropylacrylamide) grafts on gold and polyethylene films are good substrates for a new, mild hydrogen-bond-based grafting method. In this chemistry, a hydrogen-bond-donating or -accepting hyperbranched graft couples to a polymeric acceptor or donor in ethanol solution through multiple hydrogen-bonds. In contrast to plain surface-functionalized polyethylene films or to functional monolayers on gold, hyperbranched grafts are more capacious and more tenacious in this hydrogen-bond graft chemistry. Substantial amounts of polyacrylamide or poly(acrylic acid) reversibly bind to the hyperbranched graft based on IR spectroscopy, fluorescence spectroscopy, and ellipsometry. Fluorescence studies using dansyl-labeled soluble polymers that were hydrogen-bonded to hyperbranched grafts show that these hydrogen-bond assemblies are stable to prolonged extraction with protic and aprotic solvents. These interfacial hydrogen-bonded assemblies do not readily disassemble unless the hydrogen-bond donor is deprotonated with base.

For several years now, our group has actively pursued the synthesis of functional surfaces through new grafting chemistry.[1−6] Here we report the use of ultrathin grafted interfaces of poly(acrylic acid) or polyacrylamides on polyethylene and gold as substrates for hydrogen-bonded self-assembly. In this chemistry, a polyvalent hyperbranched hydrogen-bond donor or acceptor interface strongly adsorbs a polymeric hydrogen-bond acceptor or donor to prepare a functionalized interface that is stable to prolonged extraction with protic or aprotic solvents. The hydrogen-bonded interfacial grafts so formed disassemble on deprotonation of the hydrogen-bond donor (Figure 1). This is a mild and simple grafting method leading to functional thin films. This chemistry complements covalent and ionic grafting chemistry and should be of general applicability in modification of brushlike grafts on various substrates.[1,7−12]

This approach to surface functionalization has its roots in chemistry of polymeric hydrogen-bond donors and acceptors in solution and in the solid state.[13,14] It has parallels in ionic assembly chemistry that leads to layer-by-layer polyelectrolyte grafts.[9] Indeed, Rubner's group has demonstrated that hydrogen-bonds can be used in place of ionic interactions to prepare layer-by-layer assemblies.[15] The interpolymer interactions in all of these cases exploit the advantages of polyvalency.[16] In the case of surface functionalization using hydrogen-bonds, the effectiveness of weak hydrogen-bonds is magnified by the formation of hundreds of intermolecular hydrogen-bonds between the soluble polymer and the hydrogen-bond-donating or -accepting interface. Our earlier work had shown that hyperbranched poly(acrylic acid) (PAA) interfaces on gold and polyethylene are permeable to other solvents and to other polymers.[7,17] Moreover, hyperbranched interfaces containing carboxylic acid groups or carboxylic acid derivatives behave much like the carboxylic acid groups of poly(acrylic acid) (or its derivatives) in solution. Thus, interfaces containing these groups should also behave like hydrogen-bond donors. We have also shown that the carboxylic acid groups of these PAA grafts can be converted into amides.[2,7,18] After such a conversion, the hydrogen-bond-donating PAA originally present would be converted into a hydrogen-bond-accepting amide. We reasoned that either an acid- or amide-functionalized interface should exhibit polyvalent hydrogen-bond interactions with soluble polymers—chemistry that could provide a reversible method of surface modification. The results described below show that this is indeed the case and that the interfacial character of these hyperbranched grafts results in more tenacious and capacious hydrogen-bond grafting than is seen with a simple functionalized surface.

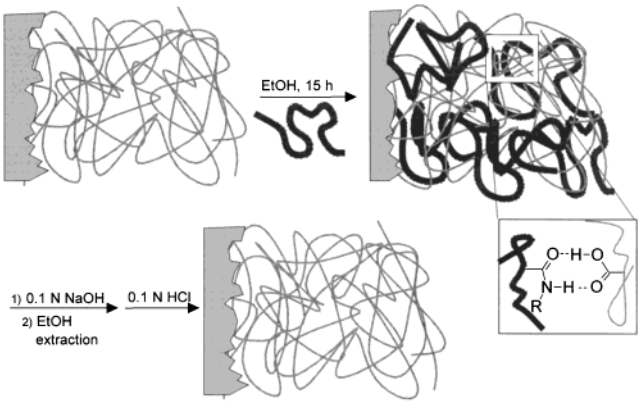

Figure 1. Schematic depiction of hydrogen-bond assembly of a hydrogen-bond acceptor polymer within a hydrogen-bond donor hyperbranched poly(acrylic acid) film and subsequent disassembly on treatment with base.

Results and Discussion

Our initial studies focused on poly(acrylic acid) hyperbranched grafts in the form of 3-PAA/PE or 3-PAA/Au films as hydrogen-bond-donating hyperbranched ultrathin films. These hyperbranched grafts are available via published procedures starting with oxidized polyethylene (PE−CO_2H) or a self-assembled monolayer

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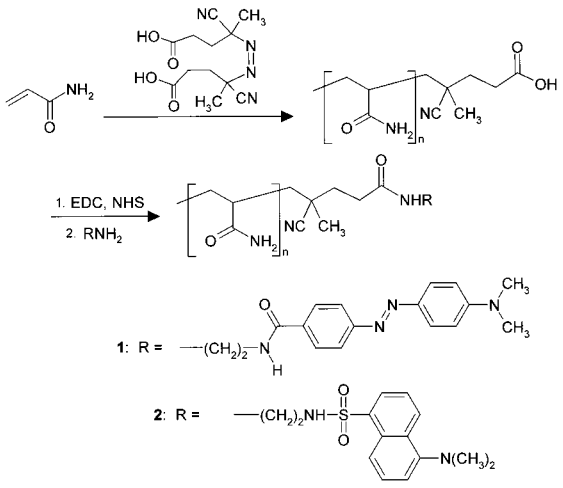
(SAM) on gold prepared using mercaptoundecanoic acid (MUA/Au).[2,7] They consist of 200−300 Å thick lightly cross-linked grafts of poly(acrylic acid). They are prepared using diamino-terminated poly(*tert*-butyl acrylate) by a multistep graft-onto-a-graft synthetic strategy using poly(*tert*-butyl acrylate) with a M_n of 16 000 Da.[2] To verify that the hyperbranched grafts were more effective than a simple functional surface in this hydrogen-bonding assembly process, control reactions were carried out using either the starting oxidized PE film or the MUA/Au carboxylic acid containing SAM. A hydrogen-bond-accepting soluble polyamide substrate, poly(*N*-isopropylacrylamide) (PNIPAM) or polyacrylamide (PAM), was prepared using radical polymerization with AIBN. To facilitate characterization of these interfaces, dansyl fluorescent tags were also attached to these polymers. Dansyl-labeled acrylamide polymers were prepared using a carboxylic acid-containing AIBN derivative as the initiator. Subsequent conversion of the terminal carboxylic acids of the product polymer into amides with an amine-containing dansyl derivative then led to a dye- or fluorescently-labeled polymer (eq 1). Such terminally functionalized polymers contain low loadings of fluorophore, ca. 0.1 mol % assuming DP's of 2000 and two terminal functional groups/chain. Labeled PNIPAM copolymers with high loadings of dansyl groups (10 mol %) were also available from a PNIPAM-*c*-NASI (*N*-acryloxysuccinimide) copolymer (eq 2).[19]



Hydrogen-bond grafting of a polyacrylamide to a hyperbranched 3-PAA/PE film was followed by a number of analytical techniques. First, an ATR-IR spectrum of a film modified by hydrogen-bonding using a solution of PNIPAM showed an increase in the amide I band at 1656 cm^{-1}. Second, XPS spectroscopy (Figure 2a) of a film modified with PNIPAM showed 5.8 ± 0.3 atom % N_{1s}. Washing the film with THF in a Soxhlet apparatus for 15, 30, or 45 h reduced this value only slightly (5.6, 4.8, and 4.8 atom %, respectively). In contrast, an oxidized PE film (PE−CO_2H) (H_2SO_4, CrO_3) containing only surface CO_2H groups treated with PNIPAM had an initial 4.2 atom % N_{1S} loading. In this latter case, the % N_{1S} loading on the PNIPAM-treated PE−CO_2H decreased to 0.9 atom % with 15 h of THF washing. Qualitatively, these loadings of 4−5 atom % N suggest that the PAA hyperbranched grafts and PE−CO_2H bind approximately equal amounts of polyacrylamide. However, the capacity of these films is undoubtedly affected by many factors (e.g., solvent, polymer compatibility,

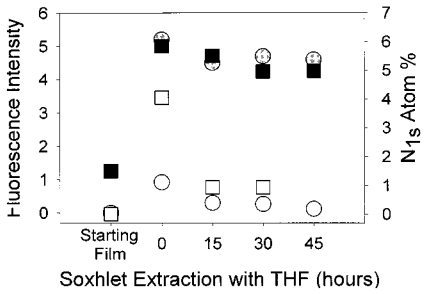


Figure 2. (a) XPS data of films of PNIPAM in 3-PAA/PE (■) or on oxidized polyethylene (□) showing the N_{1s} atom % initially, after hydrogen-bonding of the PNIPAM and after washing for 15, 30, or 45 h. (b) Fluorescence data for dansyl-labeled PNIPAM hydrogen-bonded to either 3-PAA/PE (●) or to oxidized polyethylene (○) initially and after washing for varying periods of time.

relative size of guest and host polymer, and any molecular recognition elements present).

Fluorescence spectroscopy using a highly loaded dansyl-labeled PNIPAM polymer (eq 2) confirmed these initial IR and XPS results (Figure 2b). Both the oxidized PE (PE−CO_2H) and 3-PAA/PE became visibly fluorescent on treatment with PNIPAM containing 10% pendant dansyl groups, fluorescing green when illuminated with a handheld UV light containing a 365 nm UV lamp. However, comparative studies of the fluorescence intensity of these dansyl-labeled oxidized PE film vs a PE film containing a hyperbranched poly(acrylic acid) graft showed a much higher initial fluorescence for the hyperbranched graft, 3-PAA/PE. Moreover, washing the PNIPAM-treated films with THF (vide infra) led to virtually no change in the fluorescence intensity of hydrogen-bound dansyl-labeled PNIPAM (λ_{max} = 470 nm) for the 3-PAA/PE substrate as judged using a fluorescence spectrometer ((λ_{ex} = 357 nm). In contrast, the fluorescence intensity for the washed dansyl-labeled PNIPAM-treated PE-CO_2H was negligible after brief washing.

More lightly loaded terminally functionalized dansyl-labeled PAM polymers were also used to fluorescently label both PE−CO_2H and 3-PAA/PE. As was true in the PNIPAM example above, the fluorescence of PE−CO_2H treated with dansyl-labeled PAM was less than that of a similarly treated 3-PAA/PE film. Moreover, the fluorescent label could be removed from the PE−CO_2H film by washing, but the dansyl-labeled PAM remained more tenaciously bound to 3-PAA/PE. Qualitative labeling studies were also carried out with the methyl red-labeled PAM derivative **1**. 3-PAA/PE films treated with this dye-labeled polyamide had a consistent red color across the film. These fluorescence labeling studies and the XPS results described above show that the PNIPAM and PAM hydrogen-bond acceptor macromolecule can indeed diffuse into the hyperbranched PAA graft interfaces to form a robust, hydrogen-bonded composite of PAA and PNIPAM or PAM.

The hydrogen-bound polyacrylamide polymers could be removed by deprotonating the carboxylic acid groups of poly(acrylic acid) in 3-PAA/PE or on the oxidized film (PE-CO_2H) in a basic ethanol solution for 1 h and then washing the film in ethanol for 15 h. The removal of the dansyl-labeled polymers was followed visually by ATR-IR spectroscopy (after reprotonation) and by fluorescence spectroscopy (emission at 470 nm dropped to zero). The removal of the hydrogen-bound polyacryl-

Table 1. Ellipsometric Data (in Å) for PNIPAM or PAM in 3-PAA/Au or on MUA/Au Films

film	original film thickness	after hydrogen-bond assembly	after 1 day in ethanol	after 5 days in ethanol	after base treatment
PNIPAM in 3-PAA/Au	230	520	515	517	238
PAM in 3-PAA/Au	225	560	564	570	232
PNIPAM on MUA/Au	12	40	11	11	
PAM on MUA/Au	12	130	125	128	13

amide was supported by the decrease in the amide I and II bands to their original intensities, in the case of a 3-PAA/PE film, or complete loss of both bands, in the case of the oxidized polyethylene film.

Hydrogen-bonding of both PNIPAM and PAM to ultrathin hyperbranched films of PAA on gold (3-PAA/Au) and to a carboxylic acid-containing monolayer (mercaptoundecanoic acid (MUA)/Au) was studied by ellipsometry, FTIR-ERS spectroscopy, and XPS spectroscopy. These studies complement and confirm the results obtained using hyperbranched PAA grafts as hydrogen-bond donors for hydrogen-bond-based grafting of acrylamides. Specifically, ellipsometry data (Table 1) show that incorporation of PNIPAM or PAM occurs both on a hyperbranched 3-PAA/Au film and on a MUA/Au monolayer. Greater incorporation of the hydrogen-bond-accepting polymer into a hyperbranched graft vs a simple monolayer occurs as was seen for the PE films. Moreover, removal of the hydrogen-bonded soluble polymer from the hyperbranched graft was only effected after deprotonation of the 3-PAA/Au hyperbranched graft polymer. As noted in Table 1, the thickness of the 3-PAA/Au film increased from 230 to 520 Å upon addition of PNIPAM. A slightly greater thickness change of 225 to 560 Å occurred on binding of PAM to 3-PAA/Au. Both PAM and PNIPAM remain hydrogen-bonded to the 3-PAA surface even after soaking the films in aqueous ethanol and ethanol, respectively, for 5 days. Less PNIPAM or PAM was attached to a simple carboxylic acid containing monolayer—MUA/Au. The thickness increase for PNIPAM hydrogen-bonded to SAM—MUA was from 12 to 40 Å with a larger thickness increase being seen for PAM hydrogen-bonded to the same surface, 12 to 130 Å. Soaking the SAM—MUA—PNIPAM film in ethanol for 1 day easily washes off PNIPAM. In contrast, PAM remains attached to the SAM—MUA film even after 5 days of soaking in aqueous ethanol. In all cases, these polyacrylamides were removed from the carboxylic acid-containing surface or interface by deprotonating the surface and washing with ethanol.

The role of the supported polymer and soluble polymer in this hydrogen-bond-based grafting could also be reversed. Using 3-PAA/PE films whose hydrogen-bond donor grafts were modified to form a hyperbranched hydrogen-bond-accepting polyamide graft (three cycles of treatment of 3-PAA/PE with (i) $ClCO_2Et$ and (ii) $H_2NCH(CH_3)_2$), a hydrogen-bond-acceptor hyperbranched graft was prepared. This polymer, 3-PNIPAM/PE, was then used to assemble a soluble poly(acrylic acid) into this polyamide interface using hydrogen-bonds. In this way, the role of donor and acceptor macromolecule can be reversed. Hydrogen-bond assembly in this instance was successfully followed both by ATR-IR and fluorescence spectroscopy. Poly(acrylic acid) used for this grafting chemistry (M_w = 450 000) was obtained commercially. The necessary poly(acrylic acid) polymer containing pendant dansyl labels was prepared using the chemistry shown in eq 3. The loading of dansyl groups on the resulting polymer was estimated to be ca. 0.15 mol % on the basis of the stoichiometry of the amidation reaction.

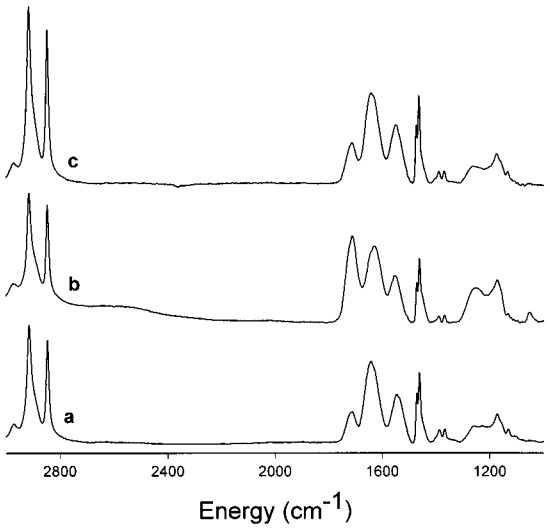
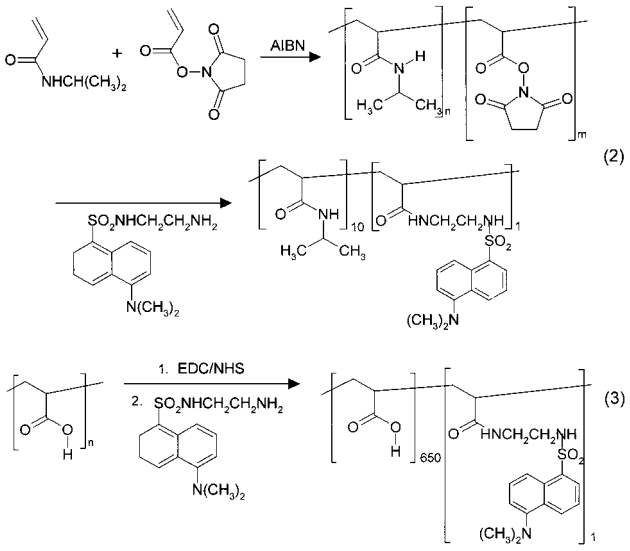


Figure 3. ATR-IR spectra of a 3-PNIPAM/PE film showing the reversible hydrogen-bond-based grafting of poly(acrylic acid): (a) starting 3-PNIPAM/PE films (b) after incorporation of poly(acrylic acid) and (c) regeneration of the starting film after base treatment to remove the PAA and reacidification to re-form any $-CO_2H$ groups.



In hydrogen-bond grafting experiments using soluble PAA as the hydrogen-bond donor, the 3-PNIPAM/PE substrate was treated with an ethanolic solution of the PAA for 15 h. After hydrogen-bond assembly, the intensity of the carbonyl peak in the ATR-IR spectrum of this film at 1715 cm^{-1} significantly increased (Figure 3b). Prolonged extraction of this film with either EtOH (24 h) or THF (48 h) led to no significant change in this IR spectrum. However, treatment of this film with 0.1 N NaOH followed by extraction with ethanol and acidification re-formed the original film (Figure 3c).

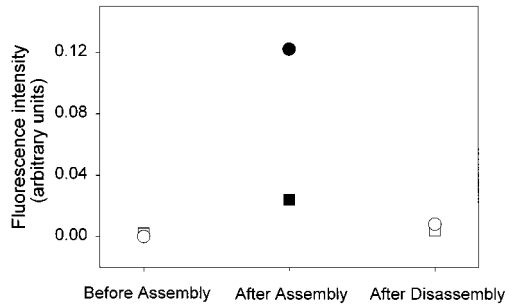


Figure 4. Fluorescence data for a 3-PNIPAM/PE (circles) or a PE−CO_2H (squares) film showing the reversible hydrogen-bond-based grafting of poly(acrylic acid): (a) the starting 3-PNIPAM/PE or PE−CO_2H films (open circle and square); (b) after incorporation of the dansyl-labeled poly(acrylic acid) (filled circle and square) and (c) regeneration of the starting film after base treatment to remove the PAA and reacidification to re-form any −CO_2H groups (open circle and square).

Repetition of this process with a fresh solution of PAA again produced a film like that shown in Figure 3b. Thus, this hydrogen-bond grafting is fully reversible and repeatable.

Results using the fluorescently labeled poly(acrylic acid) polymers paralleled the results seen above and seen earlier with PAM and PNIPAM binding to 3-PAA/PE or 3-PAA/Au. This grafting too was reversible. Treatment of the films with base led to loss of the fluorescent label. This is illustrated by the data in Figure 4.

We have also examined PAA grafting into PNIPAM grafts on gold. In these cases, a 3-PAA/Au film was converted into a poly(*N*-isopropylacrylamide) derivative by three successive treatments with $ClCO_2Et$ and $HNCH(CH_3)_2$. The resulting amidated film was then exposed to a solution of PAA. FTIR-ERS spectra of the product film before and after assembly of PAA into this film were comparable to the spectra shown in Figure 3. Ellipsometric measurements were also performed on these films. Experiments contrasting the behavior of a PNIPAM-modified hyperbranched graft on gold (3-PNIPAM/Au) with the *N*-isopropylacrylamide derivative of MUA/Au show that the change in film thickness increase seen is nearly as large as the changes seen for earlier experiments using soluble PNIPAM and a hyperbranched 3-PAA/Au graft (Table 1). In the former example, a 290 Å change in thickness was seen. In the case of 3-PNIPAM/Au, the initial amidated film is substantially thicker, but the change in thickness of about 260 Å indicates that a similar amount of soluble polymer (PAA in this case) was bound into the 3-PNIPAM/Au film by hydrogen-bonding. The results in Table 2 also show that the amount of PAA absorbed onto an amide modified MUA/Au film is negligible. Experiments in which thickness changes were monitored as the 3-PNIPAM/Au film was first grafted with PAA, then drafted with base and reacidified, then grafted again with PAA, and finally degrafted and reacidified a second time also show that the thickness changes and grafting is reversible.

In summary, hydrogen-bonding into a polyvalent, covalently bound thin film of poly(acrylic acid) and a soluble hydrogen-bond acceptor polyacrylamide is a mild way to functionalize a surface. The hydrogen-bonded polymeric ensemble so formed is stable to extensive washing and addition of external acid. The assembly disassembles on deprotonation, regenerating the initial surface after acidification. Reversing the role of hydrogen-bond acceptor and donor lead to similar results. Such processes are a mild reversible method for surface modification that complements existing covalent chemistry and ionic chemistry. Such processes could serve as new, mild methods to immobilize reagents, catalysts, or sensing agents at functionalized grafted interfaces.

Experimental Section

General Procedures. All reagents and solvents were obtained from commercial sources and used without further purification unless otherwise stated. ^{1}H and ^{13}C NMR spectra were obtained using a Varian XL200 E or Unity p300 spectrometer. Chemical shifts are reported in ppm using HMDS (0.055 ppm) as an internal reference. ATR-IR spectra were obtained using a Mattson Galaxy 4021 FT-IR spectrometer with a Wilks model 10 ATR accessory at an angle of 45° using a KRS-5 crystal and were recorded with a resolution of 1 cm^{-1}. FTIR-ERS spectra were measured using a Bio-Rad FTS 40 spectrometer equipped with a Harrick Scientific Seagull reflection accessory and a liquid N_2-cooled MCT detector. Spectra were obtained using p-polarized light at an 85° angle of incidence with respect to the Au substrate. Spectra were measured at 4 cm^{-1} resolution using between 100 and 256 scans. Ellipsometric measurements were performed on dry films in air using a Gaertner L2W26D ellipsometer with a 70° angle of incidence. Thicknesses and refractive indices were calculated assuming a standard homogeneous film model using Gaertner software. In these thickness calculations, we assumed an index of refraction of 1.46 for the 3-PAA/Au films and 1.55 for films containing covalently or hydrogen-bound polyamides. X-ray photoelectron (XPS) spectra were acquired using a Perkin-Elmer (PHI) model 5500 spectrometer using a Mg Kα source and a takeoff angle of 45°. The films used for XPS experiments were cut into 0.5 × 0.5 cm pieces. Two films were put side by side on the holder and held in place by a metal ring. A survey scan was taken first, and then a multiplex scan was done. The number of sweeps was set to 10, and the acquisition time was set to 30 min. The voltage was set to 15 V. The films had a brown tinge after XPS data were collected. Fluorescence spectra were recorded on a SLM Aminco SPF-500C fluorescence spectrophotometer. The polyethylene films were placed in a quartz cuvette and held in place with a Teflon yoke. The cuvette was made immovable by placing a piece of Teflon between the cuvette and the sample holder. The shutters on the instrument were closed except when data points were being collected. When working with dansyl-labeled films, the spectra were obtained with bandwidths of 4 and 2.5, an emission wavelength of 470 nm, and an excitation wavelength 357 nm. The spectra were collected using a wavelength range of 300 and 600 nm.

Poly(*N*-isopropylacrylamide-*c*-*N*-acryloxysuccinimide). Preparation of the p(NIPAM-*c*-NASI) copolymers and derivatization of these copolymers with amines follows an established procedure.[1,15] In the case of the PNIPAM derivatives used here, the M_v was determined to be 7.5 × 10^5 Da using values of 9.59 × 10^{-3} and 0.65 for *K* and α, respectively, in THF at 30 °C.[20]

1-(Dimethylamino)-5-naphthalenesulfonyl Ethylenediamine (Dansylamine) Labeled PNIPAM (PNIPAM-*c*-Dansylamine). Labeling PNIPAM-*c*-NASI with dansylamine was accomplished by dissolving 0.2 g of PNIPAM-*c*-NASI in 20 mL of THF and then adding 0.05 g of dansylamine. This reaction stirred for 15 h. The product labeled PNIPAM copolymer was precipitated using hexanes (∼150 mL) to yield 0.195 g (86%) of the fluorescent copolymer: IR (KBr, cm^{-1}): 2970 and 2920 (C−H stretch), 1652 (amide I), 1532 (amide II). ^{1}H NMR (300 MHz, D_2O): δ 1.15 (br s, 6H), 1.40−2.09 (m, 3.1H), 2.7 (br t, 0.2H), 2.95 (br m, 0.8 H), 3.96 (br s, 1H), 5.4 (br s, 1.1H), 7.2 (br d, 0.1H), 7.45−7.6 (br m, 0.2H), 8.2−8.3 (br m, 0.2H), 8.55 (br d, 0.1H). The emission maximum of this polymer was at 492 nm (excitation at 357 nm) in ethanol suspension.

Table 2. Ellipsometric Film Thickness Data (in Å) for PAA Binding into or onto 3-PNIPAM/Au or on the *N*-Isopropylacrylamide Derivative of MUA/Au

film	original film thickness	after hydrogen-bond assembly	after disassembly with base	repetition of hydrogen-bond assembly	after second dissassembly
PAA in 3-PNIPAM/Au	607	863	612	829	612
PAA on SAM amide	10	20	9		

α,ω-Diacidopoly(acrylamide) Synthesis (PAM). The α,ω-diacidopoly(acrylamide) (PAM) polymer was synthesized by radical polymerization of 5 g of acrylamide using 0.197 g of the initiator 4,4′-azobis(4-cyanovaleric acid) in 60 mL of 1,4-dioxane under a nitrogen atmosphere for 15 h at 120 °C. The polymer precipitated from the reaction solution after 5 h. The acid-terminated polymer was purified by two precipitations in THF from water. The precipitated polymer was then characterized using ^{1}H NMR spectroscopy, FT-IR spectroscopy, titration, and viscometry. Titrations using 0.1 N NaOH provided an M_n value of 30 250 Da (assuming difunctionality). The M_v was determined to be 38 550 Da using values of 6.31 $\times$ 10^{-3} and 0.80 for K and α, respectively, in water at 30 °C.[21] The ^{1}H NMR spectrum was not very informative, showing broad peaks in the expected regions. However, the ^{1}H NMR spectrum did show that no monomer was present. The dominant peaks in the IR spectrum were the amide peaks: IR (KBr, cm^{-1}) 3429 and 3206 (N−H stretch), 2970 and 2929 (C−H stretch), 1667 (amide I), 1615 (amide II). ^{1}H NMR (300 MHz, D_2O): δ 1.4−1.8 (br m, 2H), 2.0−2.3 (br m, 1H).

1-(Dimethylamino)-5-naphthalenesulfonyl Ethylenediamine (Dansylamine)-Terminated PAM. The α,ω-diacidopoly(acrylamide) was labeled with a fluorescent amine by allowing 2 g of the α,ω-diacidopoly(acrylamide) dissolved in 50 mL of H_2O to first react with 0.362 g of EDC and 0.110 g of NHS for 30 min in an ice bath (∼4 °C). Then 0.11 g of dansylamine in 10 mL of CH_2Cl_2 was added, the biphasic mixture was stirred for 15 h. The CH_2Cl_2 layer was separated from the water layer containing the labeled polyacrylamide. Then the labeled polymer was precipitated by adding an aqueous solution of this polymer to an excess of THF. The M_n of the labeled polymer was determined by end group analysis to be 33 200 Da using fluorescence (a calibration curve for dansyl-labeled polymer was prepared from aqueous solutions containing known concentrations of the ethylenediamine derivative of dansyl chloride) and assuming two $-CO_2H$ chain ends per molecule. The fluorescent-labeled polymer was also analyzed using ^{1}H NMR and FT-IR spectroscopy. IR (KBr, cm^{-1}): 3429 and 3206 (N−H stretch), 2970 and 2929 (C−H stretch), 1667 (amide I), 1615 (amide II). ^{1}H NMR (300 MHz, D_2O): δ 1.4−1.8 (br m, 2H), 2.0−2.3 (br m, 1H). However, no peaks attributable to dansyl groups were seen in ^{1}H NMR spectra because of the low loading of terminal dansyl groups.

Methyl Red-Labeled PAM. The α,ω-diacidopoly(acrylamide) used in the synthesis of the dansyl-labeled PAM was also used to prepare a methyl red-labeled PAM. A amine derivative of methyl red was prepared bv a reported procedure[2] and coupled to the terminal carboxyl groups of the PAM as described above. The polymer so prepared had the same ^{1}H NMR and FT-IR spectrum as the dansyl-labeled PAM but had a pH-sensitive UV−vis spectrum.[22]

Hydrogen-Bonding of Polyacrylamide Polymers (PNIPAM or PAM) to Oxidized Polyethylene Films and to Hyperbranched Poly(acrylic acid) on Polyethylene Films (3-PAA/PE). These starting polyethylene films (PE-CO_2H or 3-PAA/PE) were prepared using reported procedures.[2] The polyethylene substrate film was then immersed in a solution of 0.100 g of PAM in 10 mL of 85% aqueous ethanol (or to 0.1 g of PNIPAM in 10 mL of ethanol) and allowed to sit for 15 h. The polyethylene substrate was then removed form the solution, rinsed with 85% aqueous ethanol (or ethanol for the PNIPAM-modified materials), dried under nitrogen, and then dried at reduced pressure for 15 min (1 Torr). At this point the film was either examined spectroscopically or washed in a Soxhlet apparatus. Washing entailed putting the hydrogen-bonded polyethylene substrate into a Soxhlet apparatus and washing it for 15 h with THF. ATR-IR spectroscopy of a PAM hydrogen-bonded 3-PAA/PE film included an amide I peak at 1656 cm^{-1} peak that was comparable if not larger than the acid carbonyl peak at 1710 cm^{-1}. Upon washing, it appeared that there was some deprotonation occurring in the film. The carbonyl peak at 1710 cm^{-1} lost intensity, and a new carboxylate appeared at 1560 cm^{-1}. The ATR-IR spectrum of a PNIPAM hydrogen-bonded film included an amide I peak at 1656 cm^{-1} peak that was comparable if not larger than the acid carbonyl peak at 1710 cm^{-1}. No substantive change in the ATR-IR spectrum of PNIPAM-modified hyperbranched PE films occurred on extraction. Decreases in the intensity of amide carbonyl peaks after extration were however observed for oxidized polyethylene films that had been treated with polyacrylamides.

Hydrogen-Bonding from a Solution onto SAM-MUA or 3-PAA/Au. The gold film was submerged in a solution of 0.100 g of polymer in 85% aqueous ethanol (PAM) or 100% ethanol (PNIPAM) and allowed to sit for 15 h. The film was then removed form the solution, rinsed with 85% aqueous ethanol (PAM) or 100% ethanol (PNIPAM), and dried under nitrogen. Ellipsometry and FTIR-ERS were then used to characterize these films.[7] The films were washed by soaking in 85% aqueous ethanol (PAM) or 100% ethanol (PNIPAM) for 15 h. The films were then removed from solution, rinsed aqueous ethanol (PAM) or 100% ethanol (PNIPAM), and dried under nitrogen.

Dansyl-Labeled Poly(acrylic acid). Poly(acrylic acid) (4.14 g, 450 000 M_w) was dissolved in 80 mL of water, cooled to 0 °C, and allowed to react with 18 mg of EDC and 11 mg of *N*-hydroxysuccinimide for 30 min. Then 25 mg of the ethylenediamine derivative of dansyl chloride was added, and the resulting mixture was stirred for 15 h. The mixture was washed with CH_2Cl_2, and the aqueous solution was evaporated to dryness at reduced pressure to yield the labeled poly(acrylic acid). The estimated loading of fluorophore on this poly(acrylic acid) polymer was ca. 0.15 mol %. While fluorescence of this polymer showed a peak for dansyl ($\lambda_{excitation}$ = 357 nm and $\lambda_{emission}$ = 525 nm in ethanol), ^{1}H NMR and IR spectra of the product were indistinguishable from the spectra of the starting poly(acrylic acid) due to the low loading of the fluorophore.

Hyperbranched *N*-Isopropylacrylamide of 3-PAA/PE. A 3-PAA/PE film sample was suspended in 60 mL of dry DMF and activated with 1 mL of *N*-methylmorpholine and 1 mL of ethyl chloroformate for 1 h. The film was rinsed with dry ethyl acetate, dried at 1 Torr for 30 min, and then immersed in 50 mL of DMF containing 2 M isopropylamine for 3 h. The product film was then rinsed with ethanol, acidified with 50 mL of 0.1 N HCl, rinsed again with ethanol, and then dried at 1 Torr. This procedure was repeated twice more to yield a hydrogen-bond acceptor polymer for binding to a soluble poly(acrylic acid) hydrogen-bond donor. The conversion of the PAA graft into a poly(*N*-isopropylacrylamide) graft was verified by ATR-IR spectroscopy, which showed an 80% reduction in the $-CO_2H$ peak intensity and the appearance of new amide peaks at 1645 and 1544 cm^{-1}.

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