Preparation of Hyperbranched Polymer Films Grafted on Self-Assembled Monolayers

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Highly branched polymers provide new molecular structures that have interesting properties and applications.[1−7] In this paper we report the preparation of thin films of new highly branched polymers which are relevant to boundary layer phenomena such as adhesion, wetting, and chemical sensing. Specifically, we synthesized surface-grafted, hyperbranched poly(acrylic acid) (PAA) films on self-assembled organomercaptan monolayers. These films grow in discrete steps, but unlike most layer-by-layer approaches, film thickness increases nonlinearly as a function of the number of layers because of the branched polymeric architecture. Moreover, these polymer films contain a high density of carboxylic acid groups, which can selectively bind metal ions or serve as reactive sites for subsequent derivatization.

Although we are unaware of examples of other surface-grafted, hyperbranched polymer films, several groups recently prepared surface-confined monolayer and multilayer polymeric thin films.[8−16] In a synthetically elegant approach, Whitesell and Chang synthesized 1000 Å-thick monolayers of helical peptides.[14] Decher and co-workers developed a simple method for preparing polymer multilayers by sequential electrostatic adsorption of anionic and cationic polymers.[15] In solution, a few combburst polymers were recently synthesized which have structures somewhat similar to the surface-grafted PAA films we describe here.[17] The PAA films discussed here combine many of the unique and desirable properties of the above-mentioned materials in that they are prepared stepwise, can be thick (>1000 Å), and are highly branched.

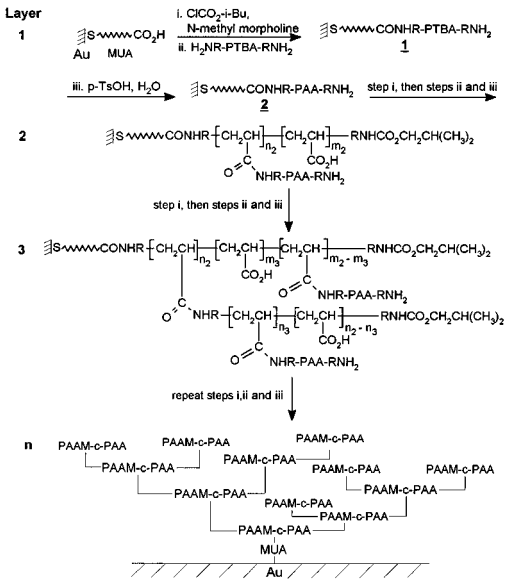

Figure 1. Hyperbranched polymer grafts prepared on a mercaptoundecanoic acid SAM confined to a gold substrate. H_2NR-PTBA-RNH_2 is amine-terminated poly(*tert*-butyl acrylate) ($R = C(CN)(CH_3)(CH_2)_2$-$CONH(CH_2)_2$), PAAM-c-PAA represents a random copolymer of poly(acrylic acid) and the poly(acrylamide) formed from poly(acrylic acid) carboxylic acid groups and the amines of a hydrolyzed PTBA derivative.

Our synthetic procedure (Figure 1) begins with a mercaptoundecanoic acid (MUA) self-assembled monolayer (SAM).[18,19] Activation of the carboxylic acid groups via a mixed anhydride[20] followed by reaction with an α,ω-diamino-terminated poly(*tert*-butyl acrylate) (H_2NR-PTBA-RNH_2) yielded the grafted polymer layer, **1**. Hydrolysis (*p*-TsOH·H_2O in benzene, 50−55 °C, 1 h) then formed a grafted PAA layer, **2**. Repetition of these steps produced additional grafting at multiple sites on each prior graft, leading to a layered, hyperbranched polymer film.

This procedure has several desirable attributes. First, it compensates for inefficiencies in reactions at surfaces. Because there are many grafting sites on each polymer chain, this method produces a thick polymer layer even if reactions proceed in relatively poor yield . Second, the grafted polymer films contain a high density of reactive functional groups that are suitable for further elaboration. Finally, because branching infers that each subsequent layer contains more polymer chains, this method leads to increasingly thicker and more tightly packed polymer layers.

We monitored each synthetic step using Fourier transform infrared external reflection spectroscopy (FTIR-ERS). Activation of the carboxylic acid groups of the MUA monolayer (Figure 2A) produced anhydride intermediates, which were stable enough to be observed spectroscopically at 1825 cm^{-1} (Figure 2B). The anhydrides were allowed to react with amine groups of H_2NR-PTBA-RNH_2 (M_n = 14 600) to form amide bonds and hence the first layer of the surface-grafted polymer. The FTIR-ERS spectrum of the grafted polymer contains a small peak at 1545 cm^{-1} that we attribute to the amide bonds and a large peak at 1733 cm^{-1} resulting from the ester groups of PTBA (Figure 2C). We then hydrolyzed the *tert*-butyl ester groups to form a PAA graft.[21] Peaks at 1394, 1369, 1258, and 1159 cm^{-1} (Figure 2C) due to the *tert*-butyl ester groups[22] disappeared after hydrolysis (Figure 2D). Changes in water contact angles from 86° to <10° and elemental analysis using X-ray photo-

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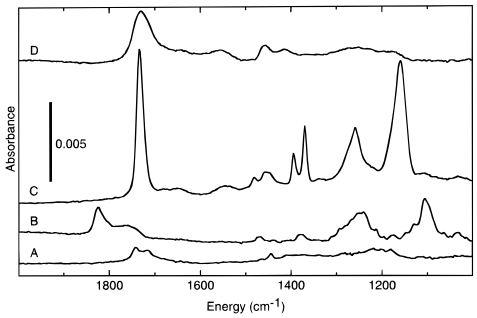

Figure 2. FTIR-ERS spectra of (A) a MUA monolayer, (B) the MUA monolayer activated with isobutyl chloroformate, (C) a layer of PTBA grafted on the MUA monolayer, and (D) hydrolyzed PTBA on the MUA monolayer.

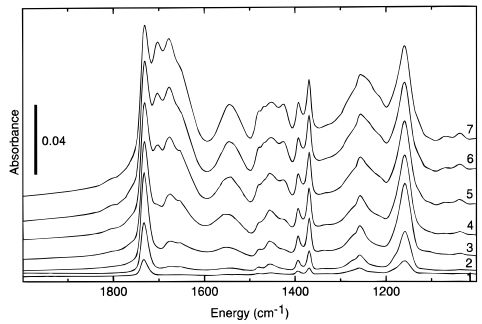

Figure 3. FTIR-ERS spectra of 1−7 layers of PTBA grafted on a MUA monolayer.

electron spectroscopy (XPS) confirm addition of the polymer and hydrolysis.

Following hydrolysis of the first layer, the newly formed carboxylic acid groups were activated with isobutyl chloroformate and allowed to react with H_2NR-PTBA-RNH_2. Subsequent hydrolysis, confirmed by contact angle measurements, yielded the second grafted layer of PAA. Through repetition of these steps, we have synthesized as many as seven polymer layers. Because each polymer chain contains several polymer grafts and each of these grafts contains additional polymer grafts, this process results in highly branched, graft polymers. Figure 3 shows FTIR-ERS spectra for films containing 1−7 grafted PTBA layers. The intensity of the C−O peaks (1258 and 1159 cm^{-1}) of the *tert*-butyl ester, carbonyl peak (1733 cm^{-1}), and amide peaks (1678 and 1545 cm^{-1}) increase with the number of grafted layers. The fact that the intensity of the amide peaks increases nonlinearly indicates that polymer chains are covalently grafted and not just physically entangled. Control experiments confirmed that grafting proceeded via a carboxamide. When we attempted to graft a layer of PTBA onto the MUA monolayer or a layer of PAA without using isobutyl chloroformate activation, the film thickness increased by only a few angstroms.

As shown in Figure 4, the ellipsometric thickness of the polymer films does not vary linearly with the number of grafted polymer layers. The thickness gained from each grafting step increases rapidly during formation of the first few layers because there are many more reactive carboxylic acid groups in each subsequent layer. This result is consistent with the trends in the intensities of the FTIR-ERS absorptions. Figure 4 also shows the ratio of thicknesses in consecutive layers. These data suggest that a high level of branching occurs in the first few layers. In outer layers, space constraints restrict branching and layer thicknesses approach a constant value.

Because of the large density of functional groups, PAA films can serve as specific metal-ion binders. After exposure to an

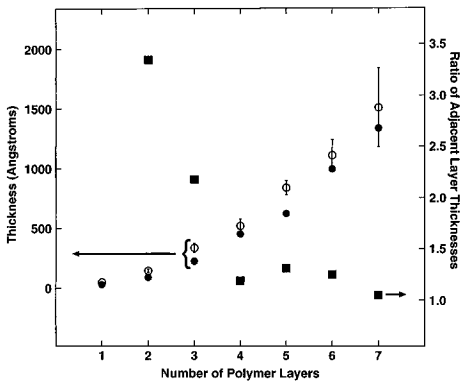

Figure 4. Ellipsometric thicknesses of hyperbranched polymer films versus the number of grafted layers before (open circles) and after (filled circles) hydrolysis.[23] The ratio of adjacent layer thicknesses (filled squares) is also shown for each layer.

equimolar ethanolic solution of $Fe(ClO_4)_3$ and $Ni(ClO_4)_2$, the intensity of the acid carbonyl FTIR absorption (1731 cm^{-1}) decreased by >80% and new peaks corresponding to the symmetric and asymmetric stretches of carboxylate appeared (1582 and 1440 cm^{-1}). These changes demonstrate metal complexation by the carboxylate receptors. In this competitive binding experiment, the films bound high levels of Fe^{3+} (XPS: O/Fe = 6, consistent with each Fe^{3+} coordinated to three carboxylates), but no detectable Ni^{2+}. This result is in accord with the formation constants of Fe^{3+}− and Ni^{2+}−carboxylate complexes.[24]

To demonstrate that PAA films can be derivatized to change interfacial properties, we reacted the carboxylic acids on the hyperbranched polymer film (four grafted layers) with ethylene diamine. The reaction occurs after activating COOH groups with isobutyl chloroformate as in the grafting process. The FTIR-ERS spectrum of the polymer film reveals large, newly formed amide peaks (1674, 1555 cm^{-1}) and a >65% decrease in the carboxylic acid carbonyl peak (1731 cm^{-1}).

In summary, hyperbranched PAA films can be easily synthesized on a MUA SAM via sequential grafting with polymeric building blocks. The film thickness increases rapidly as a function of the number of grafting steps. In addition, these films contain a high density of carboxylic acid groups that can selectively bind metal ions or be chemically modified. Hyperbranched polymer films thus provide new platforms for chemical sensing applications and for tailoring polymer surface properties for a wide variety of technological applications.

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Supporting Information Available: Preparation of H_2NR-PTBA-RNH_2, grafting procedure, table of thicknesses and contact angles, FTIR-ERS and XPS spectra of grafted PAA films (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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