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Polymer 47 (2006) 8137–8146

polymer

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Role of functionalized terminal groups in formation of nanofibrillar morphology of hyperbranched polyesters

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Received 16 July 2006; received in revised form 14 September 2006; accepted 15 September 2006
Available online 11 October 2006

Abstract

A series of amphiphilic hyperbranched polymers with a polyester–polyol core and 64 terminal hydroxyl groups were modified by substituting various terminal groups: alkyl tails, amino, and carboxyl groups. The effect of the pendant groups' chemical composition on the resulting surface morphology within Langmuir–Blodgett monolayers with respect to their ability to form nanofibrillar surface structures was investigated. We demonstrated that the amphiphilicity of the polyester core with 64 hydroxyl groups can be achieved if a fraction of alkyl tails (C15) is higher than 1/4. Nanofibrillar morphology was consistently formed as the highly polar functional groups were added to the polyester cores in combination with a significant (>30%) fraction of alkyl terminal groups. Addition of amino end groups was observed to be much more effective in promoting the nanofibrillar assembly than the addition of carboxyl end groups.

Keywords: Self assembly; Hyperbranched polymers; Langmuir–Blodgett films

1. Introduction

Hyperbranched polymers' thermal, mechanical, and physical properties can be tuned several ways by varying internal chemical structure, backbone flexibility and branching, and inner and outer functional groups' nature and distribution [1–6]. When no precise structural organization and specified placed functionalities are required, hyperbranched polymers are considered good candidates for a variety of applications requiring low viscosity and high density of functional groups [7–21]. Highly branched polymers have been recently investigated for sensor applications including aromatic hyperbranched polyesters with differing end groups for chemical sensor applications [28], hyperbranched hydrogen-bond acidic polymers for surface acoustic wave sensor applications [22], and hyperbranched polyesters with different terminal groups as a sensitive layer for solvent detection [23]. Chemical modification of hyperbranched cores with different terminal groups can alter interfacial behavior, adjusting known non-covalent interactions including hydrogen bonding, polar interaction, and π–π stacking [24–26]. For example, Li et al. [26] reported that fluorinated functional groups attached to hyperbranched polyglycidol strengthened the interaction between molecules, reflected in viscosity and thermal properties. A hyperbranched polymer core with the substituted terminal hydroxyl groups with benzoyl chloride showing aggregated morphology controlled by a quantity of benzoyl terminal groups was reported by Jiang et al. [27]. Other researchers focused on the adjustments made to the polymer core and whether it can govern self-assembly properties, reducing the influence of end groups [24]. Sparse studies have been done

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doi:10.1016/j.polymer.2006.09.035

to date for systematic exploration of factors effecting multifunctional hyperbranched polymers' self-assembly.

In the case of adsorption onto a solid surface, the surface structures are controlled by the composition of aliphatic and polar groups which determines the character of highly branched polymers' self-assembly at the air–water interface [28–30]. While much research work has gone into understanding and directing surface assembly of dendrimers [31–47] and star block copolymers [48–51], the assembly of hyperbranched molecules at surfaces remains a challenging task and has been addressed only in a few recent studies [52–58]. Moreover, there are only a handful of reports on the formation of organized nanostructures from hyperbranched molecules composed of irregular, random branched fragments with the degree of branching well below than that observed for the dendrimer architecture [59]. Generally, they are not expected to form regular supramolecular structures because of their high polydispersity, irregular architecture, and poorly defined shape. Yet as we have recently shown, multiple weak intermolecular interactions among irregular, highly branched, and polydisperse molecules can facilitate their assembly into one-dimensional supramolecular structures within Langmuir–Blodgett (LB) monolayers [59,60]. This phenomenon was observed for modified hyperbranched polyesters with initial 64 hydroxyl terminal groups partially modified with aliphatic chains and amino end groups. These were remarkably well ordered structures that show long micro- and nanofibers. However, only two examples of particular chemical compositions with a particular fraction of amino terminal groups were observed to be capable of forming one-dimensional surface structures [59,61]. The possibility of such a peculiar assembling behavior in the presence of other terminal groups (e.g., carboxyl) and a different overall chemical composition of amphiphilic shells have not been addressed.

In this paper, we focus on understanding the role of amphiphilic balances and the combination of different functional terminal groups in nanofibrillar structure formation within Langmuir monolayers of modified hyperbranched polyesters. For this study, a series of modified hyperbranched polyesters were synthesized from commercial polyol Boltorn BH40 with about 64 hydroxyl terminal groups via step-wise end-grafting of the palmitic acid group followed by either aminohexanoic acid or succinic acid grafting. The objective of this assay was to screen a larger range of outer shell compositions by varying the number of hydrophobic alkyl groups and ionic amino- and carboxyl-terminated branches. Examination of self-assembly in LB monolayers with AFM provides an insight into how the variable shell composition affects the resulting surface morphologies.

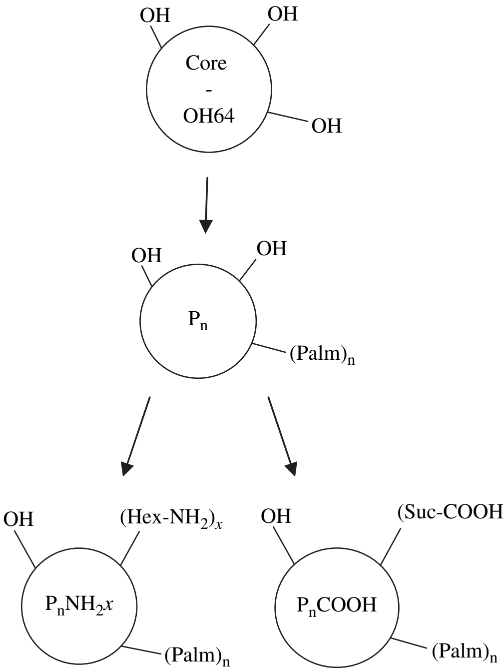
2. Experimental section

2.1. Materials

Hyperbranched polyester core *Boltorn H40* was obtained from Perstorp Polyols AB, Sweden. All additional chemicals were purchased from Aldrich and used without further purification. The initial polydispersity of hyperbranched polyester used here was 1.9. Before modification, the commercial product was purified to remove low molar weight fractions and reduce polydispersity to 1.4. Fractional precipitation of the hyperbranched polyester core and functionalization were performed according to the procedure stated elsewhere [59]. In summary, the degree of branching of the polyester core after purification was 0.4, the average number of monomeric units (the degree of polymerization) was 60, the number of hydroxyl terminal groups was 63–64, and the number average molecular weight of the initial core was 7800, all data were obtained from NMR. GPC analysis showed much lower absolute values as is expected for branched molecules.

Tailoring of the hyperbranched polymer used in this research utilized traditional methods of ester and amide syntheses [59,62,63]. Terminal hydroxyl groups of the core were esterified with palmitoyl chloride (Palm), aminohexanoic carboxylic (Hex) acid and succinic anhydride (Suc). Scheme 1 shows the major steps in the preparation of a series of amphiphilic hyperbranched polymers. At the first step, the hyperbranched polymer was modified with alkyl and carboxylic acid groups to assure its amphiphilic properties. Synthesis of aliphatic esters was performed via reaction with palmitoyl chloride. Synthesis of the compound with NH_2 terminal groups was done following the known procedure [59]. Every step of the synthesis was followed by the purification of the product using column chromatography and dialysis. Purity of the product and its polydispersity were controlled by using GPC analysis after each step.

Compounds were fully characterized by FTIR, GPC, ^1H, and ^{13}C NMR as discussed in numerous publications on hyperbranched polyesters coming from our groups as well as from



Scheme 1. Chemical modification of the polyester core. Abbreviations palmitoyl (Palm), aminohexanoic (Hex) and succinic (Suc).

other research groups [59,64–67]. The chemical composition of the synthesized polymers was estimated from ^1H and ^{13}C NMR similarly to that described in detail for similar compounds in our previous publications [59,60]. Chemical structures and molecular models built with ChemDraw and Materials Studio gave estimated dimensions of the molecules. The data for the composition and molecular weight of all compounds studied here are summarized in Table 1.

2.2. Fabrication of the surface structures

The substrates for LB deposition were atomically flat polished silicon wafers of the [100] orientation (Semiconductor Processing, Co.). Silicon wafers were cleaned by a ‘‘piranha’’ solution according to usual procedure described in detail elsewhere [68,69]. Silicon substrates were cut into pieces of 15 by 20 mm. The hyperbranched polyesters were dissolved in chloroform and LB monolayer deposition was conducted using LB troughs (R&K and KSV). A dilute solution in chloroform of 35 μL was deposited onto the Nanopure water (18 MOm cm) surface. The concentration of the solution was 0.043 mmol/L. Barriers were made to compress at the rate of 50 μm/s. The monolayers were deposited at 1 mN/m, 5 mN/m, 10 mN/m, 20 mN/m, and 30 mN/m surface pressures. All monolayer thickness measurements were obtained with a COMPEL Automatic Ellipsometer (InOm Tech, Inc.) with an incident angle of 70° with refractive indices estimated from chemical composition.

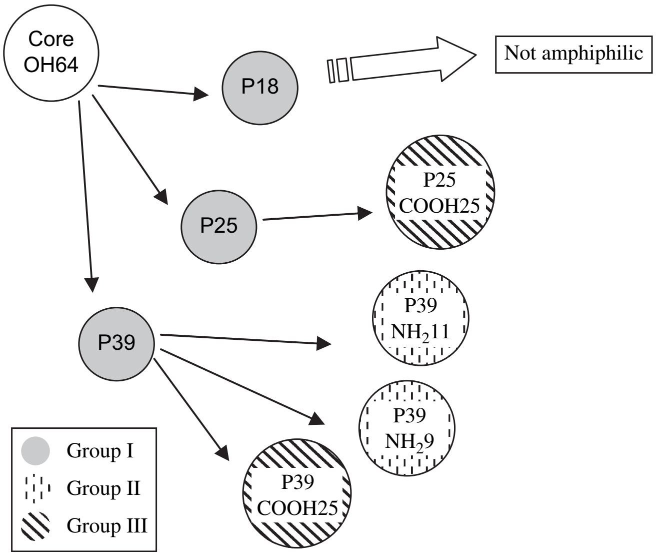
2.3. LB monolayers characterization

The LB monolayers on a silicon surface were studied with AFM microscopes Dimension 3000 and Multimode (Digital Instrument, Inc.) in the tapping mode according to the experimental procedure well established in our laboratory and described earlier [70,71]. The AFM imaging in concurrent topography and phase modes was performed in the regime of the ‘‘light’’ tapping to avoid damaging of the monolayers. The shape of the AFM ultrasharp silicon probes was evaluated by scanning a reference specimen of gold nanoparticles with a diameter of 3–5 nm. Scan sizes were collected with 10, 5, 2, and 1 μm scan sizes and at a scan rate of 0.6 Hz in most cases.

3. Results and discussion

Amphiphilic hyperbranched polyesters with identical cores and different shell compositions are separated into three groups for discussion as shown in Scheme 2. A summary of the polymers’ molecular characteristics is listed in Table 1 which also includes initial polyester core for comparative purposes. The chemical structure of the polyester core used for functionalization is presented in Fig. 1A. Also shown are molecular models for two selected compounds studied here demonstrating the overall shape and idealized distribution of the various terminal groups, Fig. 1B,C.

The first group of hyperbranched polymers is comprised of three polyester cores with different numbers of palmitic terminal groups: 18, 25, and 39. The maximum substitution number for this hyperbranched polymer is 64 since the core structure has on average 64 terminal hydroxyl groups. However, due to sterical hindrance, it is often impossible to achieve targeted substitution, thus the final number of alkyl chains attached can deviate from initially calculated. After including in the consideration that the previously explored hyperbranched polymer had 50 alkyl tails, the series considered here covers a range of contents of alkyl terminal groups from about 30% to 80%.



Scheme 2. Grouping of modified hyperbranched compounds.

Table 1
Hyperbranched polymers studied and their characteristics

Group	Name	Number of alkyl tails	Number of COOH	Number of NH$_2$	Number of free OH	M_n (GPC), kDa	PDI (GPC)	M_n (NMR), kDa
0	Core	None	None	None	64 ± 2[a]	3.8	1.4	7.8
I	P39	39 ± 2	None	None	25 ± 2	8.0	1.6	16.6
	P25	25 ± 2	None	None	39 ± 2	6.7	1.5	13.2
	P18	18 ± 2	None	None	46 ± 2	5.8	1.6	11.6
II	P39NH$_2$9	39 ± 2	None	9 ± 1	16 ± 2	10.8	1.5	17.6
	P39NH$_2$11	39 ± 2	None	11 ± 1	14 ± 2	12.4	1.5	17.8
III	P25COOH25	25 ± 2	25 ± 2	None	14 ± 2	11.3	1.5	16.1
	P39COOH25	39 ± 2	25 ± 2	None	0	13.5	1.6	19.1

[a] Here and everywhere, accuracy corresponds to estimated typical NMR uncertainty.

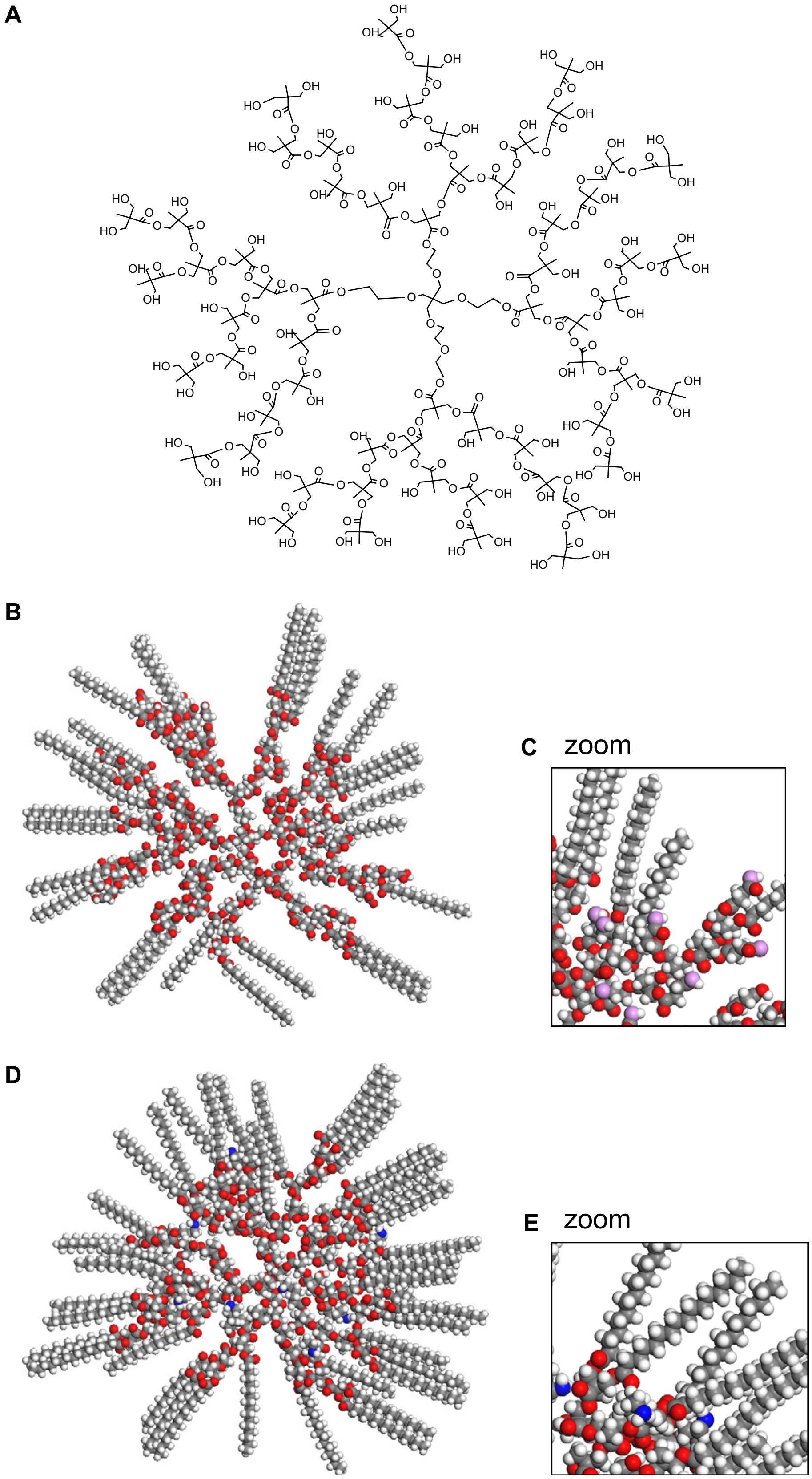


Fig. 1. Representative molecules: (A) chemical structure of core BH40, (B and C) molecular models of P25COOH25, (D and E) P39$NH_2$11. Zoomed structures (C and E) depict location of ionic group blue – amino group (E), and purple – hydroxyl of carboxylic group (E). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Here, it is worth noting that because the chemical modification reaction parameters are strongly dependent upon the molecular weight of the final compound and the degree of the substitution of the end groups, the precise control of the exact number of the substituted chains attached varied and did not correspond to any ''round'' fraction (see Table 1). However, considering relatively narrow (for hyperbranched polymers) molecular weight distribution (the polydispersity index within 1.4–1.6) the average parameters can be exploited for the analysis of the compositional trends. In all cases, the accuracy of the NMR-based derivation of the number of modified groups estimated from repeated measurements of different probes is very much consistent and usually small in comparison with differences between samples (Table 1). The presence of the low molar weight fraction as well as the presence of the high molecular weight molecules is apparently smearing the surface behavior but does not significantly mask general trends discussed below.

Group II includes two amphiphilic molecules with the same number of alkyl groups at 39 and a different number of terminal amino groups at 9 and 11 (Scheme 2). Group III represents two polymers with the same number of 25 carboxyl groups and a different number of aliphatic groups, 25 and 39, respectively (Table 1). The results obtained here are also compared with the modified hyperbranched polyester studied before with 50 alkyl tails and 14 amino groups [59]. The name of the polymer reflects the number of each palmitic and ionic group in each polymer as calculated from ^{13}C NMR analysis (Table 1).

3.1. Group I. Alkyl-substituted hyperbranched polymers: P39, P25, P18

The alkyl-substituted hyperbranched polyesters showed a small variance in the surface area per molecule as can be seen from the pressure area isotherms for all the three compounds as presented in Fig. 2. The limiting surface area calculated by the extrapolation of the steep rise in the surface pressure in the condensed monolayer state, in accordance with a usual procedure, displayed a small variation. The limiting surface area per molecule A_o for all the three polymers stayed around 15 nm^2 [72] (Fig. 2, Table 2). The P18 compound exhibited a more gradual transition in the surface pressure and the slightly lower surface pressure for the pre-collapsed state indicating less stable monolayers and thus a shift of the overall hydrophilic–hydrophobic balance from the most favorable. The variation of alkyl substitution plays a minimal role that indicates significant restructuring of the overall core shape and its predominant role in the formation of the densely packed monolayer. However, the thickness of the LB monolayers increased as the amount of the alkyl substitutions increased at both 5 mN/m pressure and 30 mN/m pressure, indicating a trend to the upward orientation of the alkyl tails and possible crystallization of the alkyl terminal chains. This trend is more clearly apparent for compounds with larger numbers of alkyl tails (Table 2). This suggestion is based on our previous results for similar hyperbranched compounds within Langmuir monolayers [52,59]. In fact, in these studies the processes of upward orientation and chain crystallization have been directly observed for hyperbranched compounds subjected to the compressive pressure by applying in situ synchrotron diffraction studies as discussed in detail in our previous publications.

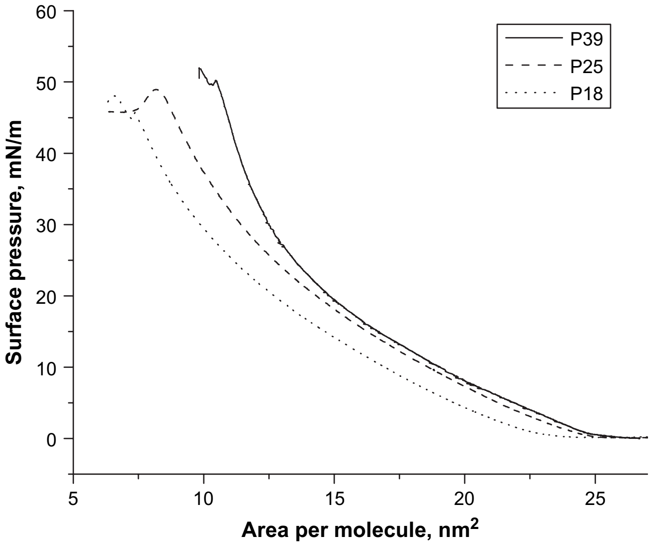


Fig. 2. Langmuir isotherms of alkyl-substituted hyperbranched polymers, Group I.

To determine the theoretical limiting surface area per whole molecule, the surface area per an alkyl tail can be calculated as described in previous publications, taking 0.2 nm^2 as the known surface area per alkyl tail in densely packed state [72]. Using the known numbers of alkyl tails as 18, 25, and 39, the total projected surface area per molecule occupied by the hydrophobic alkyl shell was estimated to be 3.6, 5, and 7.8 nm^2, respectively. However, the actual limiting surface area per molecule calculated from the surface area isotherms shows much larger values, indicating that the hyperbranched polymer core, not alkyl tails, limits the surface molecular area even for the largest number of alkyl tails studied here.

Shown in Fig. 3 is the surface morphology of LB monolayers as viewed by AFM (tapping mode) for alkyl-substituted hyperbranched molecules at low and high surface pressures. All modified hyperbranches with alkyl tails in their shells showed no characteristic fibrous structures even at high degrees of substitution. Surface roughness was very low at 0.1 nm RMS microroughness, measured within 1 μm^2 surface area. P39 compressed to 30 N/m showed a slightly higher RMS microroughness of 0.3 nm due to the formation of surface islands with an average height of 0.9 nm. This structure

Table 2
Limiting surface molecular area and the monolayer thickness (±0.2 nm here and everywhere) for Group I at pressures 5 mN/m and 30 mN/m

Name	A_o, nm^2	t_5, nm	t_{30}, nm
P18	14.5	1.6	2.5
P25	16	1.7	2.8
P39	15	1.8	3.3

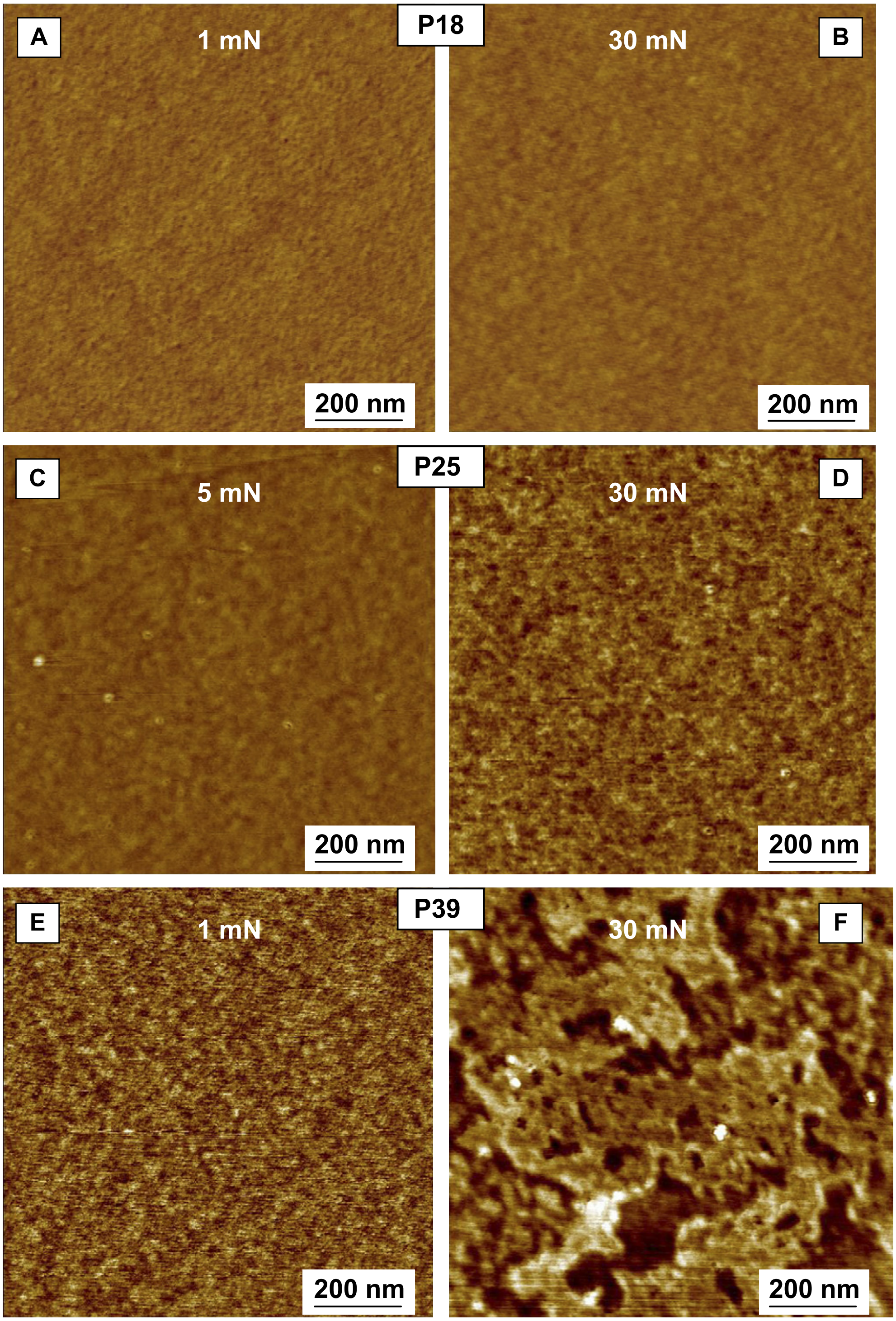


Fig. 3. AFM images of LB monolayers at different pressures, Group I. *Z*-scale 5 nm.

can be contributed to the formation of closed packed crystalline areas formed with vertically oriented alkyl tails and surrounded by less ordered regions which can be composed of low molar weight fraction. This kind of molecular ordering cannot be achieved with a lower degree of substitution because of the lower surface density, loosely packed aliphatic chain groups and the dominating role of the polyester cores in the lateral ordering.

Finally, it is worth noting that the compound with the lowest number of alkyl tails studied here loses its amphiphilicity even after minor addition of amino or carboxyl groups (Scheme 2). After modification, it becomes soluble in the water subphase and thus not capable of forming stable Langmuir monolayers. This result indicates that higher than 1/4 substitution of the polyester core end groups with alkyl tails is required to induce the stable hydrophilic–hydrophilic balance which is still sufficient to support hyperbranched molecules at the air–water interface.

3.2. Group II. Amino-alkyl-substituted polymers: $P39NH_211$, $P39NH_29$

The presence of amino terminal groups makes the polymer core more hydrophilic and aids the polymer hydrogen bonding capability, resulting in denser molecular packing. A significant change in the surface molecular area is observed upon the addition of amino groups along with alkyl tails (Fig. 4). Addition of amino groups yielded a lower A_o, indicating a more compact structure of the polyester core (Table 3). These changes are accompanied with a more gradual transition upon compression. The thickness of the LB monolayers decreased significantly upon addition of amino groups at high pressure when compared to alkyl-substituted P39, reflecting substantial reorganization of the intramonolayer structure. The change is less pronounced for the compound with 11 amino groups and is much more dramatic for the compound with 9 amino terminal groups (Table 3).

In fact, AFM shows a dramatic change in the surface morphology of both amino-containing compounds as compared with initial alkyl-modified cores (Fig. 5). Both amphiphilic hyperbranched molecules with combined alkyl and amino terminal groups are capable of forming nanofibers with dimensions very similar to those reported previously [59]. The density of the nanofibers is increasing with the surface pressures. Densely correlated bundles which combine 5–7 nanofibrils were observed at the highest pressure for the compound with 9 amino groups. Occasionally at low pressure, very peculiar structures of closely spaced parallel stacks of these nanofilaments were formed. The height of the nanofibers evaluated from AFM cross-sections is 0.8 nm.

The morphology of the nanofibrillar texture is very different for two amino-containing compounds studied here. Unlike the hyperbranched compound with 9 amino groups, the P39N11 molecules form very few nanofibers scarcely placed over the surface (5–10 per 1 μm^2), while P39N9 compound forms a dense network of filaments (Fig. 5). Dimensions of these nanofibers are similar to those described in our previous report on the hyperbranched compound which can be named P50N14, using the present naming terms [59]. Close similarity of the nanofibrillar morphologies allows us to assume that structure formation mechanisms are similar since the polymers have the same functional groups and are only slightly different in the overall composition. Driving forces for this assembly come from two major factors: hydrogen bonding among the carbonyl groups of the core structure and the amino groups of aminohexanoic acid, as well as crystallization of alkyl tails under compression.

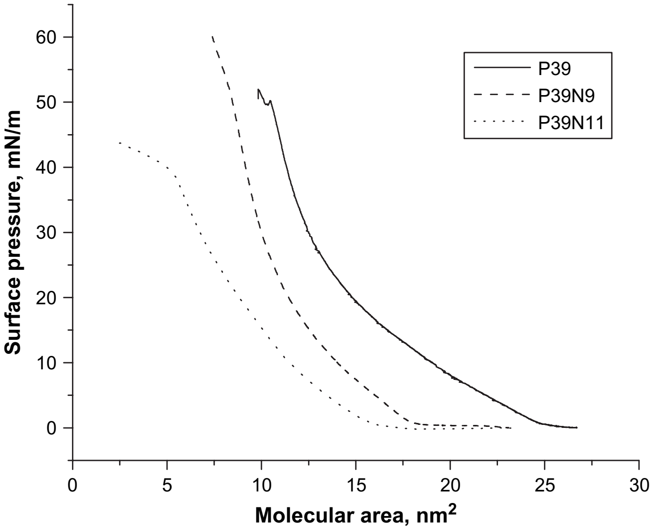


Fig. 4. Langmuir isotherms of amino-alkyl substituted hyperbranched polymers, Group II.

Table 3
Limiting surface molecular area and monolayer thickness for Group II at pressures 5 mN/m and 30 mN/m

Name	A_o, nm^2	A_1, nm^2	t_5, nm	t_{30}, nm
P39N11	13	23	1.8	2.3
P39N9	12.5	18	1.0	1.8
P39	15	25	1.8	3.3

The absence of a dense nanofibrillar network for the compound with a fewer number of alkyl tails and higher number of amino terminal groups, even at high surface pressures, can be rationalized by suggesting a stronger trend toward phase separation within LB monolayer which favors planar ordering of the alkyl tails on the expense of the association of the polyester cores. In this case, the hyperbranched molecules likely form microphase separated layers of alkyl tails and cores, which prevent the formation of one-dimensional fibrillar structures. Isolated fibrillar structures are likely formed on defects and interdomain boundaries.

3.3. Group III. Carboxyl-alkyl-substituted polymers: P38COOH25, P25COOH25

The inclusion of COOH terminal groups showed the most dramatic effect on the modified hyperbranched compounds' surface behavior (Fig. 6). Compound P25COOH25 possessed the lowest surface molecular area among all compounds studied here (Table 4). The addition of acidic COOH groups shifts the balance between the hydrophilic cores and hydrophobic alkyl tails, making the cores much more compact. The alkyl tails then take on more upright orientations at higher surface pressures. The larger amount of alkyl tails in P39COOH25 buffers the added hydrophilic effect more effectively but even in this case, significant compactness of the modified polyester cores is obvious from the pressure area isotherms (Fig. 6).

The surface morphology studies of the carboxyl-containing compounds revealed a very different pattern (Fig. 7). First, hyperbranched compound P39COOH25 formed very few fibers. Moreover, the density of the fibers for this polymer does not change much with an increase of the surface pressure. These fibers have different shapes and resemble the edges of grain

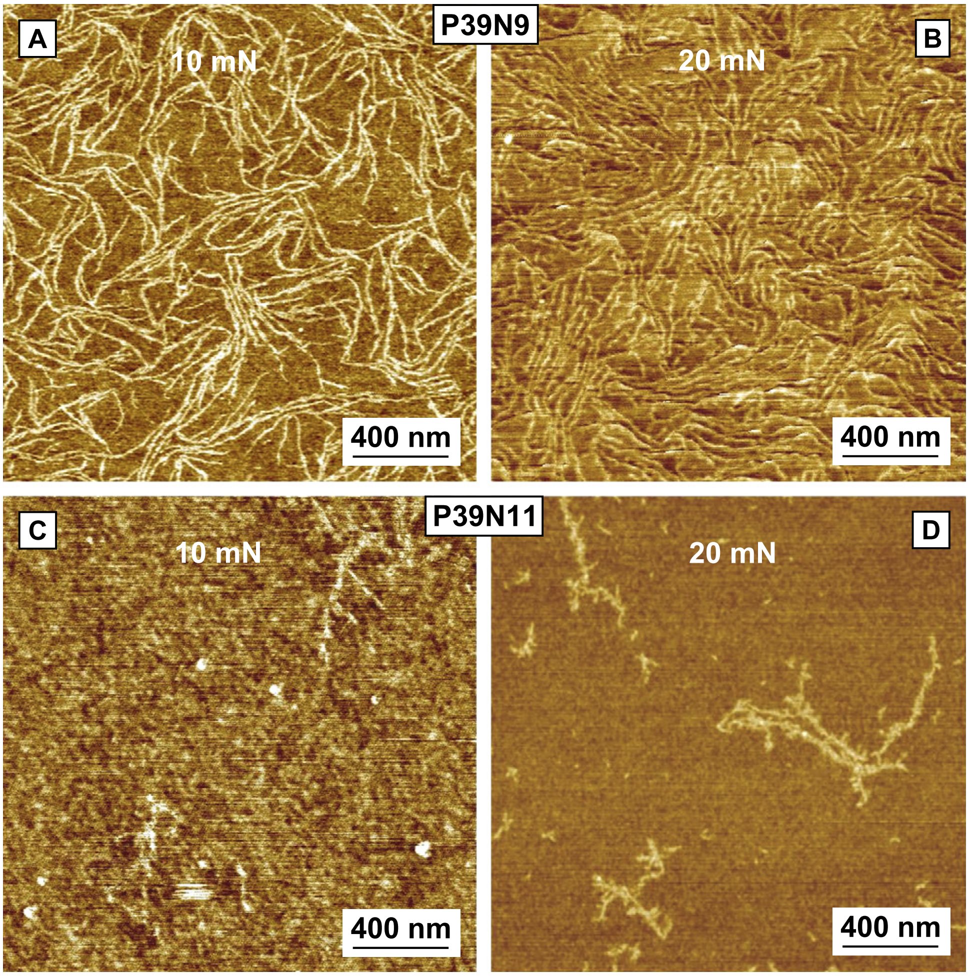


Fig. 5. AFM images of LB monolayers at different pressures, Group II. *Z*-scale for A and C – 3 nm and B and D – 5 nm.

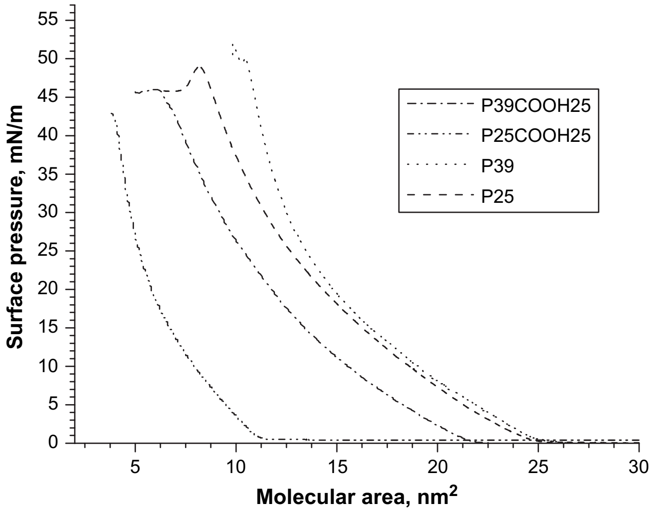


Fig. 6. Langmuir isotherms of carboxyl-alkyl substituted polymers, Group III: P39COOH25, P25COOH25, vs alkyl substituted compounds P25 and P39.

boundaries. In contrast, dendritic or fibrous structures are formed in P25COO25 with fewer numbers of alkyl tails (Fig. 7). This surface morphology is very different from that observed before and its formation is pressure dependent. At higher pressure, the density of dendritic fibers increases and at 20 mN/m, an extensive network of dendron-like filaments is observed. Cross-section measurements point to monomolecular stacking morphology of these structures. Apparently, in the case of carboxyl-terminated branches one-dimensional structures, they can be assembled within LB monolayers although they are not well developed as shown in both our previous studies and with the amino-containing hyperbranched compounds studied here. To form even imperfect one-dimensional structures, a much higher concentration of carboxyl terminal groups is required: 25 carboxyl groups (or 40%) as compared to 9 amino groups (or 14%). Obviously, this difference can be attributed to the fact that despite the carboxylic groups are capable of forming intermolecular hydrogen

Table 4
Limiting surface molecular area and monolayer thickness for Group III at pressures 5 mN/m and 30 mN/m

Name	A_o, nm^2	t_5, nm	t_{30}, nm
P25COOH25	8	1.4	2.3
P25	16	1.0	1.9
P39COOH25	14	1.8	2.5
P39	15	1.8	3.3

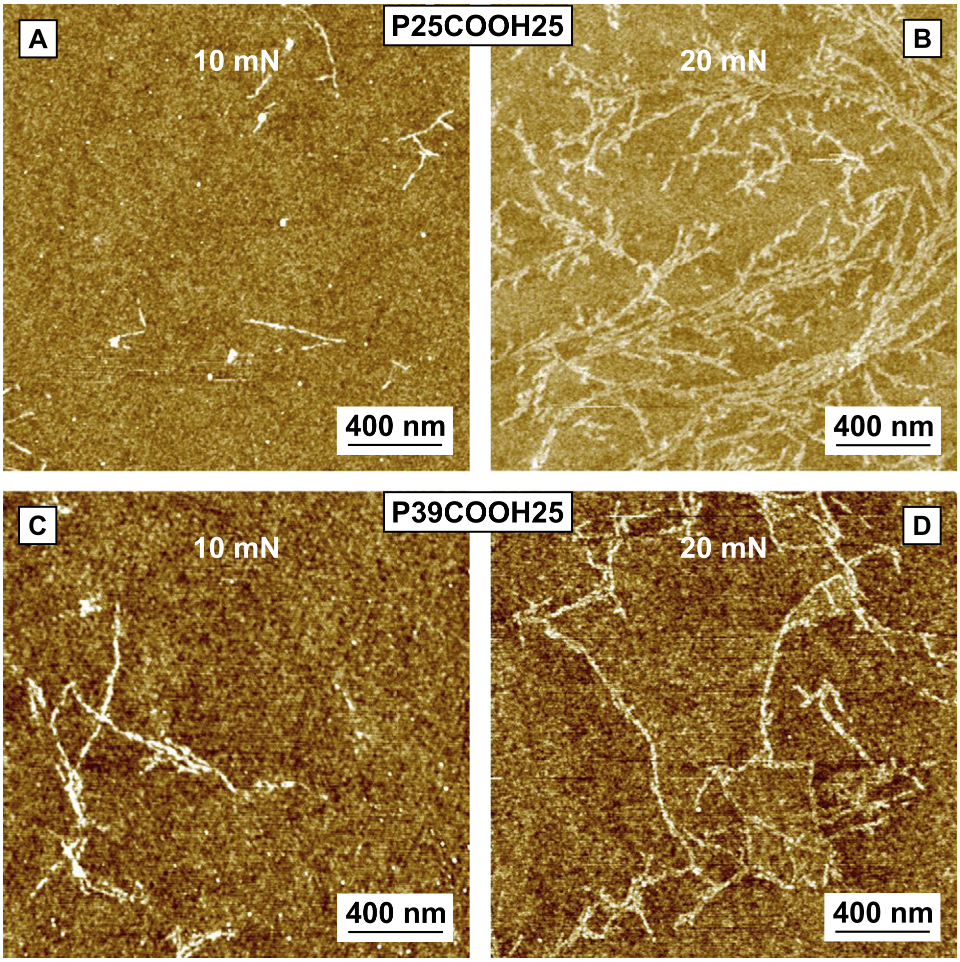


Fig. 7. AFM images of LB monolayers at different pressures, Group III. *Z*-scale for A and C – 3 nm and B and D – 5 nm.

bonds which promote the nanofibrillar assembly, their ability to support an extensive and robust network of hydrogen bonding is below the networking ability of amino-carboxylic pairs which belong to the same or neighboring molecules [73].

4. Conclusions

In conclusion, we observed that all alkyl, amino-alkyl, and carboxyl-alkyl substituted hyperbranched polyester cores with 64 branches display amphiphilic properties and form stable Langmuir monolayers at the air–water interface. Decreasing the fraction of the alkyl tails to about 30% brings the compounds on the verge of unbalanced hydrophilic–hydrophobic interactions with a slight increase in core polarity making molecules soluble in the water subphase. Addition of polar and hydrogen bond-making terminal groups to the polyester core promotes the formation of nanofibrillar morphology with few (<15%) amino groups resulting in well-defined and long individual nanofibrils and their bundles. A large amount of carboxyl groups (40%) promotes the formation of imperfect and poorly developed nanofibrillar structures within LB monolayers.

Acknowledgements

Funding from the National Science Foundation, the NSF-DMR-0308982 project and AFOSR F496200210205 grant as well as specimen donation from Perstorp Polyols AB are gratefully acknowledged. The authors thank B. Rybak for assistance with AFM measurements.

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