Modification of Surfaces and Interfaces by Non-covalent Assembly of Hybrid Linear−Dendritic Block Copolymers: Poly(benzyl ether) Dendrons as Anchors for Poly(ethylene glycol) Chains on Cellulose or Polyester

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Received October 16, 1998. Revised Manuscript Received February 22, 1999

Solution and interfacial properties of water-soluble hybrid linear−dendritic polyether copolymers are investigated by static and dynamic surface tension measurements and adsorption experiments on polymeric substrates. The results obtained show that the block copolymers are able to form mono- and multimolecular aggregates in water. Contacting a solid polymeric substrate with an aqueous solution of hybrid block copolymer increases the hydrophilicity of the substrate. Adsorption on the hydrophobic surface of poly(ethylene terephthalate) proceeds only through the dendritic blocks of the hybrid macromolecule. For more hydrophilic substrates such as regenerated cellulose, both the poly(ethylene glycol) tail and the poly(benzyl ether) dendrons adsorb on the surface, increasing its hydrophilicity.

Introduction

The interest in dendritic polymers has recently focused both on their efficient preparation and on the search for new applications.[1] In the area of interfacial sciences, several groups[2−9] have studied dendrimers and hyperbranched polymers. For example, in earlier work, we have reported on dendrons at the air−water interface and used neutron reflectivity experiments to ascertain the shape and flexibility of simple dendritic macromolecules.[2] In several other interesting studies, dendritic macromolecules were either physically adsorbed[3−5] or covalently grafted[6−9] onto various substrates.

We report here the first attempt to alter the surface properties of polymeric substrates through adsorption of well-defined hybrid linear−dendritic block copolymers.[10,11] The linear−dendritic architecture of hybrid macromolecules, combined with their amphiphilic behavior, is expected to favor the formation of unique, broadly anchored, brushlike polymeric interfaces between hydrophobic substrates and hydrophilic media. A high density of potential hydrophobic anchor groups (benzyl ether moieties) is concentrated at the dendritic

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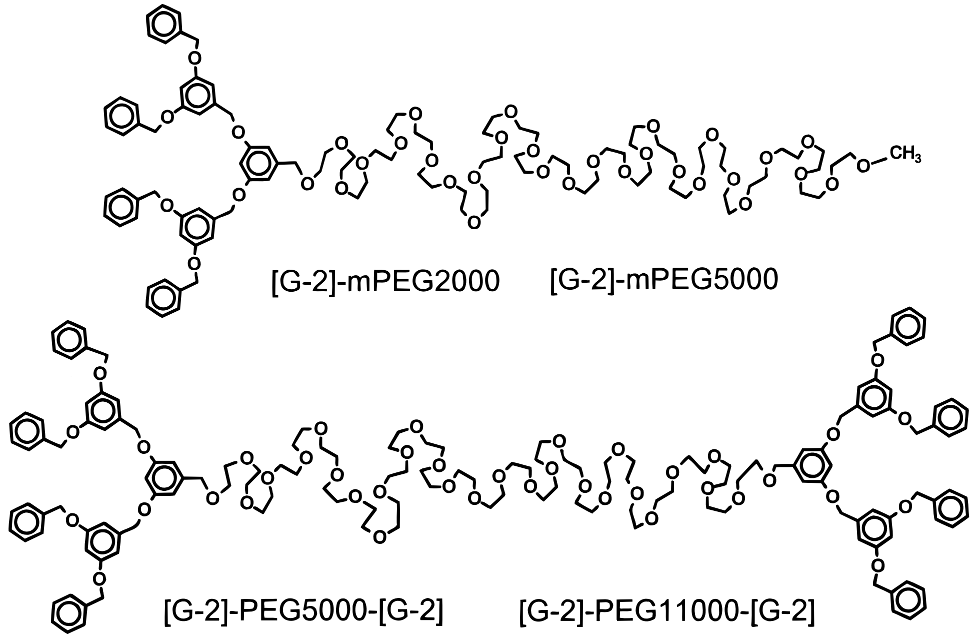

Figure 1. Schematic structures of hybrid linear−dendritic block copolymers discussed in this study.

end of the hybrid,[10,11c] while the linear tail consists of a hydrophilic segment (poly(ethylene glycol)) with a high affinity for polar solvents.

To better understand the interfacial behavior of linear−dendritic hybrids, we first investigated the properties of their aqueous solutions. AB and ABA block copolymers, in which A is a second-generation poly(benzyl ether) dendron ([G-2]) and B is a linear poly(ethylene glycol) (PEG), with varying PEG/dendron mass ratios were examined using static and dynamic surface tension measurements. The second part of this study is directed toward the modification of the surface properties of polymeric substrates such as poly(ethylene terephthalate) films and regenerated cellulose membranes by noncovalent self-assembly of the hybrid copolymers onto the surfaces via physical adsorption from their aqueous solution. These experiments are of relevance to the potential use of macromolecules for the surface modification of various materials by a simple self-assembly process.

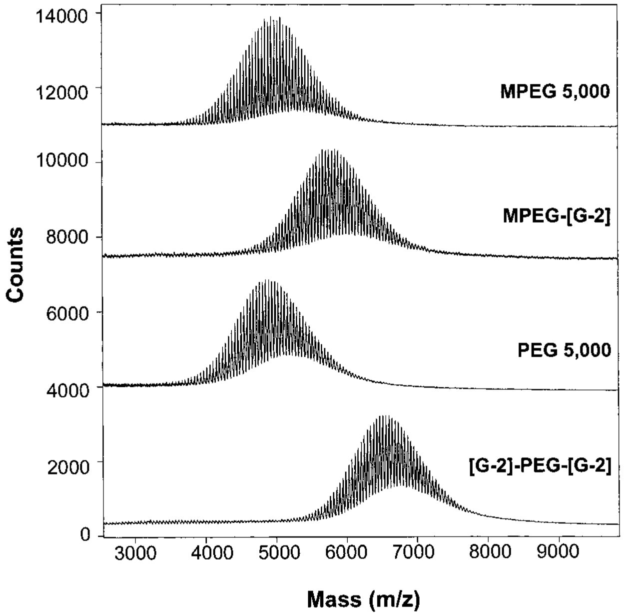

Figure 2. MALDI-TOF mass spectra of MPEG, PEG, and hybrid linear−dendritic block copolymers.

Experimental Section

Materials. Poly(ethylene glycols) (PEGs) with narrow molecular weight distributions and nominal molecular weights of 5000 and 11000 were purchased from Polymer Standards Service. Monomethyl ether of PEGs (mPEGs) with narrow molecular weight distributions and nominal molecular weights of 2000 and 5000 were purchased from Shearwater Polymers. Pluronic PE 6800 obtained from BASF is a triblock copolymer with a nominal molecular weight of 8000. It has one hydrophobic poly(propylene oxide) (PPO) central block flanked by two hydrophilic poly(ethylene glycol) end blocks, with PEG/PPO = 4/1.

Second-generation poly(benzyl ether) dendrons with a bromide moiety at the focal point were synthesized according to the well-known convergent growth procedure.[12] Their purity was verified by ^{1}H NMR, HPLC, and MALDI-TOF mass spectrometry. Hybrid linear−dendritic AB and ABA block copolymers were obtained by coupling respectively monomethyl-terminated poly(ethylene glycols) (mPEGs) and telechelic, hydroxy-terminated poly(ethylene glycols) (PEGs) with second-generation convergent dendritic bromides following the method we have described in detail earlier.[10] Their purity was verified by ^{1}H NMR, MALDI-TOF MS, and size-exclusion chromatography (SEC). Four water-soluble samples with differing architectures and PEG/dendron ratios were synthesized. Their schematic structures are given in Figure 1, and representative MALDI-TOF mass spectra measured using a Voyager DE spectrometer (Perseptive Biosystems) are shown in Figure 2. Solutions of hybrid block copolymers in doubly distilled water were prepared by dissolving determined amounts of samples in volumetric flasks. They were allowed to equilibrate for at least 1 week at room temperature under stirring.

Poly(ethylene terephthalate) (PET) films used for adsorption experiments were supplied by Toray Plastics; the films were rinsed with ethanol prior to use. Regenerated cellulose mem-

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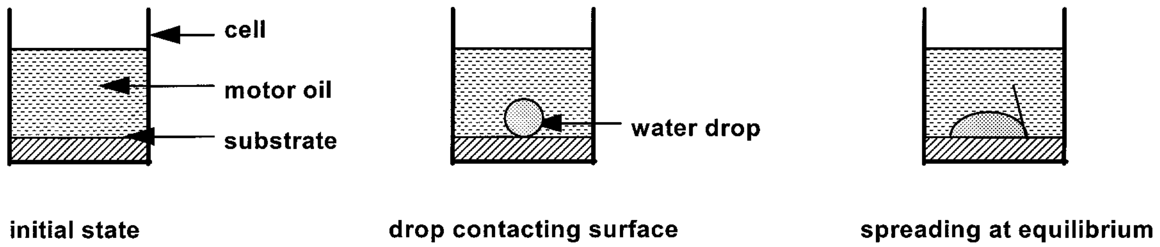

Figure 3. Scheme for contact angle measurement in a three-phase system of oil/water/solid substrate.

branes (Spectra/Por 3) purchased from Spectrum Inc. were washed with running water to remove glycerol.

Methods. Treatment of clean PET and cellulose substrates with the surface active hybrid copolymers was done in aqueous medium. The films were immersed for 2 h under stirring at room temperature in a 1 g/L solution of the chosen sample in deionized water. They were then rinsed twice with deionized water and allowed to equilibrate at 40% relative humidity and room temperature for at least 3 days.

Contact angles were measured in a three-phase system of two immiscible liquids (water and virgin motor oil) and polymer film.[13] This method gives an estimation of the hydrophilic–lipophilic balance of a solid substrate. Experiments were run as illustrated in Figure 3: the substrate was fixed to a frame with double-sided adhesive tape and immersed in a glass cell filled with motor oil. Three 1 μL drops of deionized water were released in the apolar oil medium using a micropipet. Their fall toward the film surface and their subsequent spreading was monitored with a high-speed video camera. The contact angle at the substrate/water drop/motor oil interface was measured when the equilibrium was reached.

Static surface tension measurements were made by the Wilhelmy plate method[14] using a Krüss K 10 tensiometer at a temperature of 24 ± 0.5 °C. Dynamic surface tension measurements were performed according to the maximum bubble pressure method[15] on a Lauda MPT 1 apparatus at a temperature of 24 ± 0.5 °C.

Adsorption simulations on cellulose were performed using molecular modeling products from Molecular Simulations Inc. (Cerius^2 software for construction of models and InsightII/Discover software for calculation).[16] A 10-chain layer was considered as a good starting model of an amorphous cellulose surface. This surface was constructed under two-dimensional periodic boundary conditions (no periodicity along the direction normal to the surface), and the density of the layer was adjusted to the experimental density of amorphous cellulose. Probe molecules were adsorbed in vacuo, and mean interaction energies with the surface were evaluated after using a home-designed sampling technique. Our methodology combines, in a strategy loop, both molecular dynamics and mechanics techniques and allows the exploration of all the different ways in which probe molecules can adsorb onto the surface. The number of loops necessary for a representative sampling depends strictly on the size and structural specificities of the surface. In the case of this study, the number of loops was 100.

Results and Discussion

Solution Behavior of Hybrid Linear–Dendritic Block Copolymers in Water. Two different methods were used to explore the solution behavior of hybrid copolymers in water. Thermodynamic data were drawn from static surface tension measurements using the Wilhelmy plate method, while dynamic surface tension measurements according to the maximum bubble pressure method allowed investigation of surfactant properties for very short periods of time (from 5 ms to 20 s).

The hybrid linear–dendritic block copolymers used in this study are macromolecular amphiphiles of AB or ABA type. We have reported earlier their solution properties in methanol/water and in THF[10c,d] using SEC and ^{1}H NMR measurements. These macroamphiphiles combine flexible hydrophilic linear poly(ethylene glycol) segments (B block) and semirigid hydrophobic dendritic segments (A blocks). As one might expect, their solubility in water depends on the PEG/dendron ratio. All four hybrids considered in this study were based on generation 2 dendrons and were fully soluble in water. The MALDI-TOF analysis (Figure 2) of these hybrids confirms their structure, as addition of the monodisperse [G-2] dendrons to mPEG or PEG chains does not increase the polydispersity of the latter. The changes in molecular weights observed during functionalization of both mPEG and telechelic PEG correspond to the expected values.

In comparison to common surface active molecules, which have apolar tail and polar head, our hybrids exhibit a reverse structure with hydrophobic head and hydrophilic tail. This peculiar architecture induces an interesting behavior in water. Figure 4 shows the static surface tension versus concentration curves for all four linear–dendritic hybrid block copolymers used in this work. A single point for PEG homopolymer (MW = 11000) is given for comparison purposes. Linear–dendritic hybrids exhibit typical amphiphilic behavior (see Figure 5). Below the critical micellar concentration (CMC), the surface tension decreases from $\gamma = 72$ mN/m (pure water) when the concentration increases. The hybrids behave as unimolecular micelles, with poly(ethylene glycol) chains forming a hydrophilic corona around poly(benzyl ether) dendrons. Above the CMC, the surface tension reaches a plateau. At this point the macroamphiphiles demonstrate their ability to form multimolecular micelles in water. Supramolecular aggregates of this type have also been reported elsewhere.[10c,d] For all four samples examined, surface tension values reached at the plateau are rather high when compared to those of the usual surfactants. Hybrid linear–dendritic block copolymers based on linear aliphatic polyether and dendritic aromatic polyether appear as poor surface active molecules due to their nonionic character. Nevertheless, our results regarding surfactant capacity of various samples examined here are in good agreement with the mass ratios of their hydrophilic and hydrophobic blocks. For instance, [G-2]-mPEG2000, which is more hydrophobic than [G-2]-

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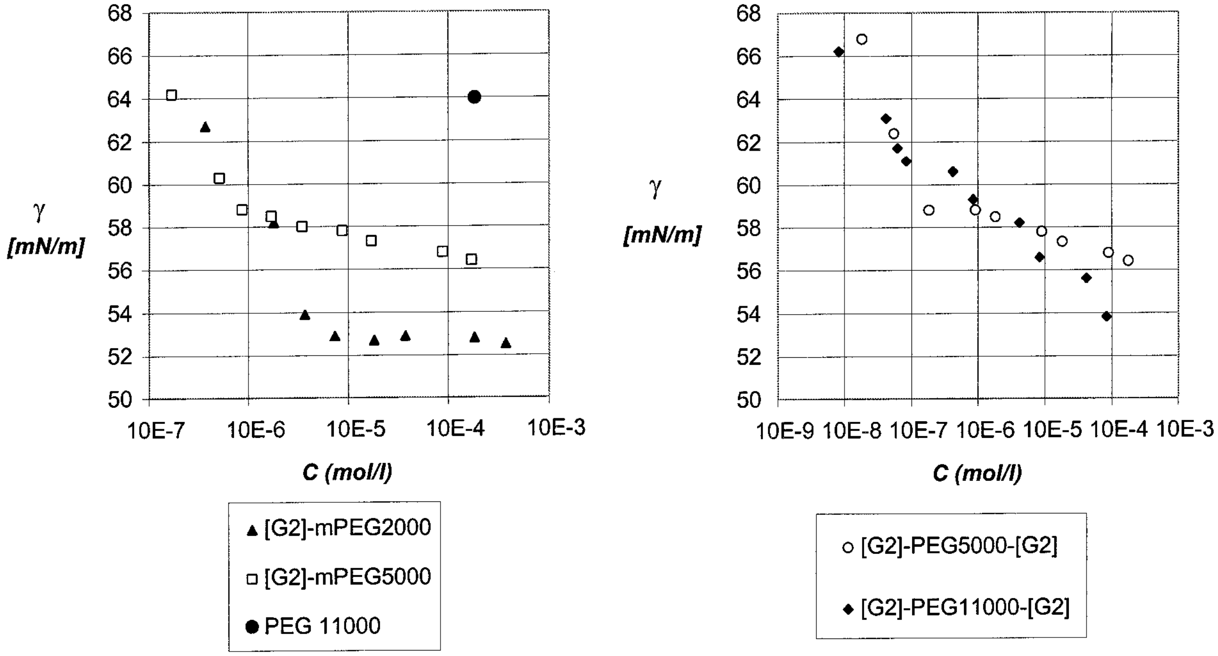
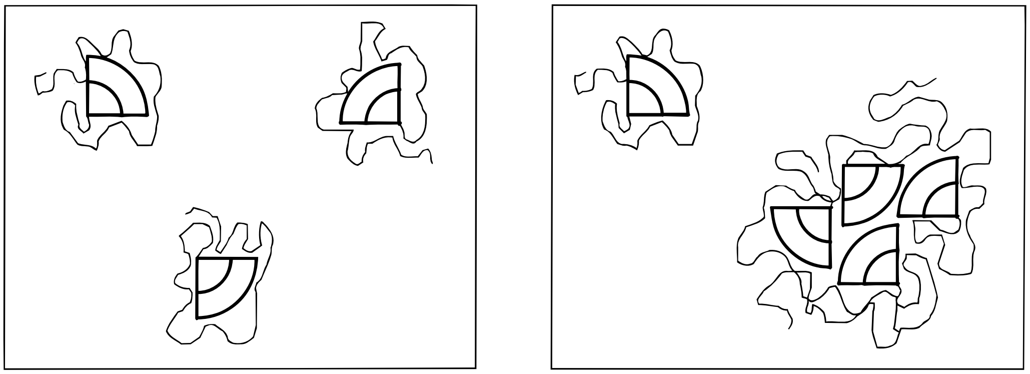


Figure 4. Static surface tension versus concentration curves for aqueous solutions of AB (left) and ABA (right) hybrid linear–dendritic block copolymers ($T = 24 \pm 0.5$ °C).



C < cmc : unimolecular micelles

C > cmc : multimolecular micelles

Figure 5. Solution behavior in water of hybrid linear–dendritic block copolymers under (left) and above (right) their CMC.

Table 1. Static Surface Tension Parameters of Hybrid Linear–Dendritic Block Copolymers in Aqueous Solution ($T = 24 \pm 0.5$ °C)

sample designation	critical micellar concentration (CMC), μmol/L	surface tension (γ) at plateau ($C = 10^{-4}$ mol/L), mN/m	area/molecule (Σ_G), Å^2
[G-2]-mPEG2000	5	52	70
[G-2]-mPEG5000	1	57.5	120
[G-2]-PEG5000-[G-2]	0.13	54	140
[G-2]-PEG11000-[G-2]	0.1	64	180

mPEG5000, also yields lower surface tension values above the CMC.

Another interesting difference between [G-2]-mPEG2000 and [G-2]-mPEG5000 is the slope of the plateau in the surface tension curves. For [G-2]-mPEG2000, the horizontal plateau shows near ideal surfactant behavior. In contrast, the tilted plateau observed for [G-2]-mPEG5000 indicates nonideal behavior. The continuous decrease in surface tension above the CMC may be induced by dynamic reorganization of micellar aggregates. Our results show that the concentration dependence of aggregate size is more pronounced when the PEG chain length increases. For instance, the CMC for [G-2]-PEG11000-[G-2] is barely visible. Also, the fact that micelle size depends on concentration prevents us from obtaining reliable data using laser light scattering. A similar observation of concentration dependence for the size of multimolecular micelles has also been reported elsewhere for hybrid linear–dendritic block copolymers in a 1:1 v/v methanol–water mixture.[10c]

CMCs determined from static surface tension measurements are gathered in Table 1. These values are typical of nonionic polymeric surfactants.[17] The fact that the CMC of [G-2]-mPEG2000 is higher than that of [G-2]-mPEG5000 is somewhat puzzling. Since the size of the hydrophilic block is smaller in [G-2]-mPEG2000

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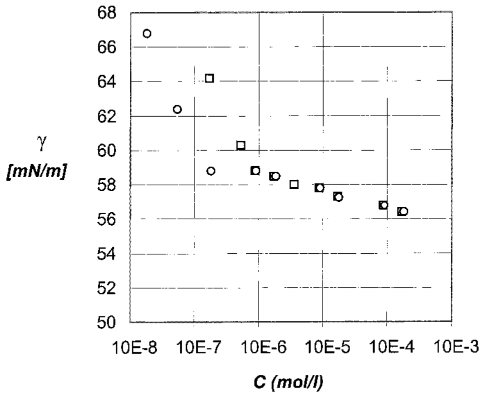

Figure 6. Surface tension versus concentration for aqueous solutions of hybrids built from similar blocks but with different morphologies ($T = 24 \pm 0.5$ °C): (□) [G-2]-mPEG5000; (○) [G-2]-PEG5000-[G-2].

than in [G-2]-mPEG5000, [G-2]-mPEG2000 would be expected to micellize at a lower concentration than [G-2]-mPEG5000. A possible explanation for this phenomenon is in the interplay of two opposite tendencies. A higher dendrimer content will increase the hydrophobicity of the hybrid and will lead to a higher propensity toward self-assembly; however, the water solubility of the material will be lower and therefore it may have difficulties forming multimolecular micelles. With [G-2]-mPEG5000, water solubility is not an issue and, despite its increased hydrophilicity, this copolymer may well form micelles faster and at lower concentrations. Also of interest is the observed solution behavior of ABA copolymers versus AB hybrids where the CMC of the ABA triblocks is much lower than that of the AB diblocks. Again, the length of the PEG block has a direct effect on both solubility and its ability to completely envelop the dendritic fragments in the hydrophilic coil. These results show that the aggregation behavior of hybrids in water is highly dependent on their architecture.

For a given architecture of the block copolymer (AB or ABA), hydrophilicity is controlled by both the length of the PEG chain and the generation number of the poly(benzyl ether) dendron. In contrast, for a given length of the hydrophilic segment and a given generation of the dendron, surfactant behavior is related to architecture. For instance, Figure 6 plots surface tension versus concentration for [G-2]-mPEG5000 and [G-2]-PEG5000-[G-2]. Both hybrids exhibit the same surface tension plateau, i.e. they behave the same way above their respective CMCs. However, the CMC of the ABA copolymer is 10 times lower than that of the corresponding AB structure, thereby confirming the higher hydrophobicity of [G-2]-PEG5000-[G-2] versus [G-2]-mPEG5000.

The area of hybrid linear−dendritic macromolecules at the air−water interface Σ_G is obtained from the Gibbs relationship:[14]

$$\Sigma_G = -k_B T \, d(\ln C)/d\gamma$$

where k_BT is the temperature in energy units, C is the bulk surfactant concentration, and γ is the surface tension. Our data (see Table 1) are of the same order of magnitude as areas measured for [G-2] poly(benzyl ether) dendrons with hydroxyl groups at their focal points determined in our earlier studies[2] using a Langmuir balance and molecular modeling. The poly(ethylene glycol) chain length has a great effect on the area of macromolecules at the air−water interface. This shows that both heads and tails of the hybrids are present at the air−water interface (Figure 7). Such a competitive adsorption is all the more probable since PEG itself causes a slight surface tension lowering of its aqueous solutions ($\gamma = 64$ mN/m for PEG 11000 at a 10^{-4} mol/L concentration). In contrast, differences in hybrid architecture (AB versus ABA block copolymer) seem to have a minor impact on the area of related macromolecules at the air−water interface (compare [G-2]-mPEG5000 and [G-2]-PEG5000-[G-2]). Hawker and co-workers have recently studied the interfacial behavior of [G-4] poly(benzyl ether) dendrons with short poly(ethylene glycol) chains at the focal point.[18] As a result of the small size of oligoethylene glycol tails when compared to the hydrophobic head of their [G-4] dendrons, they did not observe any effect of the hydrophilic chain on the areas measured at the air−water interface.

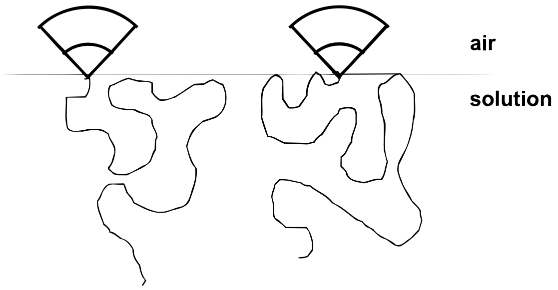

Figure 7. Most probable orientation of hybrid linear−dendritic block copolymers at the air−water interface. Both the hydrophobic and the hydrophilic part of the macromolecule are adsorbed at the solution surface.

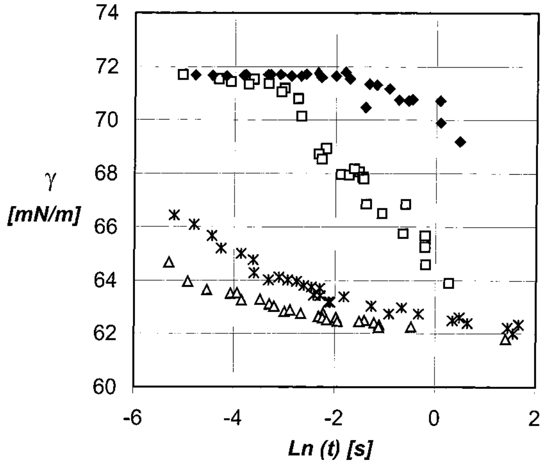

Figure 8. Dynamic surface tension of aqueous solutions of [G-2]-mPEG5000 ($T = 24 \pm 0.5$ °C): (◆) $C = 0.05$ g/L; (□) $C = 0.1$ g/L; (∗) $C = 0.5$ g/L; (△) $C = 1$ g/L.

Dynamic surface tension measurements were carried out for all four hybrid block copolymers and the two PEGs considered here. Figure 8 shows the results obtained for [G-2]-mPEG5000 at various concentrations. At any of the concentrations studied, the surface tension decreases when time increases. The hybrid exhibits typical surfactant behavior and segregates to the surface

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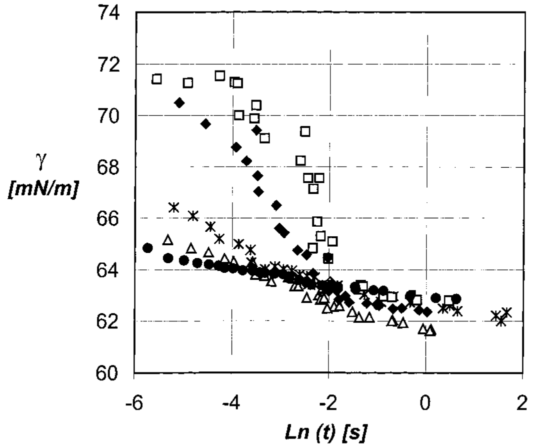

Figure 9. Dynamic surface tension of 0.5 g/L aqueous solutions of (△) [G-2]-mPEG2000; (∗) [G-2]-mPEG5000; (□) [G-2]-PEG5000-[G-2]; (◆) [G-2]-PEG11000-[G-2]; (●) PEG5000 ($T = 24 \pm 0.5$ °C).

in order to minimize energy at the air−water interface. Concentration has a great effect on the shape of the surface tension vs time curves. At lower concentrations, the surface tension is initially close to 72 mN/m (pure water) and then becomes lower as time increases. This induction period corresponds to the time during which the polymer migrates toward the interface.[19] At higher concentrations (0.5 and 1 g/L), the surface tension is lowered even for measurements made at very short times and then decreases slightly when time increases. Hence, the initial state of the air−water interface is closer to equilibrium for higher concentrations. However, the surface tension values reached at the end of the maximum bubble pressure experiments (time = 20 s) are higher than those obtained with the Wilhelmy plate method. This difference means that the interfaces do not reach equilibrium within 20 s. Therefore, it is likely that the macromolecules continue to rearrange at the air−water interface in the period between the last measurement of the maximum bubble pressure experiments (20 s) and data obtained at equilibrium with the Wilhelmy plate.

For comparison purposes, surface tension vs time curves for all four hybrids and PEG 5000 at a 0.5 g/L concentration are shown in Figure 9. Surface tensions reached at the longest interface times are always close to 62 mN/m. PEG 5000, [G-2]-mPEG2000, and [G-2]-mPEG5000 exhibit similar behaviors: the surface tension decay starts immediately as the experiment is begun, indicating that these macromolecules migrate rapidly toward the interface. Moreover, the similarity in behavior between PEG and the hybrids shows that the mobility of these AB block copolymers at the air−water interface is determined almost exclusively by their PEG segment. Quite remarkably, curves for the ABA dumbbell-like structures [G-2]-PEG5000-[G-2] and [G-2]-PEG11000-[G-2] do not show an immediate surface tension decay. Hence, it appears that ABA triblocks migrate more slowly than AB diblocks toward the air−water interface. This fact is not surprising since, as a result of its architecture, the configuration of the ABA macromolecule in solution is expected to be far from a random coil.

Table 2. Contact Angles of Water on PET, Cellulose, Modified PET, and Modified Cellulose When Immersed in Oil

treatment designation	contact angle oil/water/PET, deg	contact angle oil/water/cellulose, deg
none	164 ± 1	72 ± 2
PEG5000	160 ± 1	40 ± 3
PEG11000		50 ± 5
PEG35000	150 ± 2	
PEG1000000	130 ± 5	
Pluronic PE 6800	139 ± 2	31 ± 3
[G-2]-mPEG2000	150 ± 8	33 ± 2
[G-2]-mPEG5000	130 ± 5	26 ± 1
[G-2]-PEG5000-[G-2]	125 ± 2	36 ± 1
[G-2]-PEG11000-[G-2]	115 ± 1	54 ± 2

Modification of Surface Properties of Solid Materials. Adsorption experiments were carried out on poly(ethylene terephthalate) (PET) films and regenerated cellulose membranes. Solid substrates were treated with aqueous solutions of the various hybrid linear−dendritic block copolymers. To assess the specific role played by the dendritic segment, similar treatments were carried out in parallel with regular PEGs and with Pluronic PE 6800. The hydrophilicity of the solid surfaces was estimated through measurements of interfacial contact angles in a three-phase system consisting of oil, water, and the solid substrate. All substrates were thoroughly rinsed with water prior to contact angle measurements. Table 2 shows the results that were obtained.

1. Adsorption on a Hydrophobic Substrate (PET). As expected from the intrinsic hydrophobicity of PET, untreated films exhibit high contact angles to water. Water drops do not displace oil in order to spread on the surface. Treatment with regular PEGs produces varying effects depending on the length of the specific macromolecule considered. Treatment with short PEG chains (MW = 5000) does not alter the hydrophilicity of the PET surface. Most probably, adsorption interactions are too weak to maintain the PEG chains confined to the surface during the rinsing phase of the experiment. When the PEG chain length is increased, the solubility in water is lowered while the number of anchor points to the substrate is increased. Therefore, some modest increase in hydrophilicity is observed. Hybrid linear−dendritic block copolymers induce a much more pronounced increase in the hydrophilicity of PET. Again, contact angles to water decrease when the length of the hydrophilic segment of the macromolecule increases. With comparable mass ratios of hydrophilic and hydrophobic blocks, ABA structures are more efficient than AB diblocks (compare [G-2]-mPEG2000 and [G-2]-PEG5000-[G-2] or [G-2]-mPEG5000 and [G-2]-PEG11000-[G-2]). Nevertheless, the positive effect of the dendritic segment on promoting the attachment of PEG chains onto the surface is clearly seen in all cases. For example, [G-2]-mPEG5000 affords a hydrophilicity similar to that obtained using a PEG molecule almost 200 times larger (MW = 1000000). A similar comparison between Pluronic PE 6800 and [G-2]-mPEG5000, two macromolecules with a similar hydrophilic−lipophilic balance, yields a higher contact angle to water for Pluronic PE 6800. Therefore, despite its lower molecular weight, the hybrid block copolymer confers higher hydrophilicity to the substrate. Our results are consist-

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[19] Hua, X. Y.; Rosen, M. J. *J. Colloid Interface Sci.* **1988**, *124*, 652.

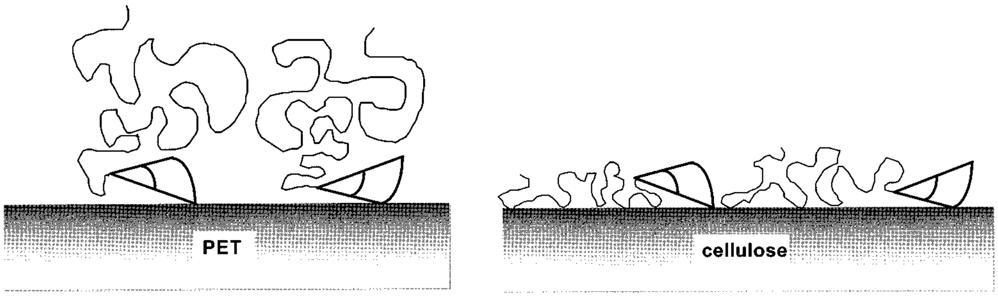

Figure 10. Possible adsorption scheme of hybrid linear–dendritic block copolymers on hydrophobic (left) and hydrophilic (right) substrates.

Table 3. Results of Adsorption Simulations of Head and Tail Fragments of the Hybrids on a Cellulosic Surface

probe molecule	absolute interaction energy between probe and surface[a] (kJ/mol)	theoretical contact area between probe and surface (nm^2)	normalized interaction energy between probe and surface[a] (kJ/mol/nm^2)
[G-2] dendron	−399.0	4.84	−164.9
[G-3] dendron	−607.0	7.55	−160.8
PEG (DP=45)	−502.0	8.64	−116.2

[a] Mean value extracted from statistics among 100 conformations of adsorbed molecules.

ent with an adsorption scheme where the hybrid is linked to the PET surface through its more lipophilic dendritic end, while its PEG tail does not interact directly with the substrate but spreads in the aqueous medium (see Figure 10).

2. Adsorption on a Hydrophilic Substrate (Cellulose). Cellulose is much more hydrophilic than PET. Polar and dispersive components of its surface free energy are comparable. Therefore, untreated cellulose membranes yield rather low contact angles to water. Our measurements are in good agreement with the values reported by Toussaint and Luner for cellulosic films.[20] Treatment with low molecular weight PEGs (5000 and 11000) induces a decrease in contact angle to water. PEG chains are able to interact with cellulose through hydrogen bonds involving the free OH groups of the polysaccharide and ether bridges of the poly(ethylene glycol) backbone. This difference in PEG adsorption behavior between hydrophobic and hydrophilic surfaces has already been noted.[21] As can be seen from the contact angle measurements, treatment with hybrid linear–dendritic block copolymers yields membranes with increased hydrophilicity. However, the correlation between the architecture of the hybrid and its ability to increase the hydrophilicity of the surface is not straightforward. Overall, it appears that AB structures are somewhat more efficient that ABA triblocks, with the lowest contact angle observed for [G-2]-mPEG5000. As in the case of PET, the dendritic head acts as an anchor point to the cellulose surface. It is also expected to limit the extent of interaction between the PEG chain and the substrate. Hence, [G-2]-mPEG5000 affords more hydrophilic surfaces than regular PEG 5000. However, competitive adsorption of both the PEG and the poly(benzyl ether) segments of the hybrid macromolecule is expected to occur since PEG itself is able to enhance the hydrophilicity of cellulose.

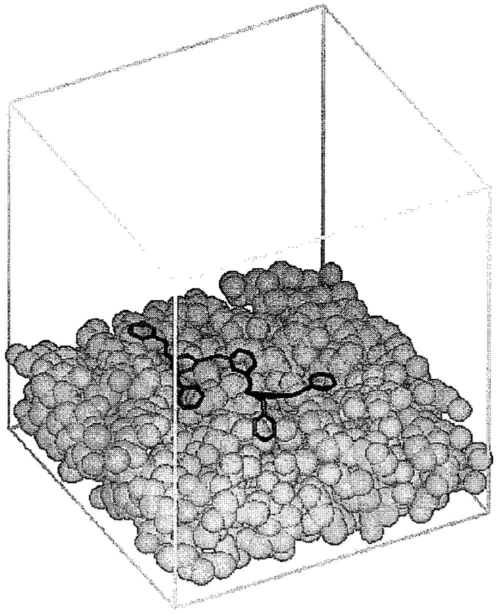

Figure 11. Molecular modeling of a [G-2] dendron probe adsorbed flat on cellulose surface after a 100-loop calculation.

Preliminary molecular modeling experiments were carried out in order to determine which part of the molecule—PEG or the dendron—is favored during the adsorption process onto the cellulose surface. The adsorption processes for the head and tail fragments were simulated separately. The main results are reported in Table 3, and the most favorable association between [G-2] dendron and cellulose is presented in Figure 11. All probe molecules tended to adsorb flat on cellulose, but this feature is mainly due to the fact that our calculations have been performed in vacuo. PEG chains interact with the surface through weak, but numerous, hydrogen bonds involving hydroxyl groups from the cellulosic surface and ether bridges from the PEG backbone. [G-2] and [G-3] dendrons mainly develop π-H interactions with the surface. These bonds involve π orbitals in dendritic compounds and hydroxyl groups of the adsorbing site. Their absolute strength is rather high, being estimated as half the value of a hydrogen

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[20] Toussaint, A. F.; Luner, P. *J. Adhesion Sci. Technol.* **1993**, *7*, 635.

[21] Schroën, C. G. P. H.; Cohen Stuart, M. A.; van der Voort Maarschalk, K.; van der Padt, A.; van't Riet, K. *Langmuir* **1995**, *11*, 3068.

bond.[22] Dendrons are also able to interact with the surface through hydrogen bonds between benzylic oxygens and cellulose hydroxyl moieties.

As observed in Table 3, it is rather difficult to predict which block, the dendron or PEG, will adsorb preferentially onto the cellulose surface. If we consider absolute interaction energies, π-H interactions established between [G-2] dendron and the surface are somewhat weaker than hydrogen bonds occurring between PEG and cellulose, while the reverse situation is observed in the case of [G-3] dendron. Recent neutron reflectivity[2b] and scattering[23] studies have confirmed the influence of generation number on shape[1] and it is expected that the generation number will have a great effect on adsorption. However, it remains to be seen whether these differences between absolute interaction energies are sufficient to displace the dendron or the PEG chain from the surface. Moreover, if we consider normalized interaction energies (ratio between absolute interaction energy and theoretical contact area between the probe and the surface), it is clear that dendron adsorption is favored. This simply means that the local anchoring of dendrons onto the cellulose surface is much more efficient than that for the PEG chains. Therefore, our simulation results tend to confirm the adsorption experiments and point toward simultaneous adsorption of both the head and tail blocks of the hybrid copolymer onto the cellulose surface (see Figure 10). More insight into the stabilization process of this system would of course involve a simulation of the adsorption of the global hybrid macromolecule and of exact linear analogues, as well as the inclusion of water molecules in the model. This work is still in progress in one of our laboratories.

Conclusions

Hybrid linear−dendritic block copolymers based on poly(ethylene glycol) and poly(benzyl ether) are a new class of surfactants that may be used to modify the surfaces of polymeric substrates in aqueous medium. Their specific architecture and composition allows hydrophilization of hydrophobic surfaces. Adsorption on apolar substrates such as PET proceeds only through the dendritic block of the hybrid. When polar and dispersive components of the surface free energy are comparable (e.g. in the case of cellulose), a competitive adsorption of PEG tails and poly(benzyl ether) heads is observed. Since contact angles for treated cellulose are lower than those for treated PET, complete coverage of the surfaces considered here was not achieved. The influence of generation number on adsorption behavior is currently under investigation, as is the balance between hydrophobicity and hydrophilicity of the dissimilar block. Also of interest are dendritic structures with terminal moieties tailored to interact strongly with specific substrates. Hybrid linear−dendritic macroamphiphiles should prove useful in interfacial applications where copolymers based on PEG are widely used.[24] Finally, it should be pointed out that only very low amounts of material are required to effect surface coverage by self-assembly and physisorption. Given these low amounts and the ready availability of simple structural analogues of the small dendrons used in this study, this approach to surface modification, or a simple variation thereof, may prove to be of practical value.

Acknowledgment. Financial support for this work carried out in part at Cornell University was provided by NSF (DMR 9796106) and the ARO MURI program (DAAG55-97-0126, sub-award to UC Berkeley). GIE-AIFOR and Rhône-Poulenc Direction Scientifique are also gratefully acknowledged for funding one of us (J.-F.S.) while on a postdoctoral fellowship at Cornell University. The authors are also indebted to Drs. V. Bergeron, J.-C. Daniel, M. R. Leduc, J. W. Leon, K. Mazeau, K. W. Pollak, J.-P. Quentin, and L. Vovelle, Mr. J. -F. Bernard, and Mr. J.-Y. Martin for stimulating discussions and for some of the experimental work presented herein.

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(24) For a relevant example of application for our macroamphiphiles, see: Crouzet, J.; Pitard, B. PCT Int. Appl. WO 98 34,648, 1998.