Synthesis and Interfacial Behavior of Polystyrene−Polysaccharide Diblock Copolymers

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ABSTRACT: Linear block copolymers of polystyrene and polysaccharide were synthesized using a block synthesis method with amino-terminated polystyrene and sodium cyanoborohydride as reducing agent. Different types of polysaccharides, dextrans, and maltodextrins with various molecular weights were used. IR spectroscopy indicated a successful coupling. Yields of reaction are 75−95 wt %. Attempts to couple long dextrans (M_w > 6000 Da) were not successful. Interfacial pressure measurements of monolayers of the copolymers on water showed interfacial behavior typical for amphiphilic compounds and different from the starting compounds, confirming the coupling reaction. Time-dependent hysteresis occurs between successive compression and expansion cycles. This is, to a large extent, due to the slow adsorption/desorption of the polysaccharide chains at the air−water interface and the formation of aggregates of copolymer at the interface. Aggregates are mainly formed by H-bonds between adjacent polysaccharide chains. The relaxation time for hysteresis, determined for polystyrene−dextran copolymer, was 85 min.

1. Introduction

Biofouling is the undesired accumulation of biological substances at surfaces and occurs on solids exposed to biological fluids such as blood, urine, saliva, tear fluid, milk, fruit juices, and seawater. It is usually initiated by protein adsorption and causes many problems in medical applications (such as implants), food technology (pollution of processing equipment), and water processing. Research has shown that coating surfaces with hydrophilic polymer brushes can prevent or reduce protein adsorption and hence retard biofouling.[1,2] So far, these brushes usually consist of synthetic polymers, often based on poly(ethylene oxide) (PEO). In biological systems the use of natural polymers may be preferred and polysaccharides seem to be the most plausible candidate. In nature, polysaccharides can be found in extracellular polymer layers and in the glycocalyx of biomembranes, having the function to prevent nonspecific adsorption of for example proteins.[3]

Polymer brushes can be prepared by physical adsorption or by chemical grafting. Physical adsorption can be performed either from a polymer solution or by using the Langmuir−Blodgett technique.[4]

The object of the research presented here was (1) to synthesize and characterize linear polystyrene−polysaccharide diblock copolymers and (2) to study the interfacial behavior of these copolymers at the air/water interface. The copolymers will be used in future research to prepare polysaccharide brushes at a solid surface, with the Langmuir−Blodgett technique, and subsequently to perform protein adsorption experiments. The polystyrene (PS) block of the copolymers serves as an anchor for the polysaccharide block at the air/water interface. Besides, the PS block will be the adsorbing part of the copolymer when brushes are prepared at a solid surface.

Copolymers can be synthesized in different ways. One possibility is to couple different small oligomers and then to grow the chains by polymerization.[5] Another route is to first synthesize one of the blocks and then couple it to another type of monomer and polymerize the second block.[6,7] A third way is to polymerize blocks separately and then perform a coupling reaction between them.[8] In the present study the last approach (coupling of prefabricated blocks) was used to couple polysaccharide to amino-terminated PS. In the context of a comparative study different polysaccharides were used (dextrans and maltodextrins) with various chain lengths. Dextrans consist of α (1→6)-linked glucosyl units and maltodextrins of α (1→4)-linked glucosyl units.

The copolymers were analyzed using IR spectroscopy. To characterize the interfacial behavior and investigate the possible application as brush material, a monolayer of these polymers was spread on an air/water interface in a Langmuir trough. PS does not dissolve in water and serves as an anchor for the polysaccharide chain, preventing the copolymer from dissolving in the water phase. The interfacial pressure as a function of the surface area was measured during sequential compressions and expansions.

2. Experimental Section

2.1. Synthesis. All solvents were purified by conventional methods. Dextrans (M_w 1500 and 6000 Da (Fluka)) and maltodextrins (Paselli MD 20, M_n approximately 850 Da; Paselli MD 6, M_n about 2800 Da (AVEBE)) were used without further purification. The Paselli-type maltodextrins are characterized by the DE value, the dextrose equivalent (20 and 6, respectively). This DE value corresponds to a number-average molar mass (M_n = (100/DE)$M_{glycosyl}$ (=162 Da)). Maltoheptaose, a maltodextrin, (M_n 1150 Da), was kindly provided by Lorant

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Table 1. Reaction Mixtures and Reaction Yield of the Polysaccharides

	polysaccharide	molar mass [Da]	polysaccharide amount [g]	PS amount [mg]	solvent	yield[a] [wt %]
Glu	glucose	180	2.0	100	DMF (10 mL)	95
Di1	Paselli MD 20	850 (M_n)	1.0	100	DMF (25 mL)	90
Di2	maltoheptaose	1150 (M_n)	2.0	200	DMF (35 mL)	90
Di3	Paselli MD 6	2800 (M_n)	4.0	100	DMF/water 30/1 (31 mL)	85
Da1	dextran	1500 (M_w)	1.2	100	DMF/water 30/1 (31 mL)	80
Da2	dextran	6000 (M_w)	4.8	100	DMF/water 50/3 (53 mL)	75

[a] Yield (in wt %) is based on the mass of polystyrene derivative before and after reaction.

Janossy (Institute of Biochemistry, University of Debrecen, Hungary). Glucose (Merck) was used to test the reaction. Amino-terminated PS (M_w 12 300 Da, M_w/M_n = 1.02) was purchased from Polymer Source Inc. and used without further purification. IR spectra were recorded on a Bio-Rad spectrometer using Win-IR software.

The coupling reaction was performed under the following general conditions: 20 mg of sodium cyanoborohydride ($NaCNBH_3$), as reducing agent, was added to a mixture of amino-terminated PS and polysaccharide dissolved in the appropriate solvent (*N*,*N*-dimethylformamide (DMF) or DMF/water). The reaction mixture was stirred for 7 days at 60 °C, and $NaCNBH_3$ (20 mg) was added every day. Subsequently, the mixture was cooled to room temperature and diluted with water (100 mL) to form a precipitate. The precipitate was filtered and washed several times with cold water to remove the excess polysaccharide. Afterward, the precipitate was dried in a vacuum desiccator (with P_2O_5) to obtain the copolymer as a white powder.

In Table 1 the reaction mixtures and yields of the coupling reaction of the different polysaccharides are summarized. The yield, in wt %, is based on the mass of polystyrene derivative before and after reaction. Hereafter, the abbreviations of the different polysaccharides, mentioned in Table 1, will be used.

2.2. Interfacial Pressure. The interfacial pressure (Π) vs area (*A*) isotherms of PS-dextrans and PS-maltodextrins at the air/water interface were determined in a Teflon Langmuir trough with a computer-controlled barrier. The interfacial pressure was measured continuously using a platinum Wilhelmy plate. Ultrapure water (specific conductivity < 0.05 μS/m, pH 6) was used for the water phase, and chloroform (Sigma) was used as spreading solvent. The concentration of the copolymer solutions ranged between 0.25 and 1.00 g/L, depending on the solubility of the copolymer. A small amount (100−400 μL) of the copolymer solution was spread dropwise with a microsyringe. After allowing the chloroform to evaporate (5 min), the Π−*A* measurement was started. The copolymer monolayer was compressed from 600 to 80 cm^2. The compression speed was 30 mm^2/s, unless mentioned otherwise. The measurements were performed at constant room temperature. Several successive compression and expansion cycles were performed with varying time intervals between compression and expansion. The reproducibility of the interfacial pressure isotherms was verified by performing experiments in duplicate. Π−*A* isotherms of the two separate polymer blocks (PS and the different polysaccharides) were determined for comparison with the isotherms of the copolymers. The Trurnit method was applied for spreading of the water-soluble polysaccharides with ultrapure water as spreading solvent.[4] The PS used (M_w = 13 700 Da, without amino end group) was purchased from Aldrich. The glycerol used in the hysteresis experiment was obtained from J.T. Baker.

3. Results and Discussion

3.1. Synthesis. The synthesis strategy was based on a coupling reaction between a polysaccharide and amino-terminated PS. In Figure 1, the coupling reaction is illustrated for dextrans and amino-terminated PS. Conventional reductive amination was chosen to couple the two blocks, with sodium cyanoborohydride as a reducing agent.[9] Polysaccharides have two structural

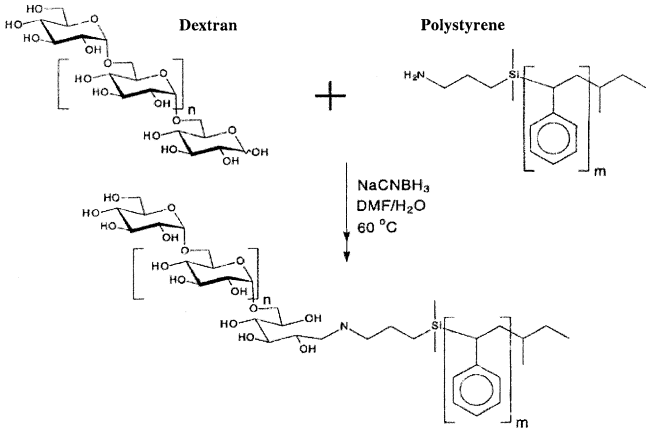

Figure 1. Synthesis of polystyrene−dextran block copolymer: Amino-terminated polystyrene reacts with dextran, in the aldehyde end group isomer (not shown), with sodium cyanoborohydride ($NaCNBH_3$) as reducing agent ($n \approx 7$ or 35 for the dextrans used, m = 120).

isomers: one containing a glucosyl end group and the other containing an aldehyde end group. The isomer containing the aldehyde end group reacts with the amino-terminated PS. Each polysaccharide chain contains only one aldehyde end group. Consequently, each polysaccharide chain reacts with only one amino-terminated PS chain, resulting in only linear diblock copolymers. The different polysaccharides used varied in linkage type and molecular weight. Glucosyl α (1→4)-linked maltodextrins and α (1→6)-linked dextrans were investigated.

To test the reaction, glucose was coupled to the polystyrene, dissolved in DMF. Subsequently, the maltodextrins and dextrans, mentioned in Table 1, were coupled to the polystyrene. The coupling reactions were performed in DMF in the case of the maltodextrins Di1 and Di2 or in DMF/water mixtures in the case of the maltodextrin Di3 and the dextrans. The choice of reaction solvent(s) proved to be very critical with respect to the solubility of the reacting polymers and consequently the conversion.

Adding water isolated the synthesized copolymers. A white precipitate was formed, which was purified by extensive washing and filtering, to remove remaining unreacted polysaccharide. Subsequently, the precipitate was dried in a vacuum desiccator and characterized by IR spectroscopy. The synthesized copolymers were used for interfacial pressure measurements without further purification. To achieve high conversion of the amino-terminated PS, large excesses (50−100 equiv) of polysaccharides were used combined with a long reaction time (7 days). The yield of reaction was 75−95 wt % (see Table 1). During purification of the precipitate, some of the copolymer is lost, leading to yields of less than 100%. Besides, it cannot be excluded that a fraction of the product consists of uncoupled PS, although a large

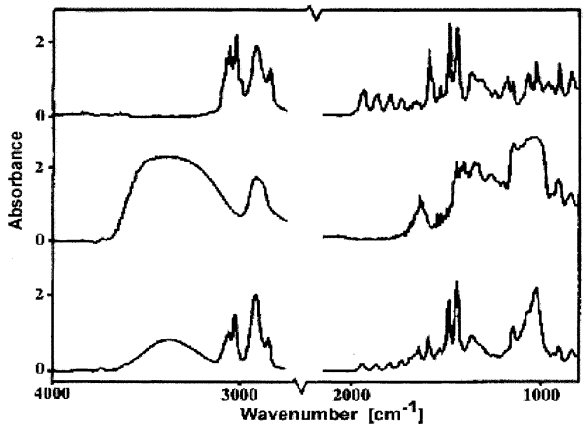

Figure 2. IR spectra of amino-terminated polystyrene (top), dextran (Da2) (middle), and polystyrene−dextran copolymer (PS-Da2) (bottom) (see text for explanation).

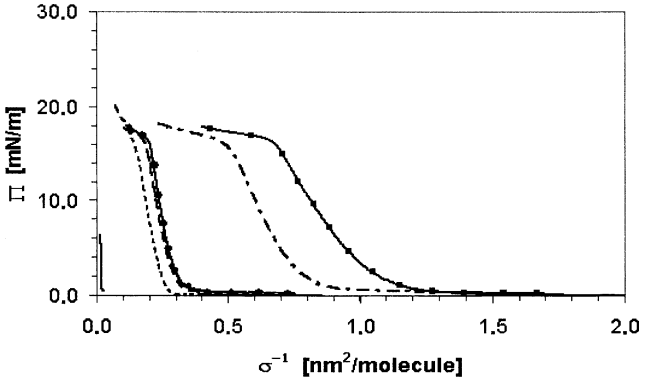

Figure 3. Interfacial pressure isotherms of polysaccharides: Glu (—), Di1 (— —), Di2 (- - -), Di3 (— - —), Da1 (●), and Da2 (■).

excess of polysaccharide was used combined with a long reaction time.

Figure 2 shows the IR spectra of the carefully dried starting compounds and the product obtained upon coupling PS with dextran (Da2). The broad peak between 3600 and 3100 cm^{-1} for dextran in Figure 2 illustrates the OH vibration of the OH groups of dextran. The sharp peaks at 1500−1600 cm^{-1} for PS indicate the C=C vibrations of the aromatic ring. Both peaks can be found in the copolymer (PS−Da2), indicating the presence of OH groups and aromatic rings in the formed product. Because of the intensive washing, the presence of remaining uncoupled polysaccharide is unlikely. Hence, it can be concluded from the IR spectra that the coupling reaction between PS and dextran was successful. IR spectra of the other synthesized copolymers exhibit similar results (data not shown).

Attempts to couple longer dextrans (M_w 9500 and M_w 15 000−20 000) with the same PS and using the same method and several different solvent systems were not successful (data not shown). For the synthesis of these copolymers a different approach is required.

3.2. Interfacial Pressure. All isotherms were recorded in duplicate and proved to be reproducible. Figures 3 and 4 display the interfacial pressure (Π) of the individual polysaccharides and PS as a function of the area per molecule (σ^{-1}) (σ is the polymer grafting density). The interfacial pressure of the polysaccharides levels off at $\sigma^{-1} < 0.7$ nm^2/molecule (see Figure 3). It indicates that at this compression level the polysaccharides are pushed into solution. Hence, the saturated

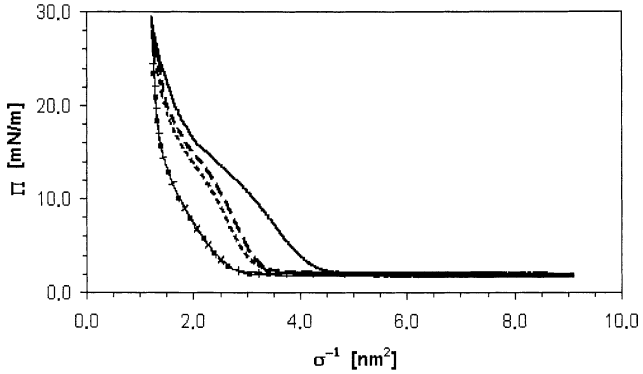

Figure 4. Interfacial pressure isotherms of PS: first compression (—), first expansion (— | —), second compression (— —), second expansion (■), and third compression (- - -).

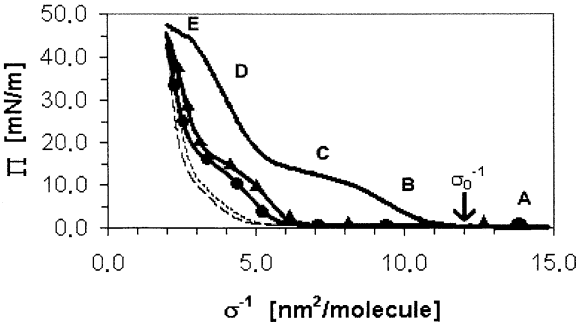

Figure 5. Interfacial pressure isotherms of PS-Da2: first compression (—), first expansion (- - -), second compression (▲), second expansion (— —), and third compression (●). σ_0^{-1} is the onset of the interfacial pressure increase; A−E indicate the different conformations of the copolymer at the air/water interface upon compression, illustrated in Figure 6.

interfacial pressure for a polysaccharide monolayer is approximately 16 mN/m.

PS can be compressed up to high interfacial pressures (see Figure 4). PS is not forced into solution at pressures ≤40 mN/m, which is plausible because of the insolubility of PS in water. The figure also demonstrates that there is a difference between successive compression/expansion cycles. This will be further discussed in section 3.3.

Figure 5 gives the interfacial pressure isotherms of PS-Da2 (M_w dextran chain 6000 Da). The first compression isotherm exhibits a pattern generally observed for monolayers of amphiphilic polymers.[4,10−12] At large area per molecule the polysaccharide block is adsorbed at the air/water interface (A in Figure 5). The PS block is in the collapsed state. Upon compression, the molecules are forced into contact and the interfacial pressure starts to increase. The increasing pressure leads to desorption of dextran from the interface (B). The onset of the interfacial pressure increase at 12.0 nm^2/molecule is indicated by σ_0^{-1} in Figure 5.

Between 8.0 and 5.5 nm^2/molecule the interfacial pressure hardly increases and assumes a semiplateau value of about 16 mN/m. In this region the dextran chains stretch out into the water phase to form a polymer brush (C). The main contribution to the interfacial pressure in this region results from the interacting dextran chains in the air/water interface, corresponding to the saturated interfacial pressure of dextran (16 mN/m). The PS block of the copolymer, at the air/water interface, prevents the dextran chains from dissolving in the water phase. At approximately 5.5 nm^2/molecule all dextran chains are desorbed from the interface.

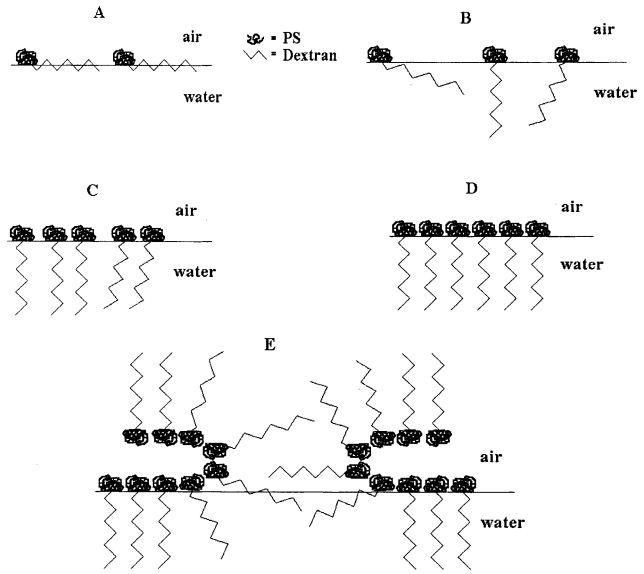

Figure 6. Conformations of PS−dextran at the air/water interface: adsorbed at the interface (A), desorption from the interface (B), polymer brush formation (C), compression of the polymer brush (D), and collapse of the monolayer (E).

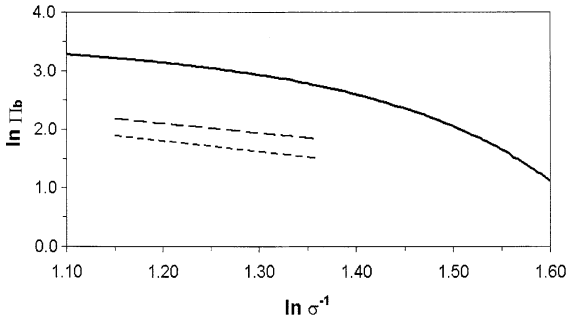

Figure 7. Interfacial pressure of Da2 brush (Π_b) vs area per molecule (σ^{-1}): experimental (—), Alexander−de Gennes model (scaling coefficient 11/6) (- - -), and SCF model (scaling coefficient 5/3) (— —).

Additional compression causes a sharp increase of the interfacial pressure, due to the repulsive interactions between the dextran chains in the polymer brush (D). At $\Pi = 45$ mN/m the monolayer collapses at an area of nearly 3 nm^2/molecule (E). The different conformations of the copolymer at the interface are drawn schematically in Figure 6, corresponding to A−E in Figure 5.

The expansion isotherms and the second and third compression isotherm do not coincide with the first compression isotherm, indicating that during compression/expansion equilibrium is not attained. This hysteresis will be discussed in more detail in section 3.3.

For a polymer brush in a good solvent the conformation is determined by a balance between the segment−segment excluded-volume interactions, causing the chains to stretch, and the entropic cost of this stretching. Polymer brush models describe the relation between the interfacial pressure of a brush (Π_b), the chain length (N), and the grafting density (σ). According to the Alexander−de Gennes model, the pressure scales as $\Pi_b \sim N\sigma^{11/6}$;[13,14] self-consistent-field (SCF) models predict a scaling of $\Pi_b \sim N\sigma^{5/3}$.[12] In Figure 7 the interfacial pressure of the Da2 brush, $\Pi_b = \Pi - \Pi_{plateau}$, is plotted on a double-logarithmic scale vs the area per molecule (σ^{-1}) for the brush regime (region D in Figure 5). $\Pi_{plateau}$ corresponds to the saturated interfacial pressure of a Da2 monolayer, with a value of 16.0 mN/m, based on the isotherm of Da2 in Figure 3. Lines corresponding to power laws of 5/3 and 11/6 are drawn for comparison. Figure 7 demonstrates that the dextran brush is in reasonably good agreement with the Alexander−de Gennes model and the SCF model, although the dextran chain is relatively small ($N \approx 37$). The average scaling coefficient at high grafting densities is approximately 2.2, somewhat higher than predicted by the polymer brush models. Variation of $\Pi_{plateau}$ between 15.0 and 17.0 mN/m showed only a slight change in the scaling coefficient of Π_b (data not shown). Corrections, by assuming 25 wt % unreacted PS (= 100 − 75 wt % yield) and consequently lower grafting densities, result in a scaling coefficient of about 1.8, which is in good agreement with the brush models. However, 25 wt % unreacted PS is overestimated. The yield of less than 100% is mainly caused by loss of copolymer during purification (see section 3.1). To verify whether the polymer brush models are applicable for polysaccharide brushes, a broader range of (longer) copolymers is needed.

Table 2. $\Pi_{plateau}$ and σ_0^{-1} Values of Different PS−Polysaccharides Determined from Π−*A* Isotherms

	molar mass polysaccharide [Da]	$\Pi_{plateau}$ [mN/m]	σ_0^{-1} [nm^2/molecule]
PS−Glu	180	16[a]	8.2
PS−Di1	850	18[a]	6.5
PS−Di2	1150	17[a]	6.2
PS−Di3	2800	17[a]	5.9
PS−Da1	1500	16	8.0
PS−Da2	6000	16	12.0

[a] The values of $\Pi_{plateau}$ for PS−glucose and the PS−maltodextrins are average values of Π in the semiplateau region.

The other synthesized copolymers, PS−Da1 and PS−maltodextrins, show interfacial pressure isotherms similar to those of PS−Da2, including hysteresis. However, the values of σ_0^{-1} and $\Pi_{plateau}$ are different, as shown in Table 2. The PS−maltodextrins do not have pronounced plateau behavior; the $\Pi_{plateau}$ values of the PS−maltodextrins are average values of Π in the semiplateau region.

The differences between the σ_0^{-1} values in Table 2 are due to differences in polysaccharide type and chain length: For longer polysaccharides the onset of the interfacial pressure increase starts at higher values of σ^{-1}, because larger molecules start to interact at larger area per molecule. The $\Pi_{plateau}$ values seem to be rather constant, indicating a uniform saturated interfacial pressure for the different polysaccharides.

3.3. Hysteresis; Chain Interactions and Time Dependency. Compression of PS−PEO copolymers at the air/water interface shows no hysteresis.[11] PEO is a very flexible polymer and accordingly adsorbs and desorbs rapidly at the interface.[15] In the case of PS−polysaccharide copolymers hysteresis is observed in the interfacial pressure isotherms. This may be due to loss of copolymer from the monolayer, or it may be an intrinsic property of the monolayer itself.[4]

To discriminate between these two possibilities, compression/expansion cycles were performed with PS−Da2, where time intervals in between cycles as well as the compression rates were varied. The time interval, the time between completion of the expansion and start of the compression, ranged from 0 to 900 min. The compression rate was varied from 5 to 100 mm^2/s. The difference between the onset area values (σ_0^{-1}) of the first and second compression isotherm ($\Delta\sigma_0^{-1}$) can be considered a measure for the hysteresis. The values of

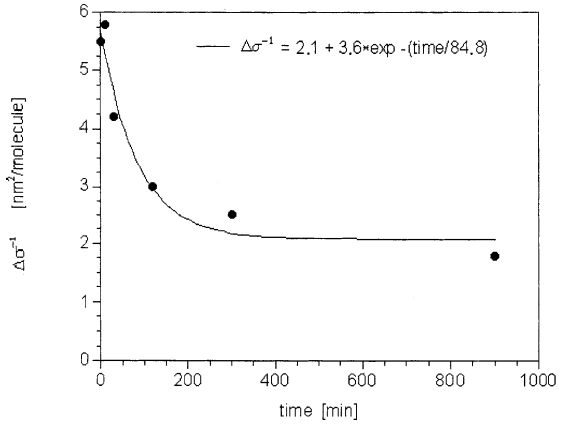

Figure 8. Influence of time interval (between expansion and compression) on hysteresis in the interfacial pressure isotherms of PS−Da2: experimental (●) and exponential curve fit (—), with relaxation time of approximately 85 min. $\Delta\sigma_0^{-1}$ is the difference between the onset area values (σ_0^{-1}) of the first and second compression.

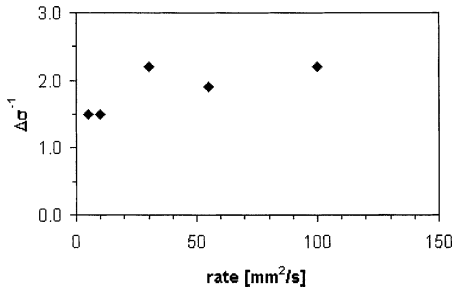

Figure 9. Influence of compression rate on hysteresis in the interfacial pressure isotherms of PS−Da2. $\Delta\sigma_0^{-1}$ is the difference between the onset area values (σ_0^{-1}) of the first and second compression.

$\Delta\sigma_0^{-1}$ are presented as a function of the time interval in Figure 8. Figure 9 displays the $\Delta\sigma_0^{-1}$ values as a function of the compression rate. When the time interval is increased or the compression rate decreased, the hysteresis diminishes ($\Delta\sigma_0^{-1}$ decreases). It suggests that, during expansion and compression, the dextran chains need some time to adsorb and desorb, respectively, from the air/water interface and adapt to a more favorable conformation. Fitting of the data in Figure 8 to an exponential relaxation function results in a relaxation time of approximately 85 min (indicated in Figure 8).

Figures 8 and 9 also indicate that it is unlikely that the (initially) adsorbed layers contained any free polysaccharide chains. These would desorb upon compression, but stay in solution upon expansion, because of the good solubility of polysaccharides in water and not adsorb at the interface again. Changing the time interval or compression rate would have no effect on the hysteresis.

Apart from the time dependency of the hysteresis, the results in both Figures 8 and 9 show a time-independent hysteresis of $\Delta\sigma_0^{-1} \approx 1.5-2.0$ nm²/molecule. This indicates a permanent change in the structure of the copolymer or loss of copolymer during the experiment.

To explain the behavior of monolayers of PS−dextrans and PS−maltodextrins upon compression and expansion, we consider the mutual interactions between the PS chains and the polysaccharide chains and the interaction of the polysaccharide chains with water.

Dextrans and maltodextrins are rather stiff molecules; desorption from and adsorption at the air/water interface are therefore presumably slow in comparison with flexible molecules like PEO. This probably leads to the observed hysteresis in the interfacial pressure isotherm (Figure 5). Furthermore, the hydroxyl groups of the polysaccharide chains may form H-bonds between neighboring glucosyl units of the same chain or neighboring polysaccharide chains.[16] In addition, H-bonds can be formed with water molecules, where water molecules can be shared by hydroxyl groups of adjacent polysaccharide chains.[16] These H-bonds contribute to the stiffness of the chains and support aggregate formation. Upon expansion, these aggregates break up only slowly because it requires activation energy.

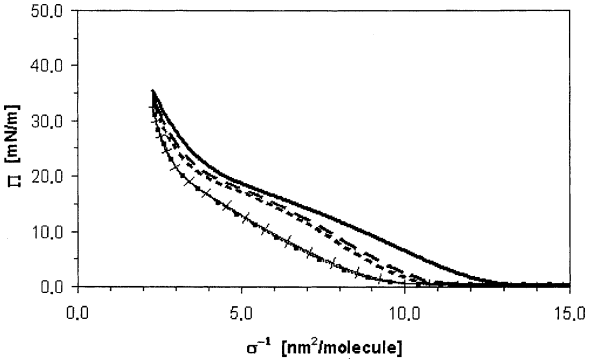

Figure 10. Interfacial pressure isotherms of PS−Da2 with 2.5 wt % glycerol in the water phase: first compression (—), first expansion (— | —), second compression (— —), second expansion (■), and third compression (- - -).

Kumaki demonstrated that monolayers of PS at an air/water interface may also aggregate.[17] Upon compression the PS chains tend to rearrange and form aggregates, which do not, or only partially, break up during expansion. This causes a shift of the second and following compression cycles toward lower values of σ^{-1}, which can also be seen in Figure 4.

As judged from Figure 5, the influence of the interactions between the polysaccharide chains dominates the interfacial pressure behavior of the block copolymers. This is illustrated by the extent of hysteresis between PS (Figure 4) and PS−Da2 (Figure 5). In Figure 10, another set of interfacial pressure isotherms is presented for PS−Da2 with 2.5 wt % glycerol added to the water phase. Glycerol is known to prevent formation of H-bonds and also serves as a plasticizer in carbohydrate-based materials.[18] A small amount of 2.5 wt % glycerol in the water phase reduces the hysteresis considerably. This gives support to the hypothesis that the hysteresis is due to H-bonds between polysaccharide chains, in addition to the slow adsorption and desorption of the polysaccharide chains. Adding 2.5 wt % glycerol to the water phase has no significant influence on the interfacial pressure of the "pure" water.

4. Conclusion

Linear diblock copolymers of polystyrene and dextrans, and maltodextrins, were synthesized successfully. Yields of 75−95 wt % were achieved. IR spectroscopy confirmed the coupling of amino-terminated PS and the different polysaccharides. Moreover, the interfacial behavior of a monolayer of the synthesized copolymers points to a successful coupling. The interfacial pressure pattern of the copolymers is typical for amphiphilic compounds and is clearly different from those of the individual PS and polysaccharides.

The copolymers demonstrate interfacial pressure hysteresis between consecutive compression and expansion cycles of a monolayer. This is due to slow adsorption/desorption of the polysaccharide chains at the air−water interface and the formation of aggregates of copolymer at the interface. Both the PS chains and the polysaccharide chains can aggregate. However polysaccharide aggregation, due to H-bonds between adjacent chains, seems to be predominantly responsible for the observed hysteresis. Increasing the time interval between compressions and expansions or reducing the compression rate reduces the extent of hysteresis. The relaxation time for the hysteresis is about 85 min.

The synthesis method here described proved to be unsuccessful for the coupling of long polysaccharides (M_w > 6000 Da). A different synthesis approach is needed for longer polysaccharides, which will be the focus of future research, together with the preparation of polymer brushes (LB films) of the different PS−polysaccharides and protein adsorption experiments on the polymer brushes.

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