Trends in Adsorption of End-Functionalized Polystyrenes by Thin-Layer Chromatography[1]

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ABSTRACT: The thin-layer chromatographic behavior on silica and alumina of polystyrene (PS-H), hydroxyl-terminated polystyrene (PS-OH), and carboxylic acid terminated polystyrene (PS-COOH) as a function of molecular weight is reported. Functionalized samples below a critical molecular weight, which depends on elution solvent, exhibit lower R_f values than PS-H samples of the same molecular weight. Above this value, similar elution behavior is observed. The data describe molecular weight regimes in which and solvent conditions under which functionalized polymers adsorb through specific interaction between the functional group and the surface.

Introduction

Adsorption of polymers at interfaces is pivotal to a range of technologies including lubrication,[2] colloid stabilization and destabilization,[3] corrosion inhibition,[4] and adhesion.[5] We are studying polymer adsorption with the objectives of controlling the conformation of adsorbed polymer chains and ultimately, through this control, regulating interfacial properties. Our strategy is to prepare polymers containing specific functional groups ("sticky feet") in well-defined densities and locations and to allow these polymers to adsorb to a surface from a solvent (or solvent mixture) from which the polymer would not adsorb, were it not functionalized. Figure 1 describes this strategy with several examples of the large variety of topologies that could be used. We have reported[6] the adsorption of thiol-terminated polystyrene and styrene-propylene sulfide block copolymers to a gold surface from tetrahydrofuran (a good solvent for polystyrene—unfunctionalized polystyrene does not adsorb). These adsorptions are types b and e in Figure 1. Adsorptions of polystyrene functionalized with a terminal zwitterionic group[7] (type b), styrene-2-vinylpyridine block copolymers,[8] and a styrene-ethylene oxide block copolymer[9] (both type e) to mica surfaces have been reported as well.

We began this research with plans for a large number of adsorption experiments involving changes in topology (Figure 1), molecular weight, concentration, sticky foot identity, and solvent identity. We envisioned that the solvent identity would be a versatile (and easily manipulated) variable for controlling the structure of adsorbed films and planned a variety of adsorption experiments based on this variable, some involving sequential adsorptions of different polymers from different solvents. With this large number of experiments before us, we needed a simple and rapid technique to test and optimize adsorption conditions and we assessed thin-layer chromatography (TLC) in this regard. Thin-layer chromatography has been used for a variety of preparative and analytical purposes including homopolymer fractionation, molecular weight determination, identification of linear polymers with specific end groups, identification and separation of stereoregular homopolymers, and separation of random copolymers according to their composition; this field of research has been reviewed.[10-12] A recent report[13] indicates that TLC is useful for detecting polymer adsorption/desorption transitions in binary solvent mixtures and measuring segmental adsorption energies.

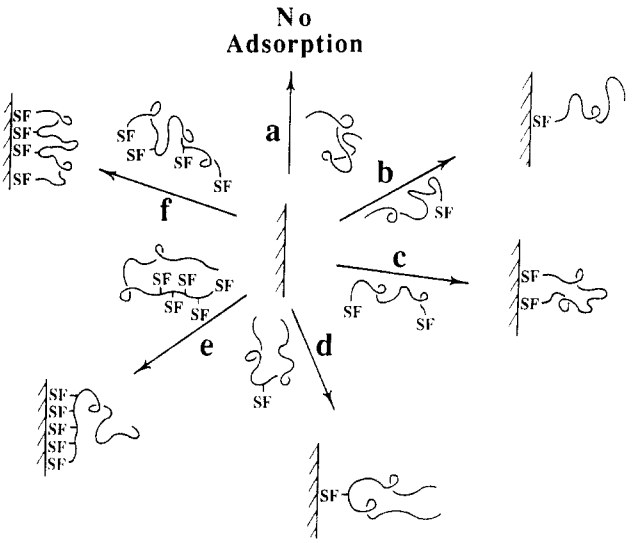

Figure 1. Pictorial representation of adsorptions of polymers to a surface from a solution that the unfunctionalized polymer will not adsorb from (SF = sticky foot).

In this paper we report TLC measurements of terminally functionalized (-COOH and -OH) polystyrenes on alumina and silica thin layers as a function of molecular weight. The results show that this simple technique is useful for predicting adsorption behavior and, of particular interest to us, useful for determining the molecular weight regime in which and solvent conditions from which functionalized polymers adsorb through specific interaction between the functional group and the surface.

Experimental Section

Materials. Styrene (Aldrich) and ethylene oxide were stirred over and distilled from calcium hydride (styrene at reduced pressure) and stored under nitrogen at -20 °C. Each was redistilled (trap-to-trap) from dibutylmagnesium (Alfa) immediately prior to use. Benzene and tetramethylethylenediamine (TMEDA; Aldrich) were distilled from calcium hydride (TMEDA at reduced pressure) and redistilled from *n*-butyllithium (Aldrich) (trap-to-trap) just prior to use. Carbon dioxide (Matheson; bone dry) was used as received; *sec*-butyllithium (Aldrich) was used as received and titrated periodically with 4-biphenylmethanol.[14] THF was distilled from sodium benzophenone dianion; chloroform was distilled from phosphorus pentoxide. High molecular weight polystyrene samples were purchased from Pressure Chemical.

Polymer Syntheses. Literature procedures[15,16] were followed for the preparation of polystyrenes (PS-H), carboxylic acid terminated polystyrenes (PS-COOH), and alcohol-terminated

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polystyrenes (PS–OH). We found that the best method for PS–COOH synthesis was to add TMEDA to the benzene solution of polystyryllithium, remove the solvent by freeze drying, and treat the resulting solid with gaseous CO_2 for greater than 6 h (the orange color of the solid polystyryllithium disperses long before the reaction is complete) before acidifying with HCl/THF. Samples prepared by this method contained small amounts of PS–H and ketone ($PS_2C{=}O$). These impurities can be resolved (by TLC) from PS–COOH, and their presence does not compromise the reported results; so they were used without purification.

Thin-Layer Chromatography (TLC). Silica gel thin layers (250 μm thick, 60-Å mean pore diameter) supported on 20 × 20 cm glass were obtained from Aldrich. Preparative alumina thin layers (250 μm thick) were obtained from Analtech, Inc. Both plate types were conditioned at 150–200 °C for at least 1 h prior to use. TLC was carried out by applying 5–10 μg of polymer as a spot (2–3-mm diameter) 4 cm from the bottom of the plate. Elution (the solvent front was allowed to proceed 6–9 cm) was carried out in a filter-paper-lined TLC tank (Aldrich) filled to 3-cm depth with eluent. After elution the TLC plates were dried in an oven at 150–200 °C for 15 min and the samples were viewed as dark spots in a fluorescent background under a UV (λ = 254 nm) lamp. R_f values are reported in the standard fashion (R_f = elution distance of sample/elution distance of eluent). R_f values obtained on different TLC plates of the same adsorbant material were normalized to the R_f values of low molecular weight PS–H standards (freshly synthesized) run on the same plate. Two low molecular weight standards (benzophenone and 2,6-di-*tert*-butyl-4-methylphenol) were run on each plate to ensure that the activity of different plates was the same. R_f values are reproducible within 5% for TLC plates from a given source. The absolute R_f values obtained for a given polymer on a given adsorbant are dependent on the source of the TLC plates. Similar trends, however, have been seen on all TLC plates, regardless of the source.

Results and Discussion

Polystyrene (PS–H), carboxylic acid terminated polystyrene (PS–COOH), and alcohol-terminated polystyrene (PS–OH) samples were prepared by anionic polymerization of styrene in benzene using *sec*-butyllithium as the initiator and reaction of the resulting polystyryllithium with methanol (for PS–H), CO_2 (in the presence of TMEDA) followed by HCl/THF (for PS–COOH)[15] or ethylene oxide followed by HCl/THF (for PS–OH).[16] PS–H samples with molecular weights greater than 1 000 000 were purchased.[17]

Thin-layer chromatography was carried out by using commercial silica and alumina chromatogram plates. Figure 2 shows plots of R_f vs molecular weight for PS–H (○), PS–OH (■), and PS–COOH (▲) eluted with benzene on silica and alumina thin layers, respectively. The shape of eluted samples of PS–H samples with $M_n < \sim 100\,000$ was close to the shape of the initial spot. PS–H with M_n between 100 000 and 600 000 exhibited a thin line (3–6 mm in length) with convex outer boundaries. PS–H with $M_n > 600\,000$ exhibited an inverted ω-shape with polymer concentrated along the convex lines. All functionalized polymers that eluted had a convex line shape. Because of this "spreading", all R_f values were computed from averages of the maximum and minimum elution distance. This difference ranged from 4 to 10 mm.

Benzene is a good solvent for PS–H, and high R_f values (○) are observed for samples with molecular weights less than $\sim 10^5$ on both alumina and silica.[18,19] Samples with M_n values higher than these adsorb to the aluminum oxide or silica surface and exhibit lower R_f values. These samples are of the critical molecular weight (have the critical energy[20,21]) necessary for adsorption on the "TLC time scale". Samples with $M_n > 2 \times 10^6$ have R_f values equal to 0, and thus they do not desorb from either silica or alumina into benzene. It should be recognized that

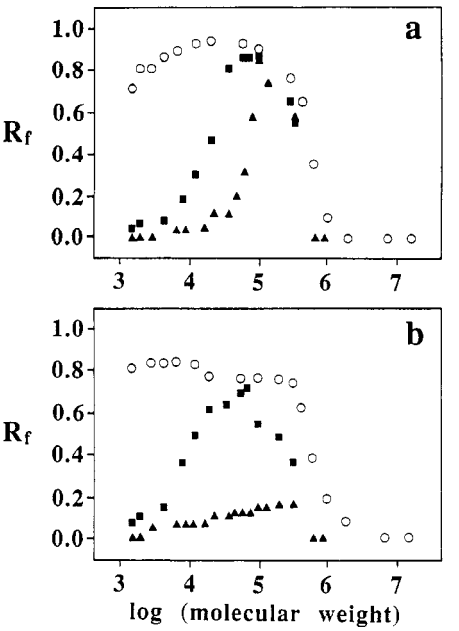

Figure 2. (a) Plots of R_f vs molecular weight for PS–H (○), PS–OH (■), and PS–COOH (▲) eluted with benzene on silica. (b) Analogous data on alumina.

adsorption/desorption kinetics play a critical role in TLC (R_f) measurements and that these conditions do not reproduce static adsorption experimental conditions but merely reflect relative propensity for adsorption and desorption. Under static conditions with greater contact time, samples with lower molecular weight than one would naively predict from these plots may adsorb from polymer solution and likewise higher molecular weight samples may desorb into solvent.

The low molecular weight samples of PS–COOH and PS–OH exhibit elution behavior markedly different from PS–H samples of the same molecular weight. PS–COOH samples with $M_n < 37\,000$ show R_f values less than 0.1 on silica (▲, Figure 2a). The carboxylic acid group is an effective sticky foot in this molecular weight regime under these conditions. As the molecular weight is increased, adsorption becomes less favorable, and at $M_n = 99\,000$, the observed R_f is essentially the same as a PS–H sample of similar molecular weight. At this molecular weight, the sticky foot/surface enthalpic interaction is not sufficient to overcome the combination of entropy loss of the large chain, the loss of polymer/solvent interactions, and the loss of solvent/surface interactions incurred on adsorption. This effect was observed for thiol-terminated polystyrenes (PS–SH) adsorbed to gold from THF solution.[6] Increasing molecular weight further causes the R_f to decrease as the critical molecular weight for adsorption of unfunctionalized PS–H is reached. The carboxylic acid is a strong sticky foot for alumina support (▲, Figure 2b), and only small differences in elution behavior are observed as the molecular weight is varied. The hydroxyl group is a relatively (to COOH) weak sticky foot, and R_f value changes for PS–OH are observed at lower molecular weights than are observed for PS–COOH on both silica and alumina. All PS–OH samples elute to some extent under these eluent conditions.

We have used several different solvents and mixed solvents as eluents, and, through this variable, the molecular weight below, which end-functionalized polystyrenes elute differently than unfunctionalized polystyrenes, can be controlled. Benzene (the data described above) gives us the largest molecular weight range in which a single terminal sticky foot affects adsorption.

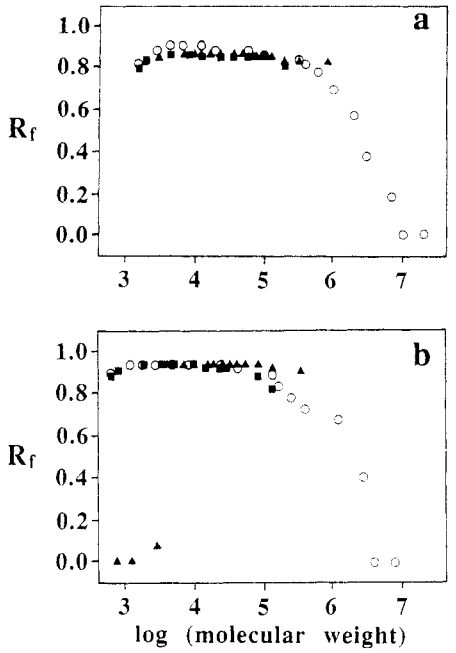

Figure 3. (a) Plots of R_f vs molecular weight for PS–H (○), PS–OH (■), and PS–COOH (▲) eluted with THF on silica. (b) Analogous data on alumina.

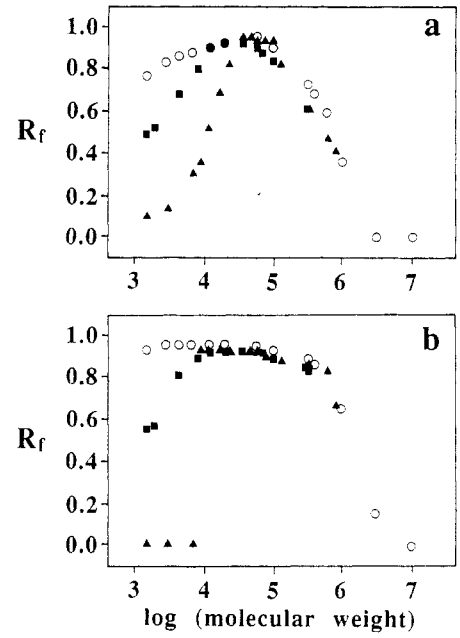

Figure 4. (a) Plots of R_f vs molecular weight for PS–H (○), PS–OH (■), and PS–COOH (▲) eluted with chloroform on silica. (b) Analogous data on alumina.

To assess the effects of multiple sticky feet, we will most certainly need to use better displacing solvents (which yield higher R_f values for one sticky foot). Figures 3 and 4 show data analogous to that presented in Figure 2 for THF and chloroform. THF is a much better displacer than benzene for PS–COOH and PS–OH. On silica, one terminal sticky foot has no apparent effect at any molecular weight; on alumina only very low molecular weight PS–COOH samples adsorb. Figure 3 shows that chloroform behaves as a displacer intermediate in strength between THF and benzene.

We emphasize that a single oxygen-containing functional group on polystyrene can dramatically affect adsorption behavior. The data herein indicate this explicitly for polystyrene samples with molecular weights less than ~100 000. That the chromatographic behavior of higher molecular weight functionalized and unfunctionalized polystyrenes is similar does not indicate that their adsorption behavior (kinetics, conformation, etc.) is similar. This is a warning that researchers should be extremely cautious of the purity of polystyrene (and, indeed, any polymer) samples used for adsorption experiments. Slight oxidation, which cannot be detected by microanalysis or GPC, is evident by TLC. Polystyrene is unstable with regard to photooxidation[22] (which introduces oxygen-containing functionality) and should be stored under nitrogen in the dark immediately after preparation and tested by TLC prior to adsorption experiments. We have found, using TLC, that the majority of commercial samples, as well as old samples that we prepared and stored under ambient laboratory conditions in screw-cap vials, contain an oxidized component.

In summary, TLC can be used to help establish conditions (herein we describe solvent and molecular weight) under which functionalized polymers will adsorb and their unfunctionalized counterparts will not—conditions under which sticky feet can be used to control adsorbed polymer architecture.

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