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Spontaneous Adsorption of Polystyrene from Solution to the Cyclohexane–Poly(vinylidene fluoride) Interface

The adsorption of polymers from solution to solid surfaces in contact with the solution is central to a spectrum of technologies including adhesives, coatings, colloid stabilization, lubrication, biocompatibility, and enhanced oil recovery. Basic elements of polymer adsorption are current foci of research in a number of experimental and theoretical groups;[1-14] several reviews are available.[15-19] The overwhelming majority of experimental studies has involved inorganic (usually metal oxide) adsorbent substrates for three practical reasons: (1) Metal oxide surfaces contain polar functionality (M–OH, M–O–M) that imparts a high surface energy;[20] thus adsorption readily occurs due to polymer segment–surface functionality interactions. (2) High surface area inorganics (in particular, silicas) are available that adsorb sufficient amounts of polymer to allow quantitative adsorbance measurements using standard analytical techniques. (3) Several of the most powerful techniques available for determining adsorbed polymer structure require molecularly smooth (surface force balance) or optically flat (both external and internal reflection techniques) surfaces and inorganic substrates either are required or are most convenient.

Organic substrates have not been extensively studied, and they offer a key advantage that has not been exploited: their chemical versatility. It is recognized that adsorption of polymers to polymer latices can be controlled by using negatively[21] and positively[22] charged latex particles, but much finer control is possible. Organic polymer films can be surface-modified to contain a submonolayer to several monolayer level of specific versatile organic functional groups,[23-27] and these surfaces can be further derivatized[28] to yield a range of substrates differing only in surface chemistry. We have been developing the surface chemistry of chemically resistant polymers[23-26,29,30] and have described[23] their advantages as substrates for studying surface reactivity; many of these advantages will apply toward their use as adsorbents.

We are currently studying the adsorption of functionalized polymers to complementarily functionalized polymer film samples.[31] We report in this paper the results of a series of control experiments that were (initially) counterintuitive, involving adsorptions of unfunctionalized polymers to an unfunctionalized surface.

Poly(vinylidene fluoride) (PVF$_2$) film[32] was exposed to cyclohexane[33] solutions of polystyrene[34] at 36 °C (slightly better solvent conditions than θ) under nitrogen for a particular duration; the polymer solution was removed, and the film sample was washed (under nitrogen) with 3 aliquots of cyclohexane at 36 °C (the solvent was in contact with the film for 15 min during each wash) and then dried at reduced pressure. Figure 1 shows a plot of the C:F atomic ratio (determined by XPS[35]) of PVF$_2$ film samples that had been exposed to 2 mg/mL of polystyrene/cyclohexane solutions versus the polystyrene molecular weight. The data were recorded at a takeoff angle of 75° (measured between the plane of the film and the entrance lens of the detector optics) and indicate the composition of the outer ~40 Å.[36] PVF$_2$ ($\text{-}\!(CH_2CF_2)\!\text{-}_n$) has a C:F ratio of 1, and an increase in this ratio indicates the presence of adsorbed polystyrene. No adsorbance is observed for polystyrene of M_n = 3100, 4200, or 7100, but adsorbance is clearly indicated for samples with $M_n \geq 20\,000$. The adsorbance reaches an apparent plateau above M_n = ~100 000; higher molecular weight samples were not studied. Figure 2 shows plots of the C:F ratio (determined by using the same conditions as for the data in Figure 1) as a function of concentration and adsorption time for a polystyrene sample with M_n = 423 000. These plots indicate that 2 mg/mL is above the plateau concentration and that a final-state adsorbance has been reached well before 24 h (the conditions used for the experiments reported in Figure 1). Figure 3 displays C_{1s} region XPS spectra for virgin PVF$_2$ and PVF$_2$ adsorbed with polystyrene of M_n = 423 000 recorded at takeoff angles of 15° (representing the composition of the outer ~10 Å[36]) and 75° (outer ~40 Å). The presence of a thin polystyrene overlayer is indicated by the appearance of a low binding energy C_{1s} photoelectron line and the takeoff angle-dependent intensity of this line (relative to the PVF$_2$ signals). The $\pi \to \pi^*$ shakeup peak that occurs at a 6.7 eV higher binding energy than that of the main polystyrene peak is obscured by the *C*F$_2$ photoelectron line.

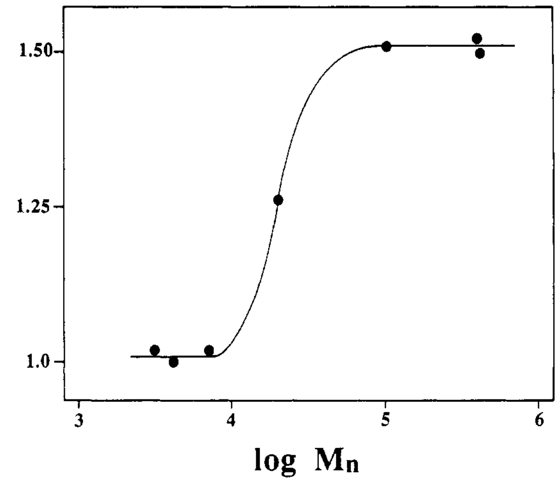

Figure 1. Plot of the C:F atomic ratio determined by XPS (75° takeoff angle) vs polystyrene molecular weight for polystyrene-adsorbed PVF$_2$ film (2 mg/mL in cyclohexane at 36 °C, 24 h).

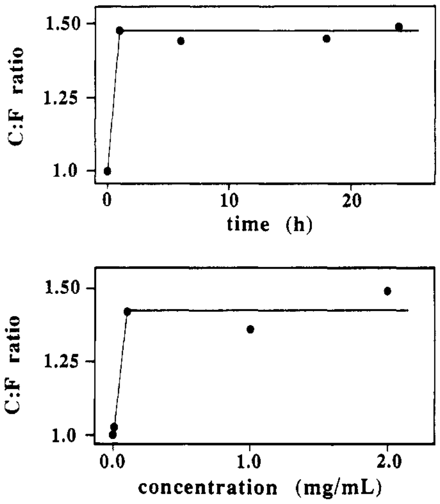

Figure 2. Plots indicating the effects of time (upper, 2 mg/mL of polystyrene, M_n = 423 000, in cyclohexane at 36 °C) and concentration (lower, polystyrene, M_n = 423 000, in cyclohexane at 36 °C, 24 h) on polymer adsorption (C:F ratio).

These experiments indicate that, above a critical molecular weight[37,38] of ~20 000, polystyrene spontaneously adsorbs to the PVF$_2$–cyclohexane interface. After some period of time less than 24 h, the adsorption is irreversible; the polystyrene cannot be washed from the film with the solvent used for adsorption. We interpret this adsorption tendency as completely analogous to polymer adsorption

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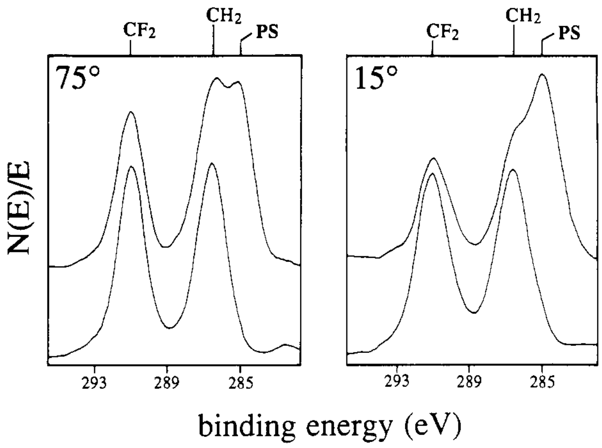

Figure 3. C_{1s} regions of XPS spectra (75° and 15° takeoff angles) of virgin PVF_2 (lower spectra) and PVF_2 film adsorbed with polystyrene, M_n = 423 000 (upper spectra).

to inorganic substrates: at sufficiently high molecular weight, the sum of the sytrene segment–PVF_2 surface enthalpic interactions outweighs the polystyrene conformational entropy loss. We recently reported[39] the adsorption of poly(L-lysine) to the water–poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) interface. Water does not "wet" FEP, and we proposed that decreasing interfacial free energy (lowering the surface tension of water) is a major driving force for adsorption and that FEP–poly(L-lysine) enthalpic interactions are negligible. The polystyrene/cyclohexane/PVF_2 system is different: polystyrene is repulsed from the free cyclohexane surface (there is a depletion layer).[40,41]

The XPS data indicate that very thin (<10-Å average thickness) films of polystyrene are formed but do not indicate whether they are continuous or patchy. The adsorption kinetics (Figure 2) suggests a PVF_2–cyclohexane interface that is saturated with polystyrene and argues for a continuous (solvated) film. The adsorbed films are dried prior to XPS analysis, and the drying process may substantially alter the thin film structure. ATR IR spectroscopy[42] and water contact angle analysis[43] were rather insensitive to polystyrene adsorption. The only change in the infrared spectrum was a very weak absorbance at 698 cm^{-1} (δ_{C-H} out-of-plane) that was observed in PVF_2 samples with adsorbed polystyrene with $M_n \geq$ 100 000. PVF_2 film with adsorbed polystyrene (M_n = 423 000) exhibits water contact angles of $\theta_A/\theta_R = 85°/62°$; virgin PVF_2 exhibits $\theta_A/\theta_R = 89°/67°$.

We summarize by emphasizing that weak polymer segment–polymer surface interactions, when cumulated in a sufficiently high molecular weight polymer, cause spontaneous irreversible adsorption (a phenomenon well-recognized for inorganic substrates) and may be useful as an alternative method for polymer surface modification.[44]

Acknowledgment. We thank the National Science Foundation (NSF) sponsored University of Massachusetts Materials Research Laboratory and the NSF (Grant DMR-8718420) for financial support.

References and Notes

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(31) Some of our objectives have been detailed in ref 30.
(32) PVF_2 film (5-mil Pennwalt Kynar obtained from Westlake Plastics) was extracted in refluxing dichloromethane for 30 min and dried [50 °C (0.05 mm)] to constant mass (3 days).
(33) Cyclohexane (Fisher) was stirred over and distilled from calcium hydride under nitrogen.
(34) Polystyrene samples were prepared by anionic polymerization of styrene (distilled at reduced pressure from calcium hydride and then dibutylmagnesium) with *sec*-butyllithium in benzene (distilled from sodium benzophenone dianion) and stored in a nitrogen-purged drybox in the dark. The molecular weights of samples prepared and studied were as follows (M_n (PDI)): 3100 (1.06), 4200 (1.04), 7100 (1.05), 20 000 (1.04), 102 000 (1.03), 405 000 (1.05), 423 000 (1.05).
(35) XPS spectra were recorded on a Perkin-Elmer–Physical Electronics 5100 at a pass energy of 71.5 eV with Mg Kα excitation (300 W). Atomic sensitivity factors used to determine atomic ratios were as follows: F_{1s}, 1.00; C_{1s}, 0.20 (determined using virgin PVF_2).
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(43) Dynamic advancing (θ_A) and receding (θ_R) contact angles were measured with a Ramé-Hart telescopic goniometer equipped with a Gilmont syringe and 24-gauge flat-tipped needle using doubly distilled water.

(44) For a review on standard polymer surface modification, see: Ward, W. J.; McCarthy, T. J. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; John Wiley and Sons: New York, 1989; suppl. vol., p 674.

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