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End group effect in polymer adsorption: Competitive adsorption of carboxylic acid-terminated and unfunctionalized polystyrene

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(Received 12 March 1990; accepted 30 March 1990)

We report measurements of the competitive adsorption of polystyrene chains, carboxylic acid-terminated and unfunctionalized, onto silicon oxide from dilute cyclohexane solution. The differential adsorption enthalpy from the carboxylic acid end group is found to be ≈ 5 kT. We are not aware of previous quantitative determinations. Together with our earlier quantification of the protio-deuterio adsorption isotope effect¹ and recent thin layer chromatography experiments,^{2,3} this determination of the chain end effect owing to a polar group emphasizes the significant role that trace chemical inhomogeneity can play in high polymer adsorption.

Experiments were performed at the University of Illinois using polystyrene (PS) samples synthesized at the University of Massachusetts. The anionic polymerization was terminated by adding methanol. Two deuterio samples (PS-*d*) with similar weight-average molecular weight (M_w) and number-average molecular weight (M_n) were investigated: deuterium-terminated deuterio polystyrene (PS-*d*, $M_w = 6000$, $M_w/M_n = 1.04$) and deuterio polystyrene terminated at one end by a carboxylic acid group (PS-*d*-COOH, $M_w = 6000$, $M_w/M_n = 1.07$). Hydrogen-terminated protio PS (PS-*h*) was also investigated ($M_w = 12\,000$, $M_w/M_n = 1.04$). The samples were dissolved in distilled and dried cyclohexane (Aldrich) at the total concentration 0.1 mg mL⁻¹.

Infrared measurements were made in the mode of attenuated total reflection (ATR). The PS was allowed to adsorb to the surface of a silicon prism prepared by methods described previously^{4,5}. Under ambient conditions, such as we used, it is well known that silicon is covered by a native oxide layer. The temperature of measurement was 30.0 °C. This is the theta temperature, T_θ , for PS-*d* in cyclohexane.⁶ By comparison, the theta temperature is 34.5 °C for PS-*h* in cyclohexane.⁶ Calibrations showed that Beer's law held to a good approximation for these films of low adsorbance, as

expected.^{4,5} The surface excess was calculated, as described previously,^{4,5} from the integrated carbon-hydrogen and carbon-deuterium infrared absorption peaks, after subtracting the (negligible) contribution of PS free in solution.

In Fig. 1, the surface excess (mass per unit area) of each species in the mixture is plotted against the elapsed time during competitive adsorption. Equilibration was rapid in every experiment, the surface excess stabilizing within 15 min.

First, the competitive adsorption was measured of a 50:50 mixture by weight of the unfunctionalized polymers: PS-*h* ($M_w = 12\,000$) and PS-*d* ($M_w = 6000$). The steady-

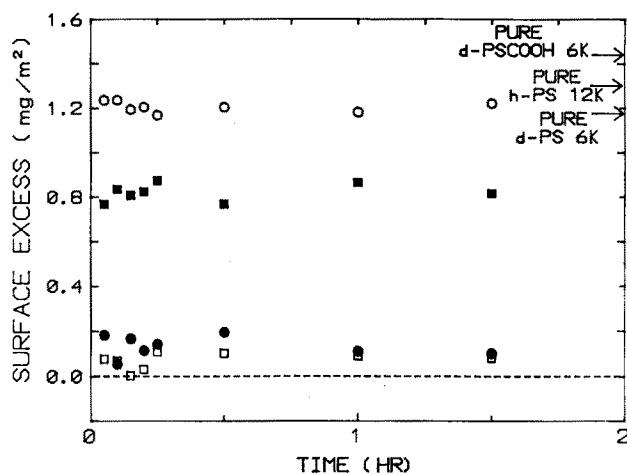


FIG. 1. Surface excess (mass per unit area) of polystyrene, plotted against elapsed time, for adsorption onto silicon oxide from cyclohexane solution (0.1 mg mL⁻¹) at 30.0 °C. Filled squares and circles: PS-*h* ($M_w = 12\,000$ g mol⁻¹) and PS-*d* ($M_w = 6000$), respectively, adsorbed from a 50:50 mixture by weight. Open squares and circles: PS-*h* ($M_w = 12\,000$) and PS-*d*-COOH ($M_w = 6000$), respectively, adsorbed from a 50:50 mixture by weight. Arrows show the steady-state surface excess of these same samples during noncompetitive adsorption in separate experiments.

state surface excess of these same samples, when they adsorbed noncompetitively in separate experiments, is also indicated in Fig. 1. In competitive adsorption, the surface excess of PS-*h* was approximately 8 times larger than that of the PS-*d*. This enrichment was less than expected solely from the entropic advantage of adsorbing chains of higher molecular weight. The adsorption isotope effect (favoring the deuterio species) was calculated by arguments presented previously¹ and was found to be $\approx 80 \text{ J mol}^{-1}$ of repeat units. This is in good agreement with our recent findings which had used commercial samples¹ and lends support to those results.⁷ It also agrees with the recent theoretical considerations of Kumar and co-workers.⁸

Next, we investigated the role of the chain end functionality. The competitive adsorption was measured of a 50:50 mixture by weight of unfunctionalized PS-*h* ($M_w = 12\,000$) and carboxylic acid-terminated PS-*d*-COOH ($M_w = 6000$). In Fig. 1, one notes the *opposite* pattern of surface enrichment than was observed for the unfunctionalized samples of similar average molecular weight. In this experiment the carboxylic acid-terminated chains, of *lower* molecular weight, were enriched at the surface. The surface excess of PS-*d*-COOH was approximately 12 times larger than that of PS-*h*. Control experiments were performed to test the conceivable possibility of chemisorption. From competitive adsorption with unfunctionalized PS of other molecular weights than for the data in Fig. 1, it emerged that the enrichment of PS-*d*-COOH was larger, the lower the molecular weight of unfunctionalized PS. In addition, previous experiments showed that adsorption of stearic acid onto this same silicon surface (from carbon tetrachloride) is reversible.⁵ The adsorption of the carboxylic acid group in the present experiments therefore appears to have been reversible, and we assume this in the following analysis.

The differential segmental sticking energy owing to the single carboxylic acid functional group was estimated. The surface excess of PS-*h* and PS-*d*-COOH in competitive ad-

sorption, expressed as fractions of the surface excess under noncompetitive conditions, was set equal to a Boltzmann factor, $\exp[-(\Delta H - T\Delta S)/RT]$. Here R is the gas constant and T is the absolute temperature. By Eq. (1) of Ref. 1, one obtains $\Delta S = 12.3 \text{ J K}^{-1}$ per mole of PS-*h*. The differential adsorption enthalpy, ΔH , is partly the result of the adsorption isotope effect (in this instance, 9.2 kJ per mole of PS-*h*) and partly the result of preferential sticking of the carboxylic acid group. Solving for the latter, one finds $\Delta H \approx 14.2 \text{ kJ mol}^{-1}$ of PS-*d*-COOH, i.e., $\approx 5.5 \text{ kT}$ per carboxylic acid end group.

We emphasize that the habitual supposition (based on the entropy of distributing chains of different length between the adsorbed state and free solution), that long macromolecules will adsorb at the expense of shorter ones, is not justified in this system. That tendency appears to be overwhelmed by the energetic preference for the surface of the single polar end group.

This work was supported by the National Science Foundation, Grants Nos. DMR-87-18136 (University of Illinois) and DMR-87-18420 (University of Massachusetts).

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Quantum Monte Carlo calculations of three-body corrections in the interaction of three helium atoms

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(Received 22 February 1990; accepted 26 March 1990)

We have used the quantum Monte Carlo (random walk) method to calculate accurate *total* electronic energies for the helium trimer in several nuclear configurations to obtain potential energies of interaction and determine three-body corrections to pairwise-additive potential energy expressions. For equilateral triangle configurations with side length 2.5 to 6.5 a.u. [1 a.u. (length) = 0.529 18 Å; 1 K (energy) = 3.164×10^{-6} a.u. (energy)] the three-body correction ranges from -5930 K at 2.5 a.u. to approximately 0

K at 6.5 a.u. Comparisons of results from simple analytic variational calculations of the same correction show the simple calculations to be remarkably accurate. The Axilrod-Teller-Muto predictions fail for side lengths less than 5.6 a.u.

The van der Waals interactions of molecules are usually discussed¹ in terms of two-body interaction energies for dimers and three-body and higher order corrections to energies given by pairwise addition of two-body interactions. In