

## Conclusion

Polystyrene that was freeze-dried from solutions of concentration below  $c^*$  was not in the form of collapsed coils. The chain dimensions were the same as those observed in normal bulk material.

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## References and Notes

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# Communications to the Editor

## Adsorption Isotope Effect for Protio- and Deuteropolystyrene at a Single Solid Surface

Many analytical methods rely on isotopic labeling. At the same time, isotopic isomers often have subtle differences in a wide range of physical properties.<sup>1</sup> Recently, we undertook measurements of adsorption exchange kinetics from liquid solution to a single solid surface.<sup>2,3</sup> It was possible to measure directly the replacement of deuteropoly(methyl methacrylate) (PMMA) by the protio species of similar degree of polymerization.<sup>3</sup> The time constant for this exchange is a measure of the surface residence time, provided that the segmental sticking energy of the two isotopic species is the same. Since PMMA is believed to adsorb at the carbonyl group, no protio-deutero isotope effect was expected and none was detected experimentally.<sup>4</sup> For polystyrene (PS) adsorbed onto a single surface of silicon oxide from cyclohexane, however, we find that the deutero isotope appears to adsorb preferentially.

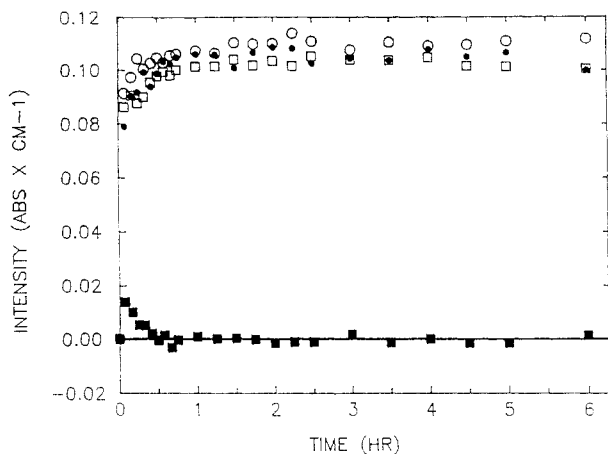
Infrared spectroscopy was employed, in the mode of attenuated total reflection (ATR), to measure PS adsorption to the native surface of a silicon infrared prism.<sup>2,3</sup> Infrared spectra were collected, and the silicon ATR prism was prepared using methods described previously.<sup>2</sup> Under ambient conditions, such as we used, it is well-known that silicon is covered by a native oxide layer.<sup>5</sup>

The temperature of measurement was 30.0 °C, which is the  $\theta$  temperature,  $T_\theta$ , for deuteropolystyrene (PS-*d*) in cyclohexane.<sup>6</sup> For protiopolystyrene (PS-*h*) in cyclohexane,  $T_\theta = 34.5$  °C,<sup>6</sup> so that PS-*d* at 30 °C finds itself in a slightly better solvent than does PS-*h*. Calibrations showed that Beer's law held to a good approximation for

these films of low adsorbance, as expected,<sup>7</sup> and that the PS free in solution (0.2 mg·mL<sup>-1</sup>) contributed only approximately 1% to the measured PS absorption peaks. At this solution concentration, PS-*d* and PS-*h* are completely miscible.<sup>6,8</sup>

In Figure 1, integrated intensities of the C-H and C-D infrared peaks, proportional to the surface excess, are plotted against elapsed time. Calibration shows that the intensity 0.10 absorbance unit·cm<sup>-1</sup> is approximately a surface coverage of 2.7 mg·m<sup>-2</sup>. The data for PS-*d* have been scaled by the calibrated fraction, 0.832, so that PS-*h* and PS-*d* intensities are proportional by the same constant to the surface excess. Three experiments are shown; comparison of (a) the adsorption of the pure deuteropolystyrene, (b) the adsorption of the pure protiopolystyrene, and (c) the adsorption of a mixture of PS-*d* and PS-*h* (48:52 parts by weight, respectively). The linear samples (from Pressure Chemical, reported to be methyl-terminated) had weight-average degrees of polymerization stated by the manufacturer to be  $N_w = 5000$  (PS-*d*) and  $N_w = 5500$  (PS-*h*), with ratios  $N_w/N_n$  ( $N_n$ , the number-average degree of polymerization) of 1.15 and 1.06, respectively. The nonideal mixing of undiluted binary mixtures of these same samples was studied previously by Bates and Wignall.<sup>8</sup>

In all three instances, the surface excess appeared to equilibrate within 1 h, and the ultimate levels adsorbed were the same within experimental uncertainty. For the mixture, at times less than 1 h the surface excess of PS-*d* rose while that of PS-*h* fell slightly. It appears that the adsorbed amounts of the two species may have taken similar values at early times, which is expected because of their similar concentrations in solution. At times greater



**Figure 1.** Integrated infrared peak intensities of polystyrene C-D and C-H vibrations, plotted against elapsed time for samples with  $N_w \approx 5000$ , adsorbed from cyclohexane solution at 30.0 °C: open squares, PS-*h*; open circles, PS-*d*, normalized as described in text; filled squares, PS-*h* in a 48:52 mixture; filled circles, PS-*d* in a 48:52 mixture. Calibration shows that the intensity 0.10 absorbance unit·cm<sup>-1</sup> is approximately a surface coverage of 2.7 mg·m<sup>-2</sup>.

than 1 h, the surface excess of PS-*h* was zero within the experimental uncertainty, indicating that the deuterio sample segregated to the surface.

The generality of this finding was tested using two additional samples of linear PS-*d*, mixed as before with PS-*h* in cyclohexane at 30 °C. Sample A (PS-*d*) had a relatively low degree of polymerization,  $N_w = 66$  (Polymer Laboratories,  $N_w/N_n < 1.03$ ). It was mixed with an PS-*h* fraction of  $N_w = 92$  (Toyo Soda,  $N_w/N_n = 1.02$ ). The 50:50 mixture in solution of total concentration 0.2 mg·mL<sup>-1</sup> gave a fractional surface excess of PS-*h* approximately 0.7 that for pure PS-*h* solution adsorbed under the same conditions and a surface excess of PS-*d* approximately 0.3 that for pure PS-*d* solution adsorbed under the same conditions. This is a larger proportion of the shorter PS-*d* at the surface than would be expected just from the mismatch of chain lengths, as will be discussed below.

Sample B of PS-*d* had a much higher degree of polymerization,  $N_w = 6300$  (Polymer Laboratories,  $N_w/N_n < 1.05$ ) and was mixed with an PS-*h* fraction of  $N_w = 12\,100$  (Toyo Soda,  $N_w/N_n = 1.05$ ). The 50:50 mixture of these two samples resulted in a surface excess comprised entirely of the deuterio species, despite the smaller proportional mismatch of the degree of polymerization than for sample A.

These consistent findings support the view that our findings reflect an isotope effect. It is true that significant differences in adsorption behavior can also result from the presence of rogue polar functional groups, for example, if chains are terminated by hydroxyl or carboxyl groups, as McCarthy and co-workers showed recently using thin layer chromatography.<sup>9</sup> However, the higher the degree of polymerization, the less important should be the influence of chain ends. We observed just the opposite: more pronounced surface segregation in the mixture with the PS-*d* fraction of higher degree of polymerization, as would be expected for a total isotope effect which increases with chain length.

The difference between the segmental sticking energies of PS-*d* and PS-*h* can be estimated from the observed surface segregation of sample A. In the spirit of refs 10 and 11, the entropy of mixing upon bringing one long chain to the surface and replacing it with  $c$  short chains

is positive. This entropic driving force can be estimated as

$$\Delta S_{\text{mix}}/k = -\ln[\varphi_{\text{long}}^{\text{ads}}/\varphi_{\text{long}}^{\text{bulk}}] + c \ln[\varphi_{\text{short}}^{\text{ads}}/\varphi_{\text{short}}^{\text{bulk}}]$$

which equals 2.55 in this instance. (The Boltzmann constant is  $k$ . The ratio  $c$  equals 92:66 = 1.4. The volume fraction in the "adsorbed phase",  $\varphi^{\text{ads}}$ , is approximated here as 0.3 for the short chains and 0.7 for the long chains. The bulk volume fraction,  $\varphi^{\text{bulk}}$ , equals  $1 \times 10^{-4}$  for both the short and long chains.) However, the shorter chains of PS-*d* adsorb more strongly than the longer PS-*h* chains, with differential adsorption enthalpy  $\Delta h$  per segment. Therefore, in bringing one long chain to the surface and replacing it with  $c$  short chains,  $92\Delta h$  opposes the entropy of mixing. Setting the Boltzmann factor equal to the difference between entropic and enthalpic factors, one obtains the rough estimate,  $\Delta h \approx 45 \text{ J}\cdot\text{mol}^{-1}$  of repeat units. It is, of course, more realistic to recognize that chains are bound to the surface by a fraction  $p < 1$  of potential adsorption sites. For PS-*h* adsorbed to colloidal silica,  $p \approx 0.5$  in the range of molecular weight of sample A.<sup>12</sup> This leads to a slightly higher estimate,  $\Delta h \approx 90 \text{ J}\cdot\text{mol}^{-1}$  of repeat units.

The primary origin of small isotopic differences in adsorption energy has long been understood to be changes in the zero-point energy normal to the surface, the vibrational energy levels being slightly lower in the case of the deuterio isotope.<sup>13</sup> Since one expects PS to adsorb at the pendant aromatic ring, it is reasonable to expect that the magnitude of the adsorption isotope effect will be similar for benzene. Already a generation ago, chromatography showed that the deuterio isotope of benzene adsorbs preferentially.<sup>1</sup> The temperature dependence of retention times in chromatography showed that for benzene the difference in enthalpy of adsorption from gas to solid is in the range 2–12 J·mol<sup>-1</sup>, depending on the chemistry of the solid support.<sup>12</sup> This is consistent with the rough estimate given above.

There is one other recent investigation of isotope fractionation by preferential adsorption: this involves segregation from the melt to the vacuum interface.<sup>13</sup> For an undiluted mixture of PS-*d* in PS-*h*, the surface energy difference between PS-*d* and PS-*h* of a high degree of polymerization was inferred to be 0.1 mJ·m<sup>2</sup> at 184 °C. This is equivalent (taking the cross-sectional area of a PS segment to be 0.67 nm<sup>2</sup><sup>14</sup>) to  $\approx 40 \text{ J}\cdot\text{mol}^{-1}$  of PS segments directly at the surface. The quantitative similarity to the estimates made above is probably coincidental. Nonetheless, in view of the fact that, of course, vacuum and silicon oxide are nonpolar and polar, respectively, it is interesting to note that the sign is the same; i.e., that PS-*d* segregates to both.

In general, the relevant question to ask about isotope effects is not whether they exist but whether they are large enough to matter. We have shown here that surface fractionation of isotopic polymer mixtures can occur even to a *single* solid surface. The differential sticking energy appears to be small per repeat unit,  $\approx 0.04 \text{ kT}$ , but large per chain macromolecule. Similar segregation behavior is expected in adsorption from the melt. This small differential energy per repeat unit provides an approach to probe equilibration times in adsorbed polymer layers when the history of adsorption is varied. A systematic study is underway.

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