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# End Chain Segregation Effects in Polymer Surfaces Observed by HREELS: A Preliminary Study

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**Introduction.** The knowledge of surface properties of polymers is important to understand, for instance, physical and chemical processes and their technological implications. Different features such as surface reactivity, electrical contact, adhesion, and fracture can be strongly dependent on the chemical nature and on the conformation of the molecular groups present at the surface.

For instance, surface tension, $\gamma_N$, of a polymer is a function of its polymerization index, $N$, usually increasing with $N$ toward a limiting value $\gamma_\infty$ reached at high $N$, but is often slightly smaller than $\gamma_\infty$.[1] This fact has been interpreted by de Gennes in terms of a surface enrichment in chain ends.[2] Such an enrichment (or possibly, in some cases, depletion) is quite obvious when chain ends are chemically very different from the chain monomers. But what about the case where chemical differences are minimal and the limiting case where the difference is essentially physical, the chain end repeat unit differing from all others only because it has a single neighbor along the chain? Surface enrichment of chain ends might have important consequences, for instance in polymer–polymer interdiffusion or polymer adhesion.[3]

While this paper was being submitted, Zhao et al.[4] published the results of a neutron reflectometry investigation of a triblock polymer similar to those used here, looking for chain end surface segregation. They obtained an upper limit of a factor 2 for surface enrichment in chain ends over the bulk value. Numerical calculations[5] have indicated that this enrichment should be confined to the outermost surface layer—over about twice the monomer size—with a slight depletion underneath. An experimental method sensitive to a comparable thickness only should therefore be well adapted.

An experimental approach to this problem is proposed here, based on the use of a vibrational spectroscopy, HREELS, which is sensitive to the surface layer of polymer films only, over a thickness ≤ 10 Å,[6] and on the isotopic labeling of chain ends by selective deuteration: a higher chain end concentration at the surface will be detected as a larger D-related signal.

HREELS consists in the energy analysis of low-energy electrons (typically with a kinetic energy of 1–10 eV) inelastically backscattered by a solid surface.[7] An electron which, by interacting with the film, has excited a molecular vibration will appear in the backscattered electron spectrum at an energy lower than the incident energy by an amount equal to the energy of that vibration: the spectrum consists of "vibrational peaks". Electronic transitions, corresponding to larger energy losses, may also be excited, corresponding loss peaks appearing in the backscattered electron spectrum. In HREELS the quantities of interest are usually vibrational frequencies rather than intensities; but we have shown elsewhere that HREELS can be used to measure the relative H/D concentration in the surface region, for instance in polystyrene films.[8,9]

Absolute quantification of HREEL spectra is not easy: differential scattering cross sections are functions of the incident electron energy $E_i$,[10] the geometry of the scattering event, and the orientation distribution of the transition dipoles relative to the ingoing and outgoing electron directions. The actual incident electron current density in an HREELS experiment is very difficult to measure. Moreover, the volume sampled by the electrons (or equivalently, the effective penetration depth) is also a function of the same variables, since all inelastic scattering channels operate in parallel (HREELS is not an absorption spectroscopy). In particular, cross sections for inelastic processes exciting electronic transitions are usually much larger than for vibrational ones, and the corresponding energy losses are large, thus greatly reducing the electron energy, so that, above the incident energy threshold for electronic excitations, the incident electron penetration depth decreases quite abruptly:[12,13] as a consequence, the depth sampled at energies above the $E_i$ threshold for electronic excitation becomes very small. This effect is particularly strong above the threshold for ionization.

Determination of cross section *ratios* for a given material at a given incident energy $E_i$ and for a given scattering geometry is much easier. This was done for the ratio $\sigma_H/\sigma_D$, corresponding to the CH and CD stretching vibrations at ca. 3000 and 2250 cm$^{-1}$, respectively, using partially deuterated polystyrenes.[8,9]

In the absence of CH-containing contaminant, the ratio $A_H/A_D$ between the areas of the CH and CD vibrational peaks is related to the ratio, $\sigma_H/\sigma_D$, between the corresponding excitation cross sections by

$$A_H/A_D = (\sigma_H/\sigma_D)(\chi_H/\chi_D) = -\sigma_H/\sigma_D + (\sigma_H/\sigma_D)(1/\chi_D)$$

where $\chi_D$ and $\chi_H$ are the molar fractions of the deuterated and hydrogenated monomers in the volume sampled by HREELS.[14]

In random copolymer films the concentration of deuterated monomers must be the same both at the surface and in the bulk, and no composition gradient perpendicular to the surface of the film should occur. So, in that case, the ratio $A_H/A_D$ directly yields the cross section ratio $\sigma_H/\sigma_D$ for the corresponding $E_i$ and scattering geometry, once the bulk average H and D mole fractions are known. These were determined using ERDA (elastic recoil detection analysis) and IR absorption to an accuracy of a few percent.[9,15] Conversely, once $\sigma_H/\sigma_D$ as a function of $E_i$ is known, the ratio $A_H/A_D$ measured on a spectrum taken under the same experimental conditions on a film containing D-labeled end groups will yield the average mole fractions $\chi_H$ and $\chi_D$ over the depth sampled in HREELS, which is a function of $E_i$. A possible end group surface enrichment may therefore be detected.

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**Table I. Characteristics of the Studied Polymers**

| | $M_n$ | $M_w/M_n$ | $x_D$ from IR of solutions | $x_D$ from ERDA of films |
|---|---|---|---|---|
| RPS | 50 000 | 1.55 | 0.58 ± 0.02 | 0.575 ± 0.01 |
| BPS1 | 10 400 | 1.10 | 0.047 ± 0.005 | |
| BPS2 | 236 000 | 1.04 | 0.20 ± 0.005 | 0.201 ± 0.006 |

In this work, thin films of random or block copolymers of normal and perdeuterated polystyrene were analyzed and the results compared with a calibration curve obtained from FTIRS analysis of dilute solutions of mixtures of normal and perdeuterated polystyrene, of random, and of block copolymers in carbon tetrachloride and with the results of ERDA of films of the same random or block copolymers.[15]

**Experimental Section.** HREEL spectra have been obtained with two different spectrometers in ultrahigh-vacuum chambers ($10^{-10}$ torr): a Kesmodel LK2000 (Lisbon) and a Leybold Heraeus ELS 22 (Thiais). Spectra obtained in both spectrometers are identical when identical conditions (incident energy and geometry) are used.

Electron primary energies, $E_i$, were varied from 0 to 10 eV; the zero of $E_i$ corresponds to the zero for the electronic current through the sample. This makes it possible to correct $E_i$ values from both spectrometers in which contact potentials are different. Incident and backscattered electron directions were at 60° relative to the perpendicular to the surface. The measured experimental resolution (elastic peak fwhm) was better than 13 meV ($\sim$100 $cm^{-1}$).

To avoid electrical charging of the film surface, films should be thin enough to allow excess charge to flow into the substrate. Such polymer films were cast on silicon wafers by dipping the substrates into solutions of the polymer in carbon tetrachloride (spectroscopic grade) and allowing the solvent to evaporate. Thicknesses thus obtained were found to be of the order of 100 Å, comparable to chain dimensions of the corresponding polymer in the bulk solid.[16]

The surface roughness of such films is probably larger than that of spun-cast films. This is, however, irrelevant in HREELS experiments such as ours, in which impact interactions are dominant,[6,7,11] so that all that matters is the distance between the surface and the center at which the electron is scattered and not the angle between the electron direction and the local orientation of the surface.

Table I shows the characterization of the analyzed polymers. RPS is a random $C_8H_8$–$C_8D_8$ copolymer with approximately equal amounts of deuterated and nondeuterated monomers. BPS1 and BPS2 are $C_8H_8$ polymer chains terminated with deuterated sequences at both ends. In BPS1, these sequences are short (about 2 monomers), while in BPS2, they are long (about 200 monomers). Isotopic compositions were determined by IR absorption spectroscopy of the corresponding solutions and directly in film form by ERDA as described elsewhere.[15] However, the D content of BPS1 is too small to allow an accurate ERDA measurement.

RPS and BPS1 were synthesized by living anionic polymerization, initiated by electron transfer using freshly prepared naphthyllithium. RPS was prepared from a mixture of $C_8H_8$ and $C_8D_8$.[9] In the case of BPS1, pure $C_8H_8$ was first quantitatively polymerized in THF at −78 °C, and the resulting chains were then capped at both ends, using $C_8D_8$, by a short ($\sim$2 units long) deuterated segment and finally deactivated using acidified methanol. Chains are, therefore, terminated using a single H atom at each end. Resulting $M_n$ and polydispersity are given in Table I. BPS2 was prepared by an anionic technique using *n*-BuLi (*n*-butyllithium) as a catalyst and methanol as the quenching reagent. Chains are, therefore, terminated by a single H atom at one end and a $C_4H_9$ group at the other end.

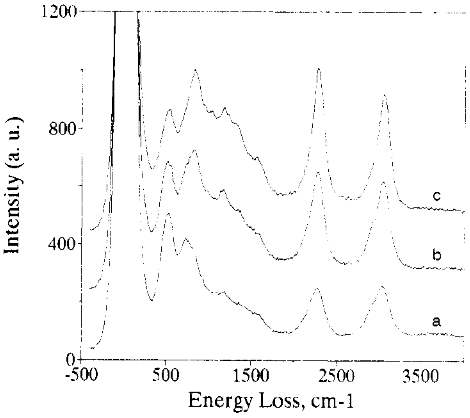

Figure 1. HREEL spectra of a random polystyrene (RPS) having molar fractions of 0.42 and 0.58 in, respectively, normal and perdeuterated monomers, taken in specular geometric conditions (incident angle of 60°) and three different incident energies: (a) $E_i$ = 3.7 eV; (b) $E_i$ = 5.7 eV; (c) $E_i$ = 7.7 eV.

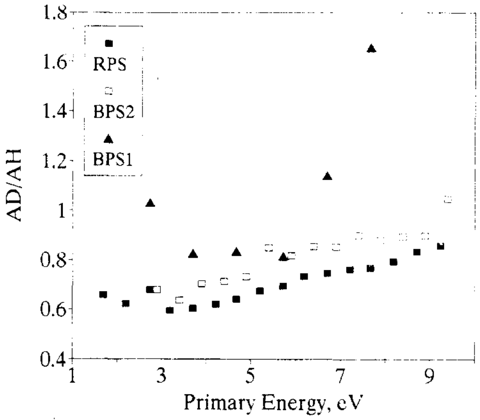

Figure 2. Ratio between areas of C–D and C–H stretching vibration peaks, divided by $x_D/x_H$, for the random polystyrene (RPS) and the two block polystyrenes (BPS1 and BPS2). Values for RPS were taken as cross section ratios.

**Results and Discussion.** HREEL spectra of the random copolymer RPS obtained at incident electron energies $E_i$ = 3.7, 5.7, and 7.7 eV are shown in Figure 1. The spectra are normalized to the elastic peak intensities (backscattered energy equal to $E_i$). Only losses concerning vibrational excitations below 4000 $cm^{-1}$ are presented. The variation with $E_i$ of the ratio $A_D/A_H$ of the CD and CH stretch peak areas using these and similar spectra is displayed in Figure 2 (solid squares). As explained above, this yields the variation with $E_i$ of the ratio $\sigma_D/\sigma_H$ of the corresponding cross sections in the chosen geometry. Uncertainties in the ratio $A_D/A_H$ are <5% for RPS, <10% for BPS2, and <15% for BSP1.

HREEL spectra of BPS1 and BPS2 were obtained in the same range of $E_i$ and the same geometry and used to determine the corresponding values of $A_D/A_H$, which are plotted in Figure 2. For easier comparison, the results as shown in Figure 2 have been scaled by the relative bulk composition, $\chi_D/\chi_H$, that is multiplied by 0.74 for RPS, 20.3 for BPS1, and 4 for BPS2. So, if there were no difference between surface and bulk isotopic compositions in these samples, all results would be superimposed onto those of RPS. Clearly, this is not so.

In the case of BPS1, the scaled values of $A_D/A_H$ are larger than expected by an amount varying between 10% and more than 100% depending on $E_i$. This rules out

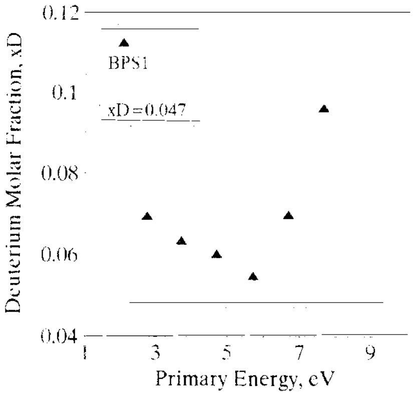

**Figure 3.** Composition of BPS1 as a function of the incident energy.

calibration errors as the cause for the differences between RPS and BPS1. Since $\sigma_D/\sigma_H$ is known from RPS, values of the mole fraction $\chi_D$ seen at different $E_i$ can be calculated and are shown in Figure 3.

These variations can be understood qualitatively by considering the variation of electron penetration depth with $E_i$: when $E_i$ increases, this depth, that is, the thickness of the layer contributing to the HREEL spectrum, increases until $E_i$ reaches the energy threshold for electronic excitation, because only vibrational excitations are possible, whose cross sections decrease.[7,11,12] Although accurate values are not yet available, a reasonable estimate of the sampled thickness is ca. 10 Å. Above the electronic threshold, the penetration depth rapidly decreases to a much smaller value of a few angstroms, since the corresponding cross section is much larger than for vibrational excitation.[12,13] This threshold in polystyrene is about 6 eV.[13]

Figure 3 can, therefore, be understood as follows: at $E_i$ = 7.7 eV, only a one to two monomer thick layer is sampled. In that layer, the deuterium concentration is more than twice the bulk value, consistent with a twofold enrichment in chain ends, predicted numerically.[5] But enrichment is confined to that layer, again as predicted: near 6 eV, the D concentration is near its bulk value, as should be the case if the sampled layer encompasses both an enriched surface layer and most of an underlying depleted one since what is measured is an *average* D concentration over the whole thickness. At very small $E_i$, the sampled depth is smaller again, and the average D concentration larger, as would be the case if only part of the depleted layer is sampled. This would imply a total thickness of the enriched plus depleted layer not much larger than 10 Å. These preliminary data cannot be discussed further. Note the importance in this experiment of having a very short—2 monomers long—deuterated end segment.

By contrast, BPS2 shows an enrichment in D of 15 ± 2%, independent of $E_i$, on the surface region sampled in the experiment—a depth up to ~10 Å. There are two reasons for observing an enrichment in D atoms extending at least to that depth: the deuterated blocks are long and the corresponding radius of gyration in the bulk solid would be ~40 Å, so a chain end at the surface corresponds to D enrichment in a comparable layer underneath; in addition, it has been observed using HREELS[14] and neutron reflectometry[17] that the surface region of similar films consisting of PsH–PsD blends (normal and perdeuterated polystyrene blends) is slightly enriched in D. However, one would then expect a larger enrichment than is observed, based on the results on BPS1. But this disregards the influence of the *n*-Bu ends: if they are strongly segregated at the surface, due to their smaller surface tension, a corresponding enrichment in H should occur. The observed result may be due to a balance of all these effects. More work is necessary, but this at least illustrates that the conditions for studying enrichment of a film surface, not corresponding to chemical differences, are relatively critical.

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