Structure at polymer interfaces determined by high-resolution nuclear reaction analysis

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We describe a method based on nuclear reaction analysis, using the reaction ^{2}H(^{3}He, ^{4}He)^{1}H, ($Q = 18.352$ MeV) to determine composition profiles of deuterated polymer chains in thin films. By detecting the emitted α particles (^{4}He) at forward angles (30°) we are able to achieve a spatial resolution of 7 nm half width at half maximum (HWHM) at the deuterated sample surface, and 15 nm HWHM at a depth of some 130 nm. We use our method to probe initial diffusional broadening at the interface between deuterated and protonated polystyrene films. Our measured profiles are in close agreement with earlier measurements (over larger spatial scales) and with mean field models for the diffusional process in this system.

The interfacial structure between bulk polymer phases or at the surface of a polymer mixture, and its development with time, has been extensively studied in recent years.[1–8] The composition profiles at such interfaces determine properties ranging from wettability[6] to transport through thin films,[3] while the time-dependent properties reflect the dynamics of entangled chains[9] and relate to effects such as spinodal decomposition kinetics.[10] The scales involved are small—often smaller than the dimension of a single polymer coil. For a miscible polymer pair the interfacial width w_c increases with time t as $w_c \sim (Dt)^{1/2}$, where D is the mutual diffusion coefficient; for highly entangled chains, D may be very small[2,3,5] [$O(10^{-15}$–10^{-20} cm^{2} s$^{-1})$], so that over accessible diffusion times (a few days, for example) w_c may range up to only some tens or a hundred nanometers.

Probing surface and interfacial profiles at these scales present a considerable challenge. Indirect methods include measurements of surface energies[11] and optical[12] and neutron scattering[13] techniques, and very recently neutron reflectometry.[14] Direct profiling methods include infrared microdensitometry[1] (spatial resolution $\sim 50\,\mu$m), microanalytical electron microscopy[4] ($\sim 3\,\mu$m), and the recent elegant studies by Kramer, Mayer, and co-workers utilizing elastic ion beam scattering[2,3] at the polymer interface (100–35 nm). Very recently[7,8] nuclear reaction analysis (NRA) was used to determine the concentration profiles of deuterated chains at polymer interfaces. Here we report on its application to probe such profiles with high spatial resolution.

While NRA has been applied previously to profile deuterium in metals, semiconductors, and other inorganic materials,[15] our extension of the technique to polymers provides a spatial resolution significantly higher than has been hitherto achieved. We describe here the basic features of NRA in this mode, and its use to determine interfacial broadening at a deuterated polystyrene/protonated polystyrene (dPS/pPS) interface.

The experimental setup is schematically illustrated in Fig. 1. A magnetically collimated beam of ^{3}He particles accelerated to energy $E_0(^{3}\mathrm{He})$ (700 keV in the present experiments) in a Van de Graaff accelerator is incident on a deuterium-labeled polymer layer as shown. As the ^{3}He particles penetrate into the bilayer, the nuclear reaction

$$^{3}\mathrm{He} + {}^{2}\mathrm{H} \rightarrow {}^{4}\mathrm{He} + {}^{1}\mathrm{H}, \quad Q = 18.352\ \mathrm{MeV} \tag{1}$$

takes places at different depths x. Outgoing α particles (^{4}He) are detected at a forward angle $\zeta = 30°$ (Fig. 1) by a passivated, implanted planar silicon detector (Canberra, model SPD-100-12-100, resolution 12 keV FWHM), and their energy spectrum is recorded on a multichannel analyzer (a PC-based Ortec ADCAM), using standard electronics.

This energy spectrum contains information on the distribution $\phi(x)$ of the deuterium atoms (^{2}H) in the sample. This is primarily because the incident ^{3}He particles lose energy by inelastic electronic processes as they penetrate the sample, so that the nuclear reaction (1) at increasing depths x takes place at progressively lower ^{3}He energies $E(^{3}\mathrm{He},x)$. This results in energies of the forward-emitted α particles which decrease rapidly as x increases. Further energy losses occur as the emitted α particles travel through the sample from the depth x to the surface of the film on their way to the detector. The energies $E(\alpha)$ of α particles reaching the detector thus provide a measure of the depth at which they were emitted by the nuclear reaction, and their energy spectrum (suitably corrected for the reaction cross section) is readily analyzed to yield the corresponding concentration

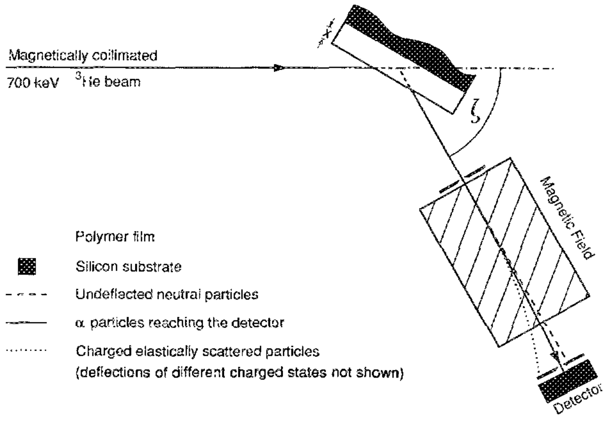

FIG. 1. Schematic illustration of experimental configuration used in the present study.

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versus depth profile of the deuterium atoms.[16]

Figure 2 shows a typical energy spectrum and the corresponding depth profile of a thin *d* PS film spin cast onto a polished silicon substrate, and demonstrates the spatial resolution achievable by this method. The thickness of the film was independently determined by ellipsometry as 13.2 ± 1 nm (dashed top-hat profile, Fig. 2), while our NRA technique yields the volume fraction profile $\phi(x)$ of the *d* PS given by the data points. The solid line is a convolution of the top hat-profile with a Gaussian whose width increases linearly with depth; it has a value of 7 nm half width at half maximum (HWHM) at the air surface (depth = 0) and 8 nm HWHM at the silicon surface.

If we assume that the surface of the spin-cast polymer film is ideally smooth, the 7 nm HWHM corresponds to the spatial resolution of the method at the surface of the polymer layer. This compares with a spatial resolution at the surface of some 40 nm HWHM attainable by forward recoil scattering (FReS) using a predetector foil to block the elastically scattered α particles[3]; the very recent modification of the FReS method using a time-of-flight approach[6] and also the backscattering methods[2] (which rely on heavy atom labeling) provide spatial resolutions of around 17–20 nm HWHM at the sample surface. Similar values (i.e., 15–20 nm HWHM) are quoted by Payne and co-workers[8] who use the same nuclear reaction (1) for deuterium profiling, but by detecting the emitted protons rather than α particles.

The innovation in our measurements relative to earlier studies[15] which provide this improved spatial resolution lies in the detection of α particles emitted in the *forward direction* (Fig. 1). In these circumstances, for an angle $\zeta = 30°$, a so-called "energy amplification" effect[17] of ~100% is obtained[17]; i.e., an energy loss $\delta E(^3\text{He})$ of the incident ^{3}He atoms due to their penetration into the sample is amplified approximately twofold for the forward emitted α particles.[17] Together with the lower values of incident energies $E_0(^3\text{He})$ (which imply a large $[dE(^3\text{He})/dx]$, this results in values of $[dE(\alpha)/dx] \cong 2$ keV/nm (this value increases[17] at greater depths x). The enhanced value of this (energy loss)/(depth) ratio in the present approach is the main reason for the improved spatial resolution (by a factor of 2.5–3), relative to elastic scattering methods. Earlier deuterium profiling studies using this reaction[15] were not carried out at forward angles (i.e., ζ was always $\geqslant 70°$) and so did not benefit from the "energy amplification" effect. This is probably because of the much greater cross section for *elastic* scattering processes, which meant that the nuclear reaction signal was "swamped out" by elastically scattered particles, especially in the higher atomic number materials used. For polymeric materials the mean atomic number is lower, but we also use a magnetic filter (Fig. 1) to remove the large flux of elastically scattered particles. The lower energy of these ($\leqslant 700$ keV) relative to the α particles (~4–6 MeV) results in deflections in the magnetic field (Fig. 1) that are sufficiently different from that of the α particles (Fig. 1, solid line) to cause them to miss the detector entry slit. The electronic "dead time" in our measurements is negligible (always < 1%). Satisfactory counting statistics (~100 counts/1.6 keV channel, for a 2 nA ^{3}He beam impinging on *d* PS) are obtained in about 40 min.

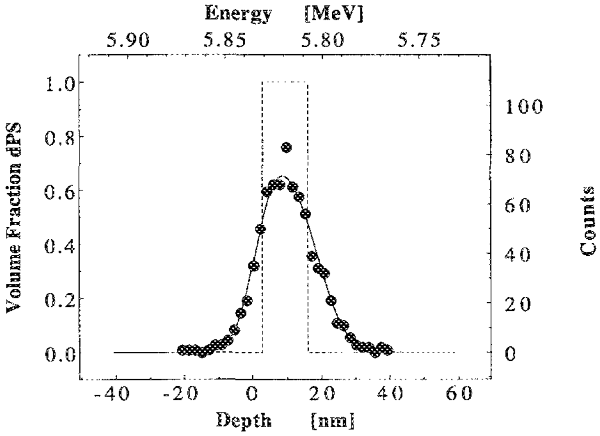

FIG. 2. Energy spectrum (top and right-hand axes) and corresponding measured volume—fraction vs depth profile (bottom and left-hand axes) of a thin *d* PS film on a polished silicon substrate. The dashed line is a top-hat representation of the ellipsometrically determined 13.2-nm-thick film. (For this thin film the energy spectrum and the depth profile correspond linearly to within 2%.) The solid line is a best-fit Gaussian to the depth profile (7–8 nm HWHM).

We have used this method to probe the broadening of the interface between *d* PS and *p*PS films. A film of *p*PS, thickness ~110 nm (weight average molecular weight $M_w = 9 \times 10^5$, polydispersity index = 1.08 obtained from Pressure Chemicals) was spin cast from toluene on a polished silicon wafer, and a similar film of *d* PS ($M_w = 1.03 \times 10^6$, polydispersity index = 1.07 from Toyo Soda) was cast, floated onto water, and laid on top to form a bilayer.

The composition profile of the unannealed bilayer was determined using NRA as described above, and is shown in Fig. 3(a). Similar bilayers were then placed in a vacuum oven at 160 ± 1 °C and allowed to interdiffuse for differing lengths of time. A typical diffusion-broadened profile is shown (following a time 7.2×10^3 s) in Fig. 3(b), where the dashed line corresponds to the *d* PS/*p*PS interface in the unannealed bilayer [from Fig. 3(a)].

The distribution $\phi(x,t)$ at time t of a concentration step function which undergoes diffusion broadening is given by the solution to

$$\frac{\partial \phi(x,t)}{\partial t} = \frac{\partial}{\partial x}\left[D(\phi)\,\frac{\partial \phi}{\partial x}\right], \tag{2}$$

with the boundary conditions appropriate to a step function at $t = 0$. $D(\phi)$ is composition dependent, as shown explicitly by Green and Doyle,[5] due both to the asymmetry in polymer lengths[2,5,18] and to non-negligible "thermodynamic slowing down" effects[5] at 160 °C. The value of $D(\phi)$ as a function of ϕ may be evaluated in terms of the known polymer sizes and mobilities,[19] and the experimentally determined segment interaction parameter[20] (all taken at 160 °C). We have solved Eq. (2)[18] using this explicit value of $D(\phi)$. The resulting profile $\phi(x,t)$ for $t = 7.2 \times 10^3$ s was then convoluted with a Gaussian of 15 nm HWHM [to correspond to the instrumental broadening at a depth of ~120 nm, as in Fig. 3(a)] and is plotted as the solid line in Fig. 3(b). The fit to our data—with no adjustable parameters—is very good. In particular, we clearly distinguish a broadening of the profile half

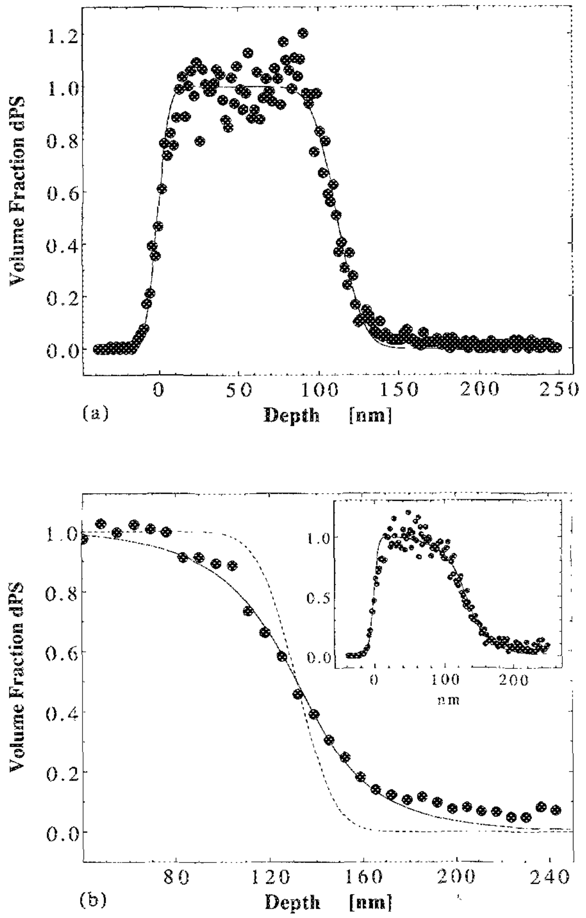

FIG. 3. (a) Volume fraction—depth profile of a ~110-nm-thick *d* PS film laid on top of a similar *p*PS film on top of a polished silicon substrate. The solid lines at the surface and at a depth of ~110 nm are convolutions of step functions with Gaussians of 7 and 15 nm HWHM, respectively. (b) As in part (a), but following 7.2×10^3 s diffusion broadening at 160 °C. The inset shows the full depth profile, while the main profile shows the broadened interfacial region, with a 5:1 data integration. The broken line corresponds to the unannealed profile in part (a), while the solid curve is the profile theoretically calculated from Eq. (2), similarly convoluted to take account of instrumental broadening.

width of some 20 nm at the interface, at ~120 nm depth. Other experiments (not presented) show that even a 10 nm broadening can be unambiguously resolved at this depth above the scatter in the data.

To summarize: we have extended the NRA approach based on the ^{2}H(^{3}He,^{4}He)^{1}H reaction to direct depth profiling of deuterium in bulk polymers. By working at forward detection angles and magnetically filtering the elastically scattered particles, we are able to achieve spatial resolutions which, at ~10 nm, are appreciably higher than those previously reported using the same approach in inorganic materials. We have utilized this to measure the initial interfacial broadening in a *d* PS/*p*PS couple, and our results are very well fitted by a mean field model which takes into account thermodynamic slowing down. Our technique complements elastic ion beam scattering methods, and provides a bridge to the recent studies of polymer interfaces using the more indirect technique of neutron reflectometry.

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