Concentration Profile of a Dissolved Polymer near the Air-Liquid Interface: X-Ray Fluorescence Study

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The x-ray fluorescence, at the near-total external reflection configuration, was employed to study the concentration profile of a dissolved polymer near the liquid-gas interface. The determined experimental concentration profile conformed with a hyperbolic cotangent squared dependence with a concentration excess ratio of about 100:1 of the surface relative to the bulk. This experiment presents the first direct measurement of that kind at the air-liquid interface and demonstrates the effectiveness of this new method to study nondestructively interface structures on the scale of tens to hundreds of angstroms.

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In this Letter we describe an experiment which probes the structure of the interface between a polymer solution and its vapor on the length scale of tens to hundreds of angstroms in the direction perpendicular to the interface. This method, near-total external fluorescence (NTEF), is a nondestructive technique which can be applied at ambient pressures, and as such is particularly suited for study of the extremely flat gas-liquid interfaces. We have applied this technique, for the first time, to study the concentration profile in dilute polymer solution in the vicinity of the air-liquid interface. The interfacial properties of dilute, electrically neutral, polymeric interfaces have received considerable attention both theoretically[1-4] and experimentally.[5-8] The accurate description of a polymer interface is important for such applications as phase separation of polymer solutions, polymeric coatings, steric stabilization of coilloids, lubrication, etc.

The NTEF method is based on the fact that the real part of the index of refraction $\hat{n}$ for matter, where $\hat{n} = 1 - \delta_1 + i\delta_2$, is smaller than unity in the x-ray wavelength regime.[9] Hence an x-ray beam grazing an interface at a subcritical angle is drastically attenuated inside the material. This exponentially decaying x-ray beam then penetrates distances typically of several tens of angstroms. The intensity at a distance z from the interface can be derived directly by application of the requirement for the continuity of the tangential electric and magnetic fields across the interface.[10] To a good approximation for small glancing angles α, the wave intensity is given by

$$I(z,\alpha) = I_0 T(\alpha) \exp[-\beta(\alpha) z], \tag{1}$$

where I_0 is the incident intensity and $\beta(\alpha) = 2k\,\mathrm{Im}(U)$ is the absorption coefficient for the evanescent beam. k is the incident wave vector, glancing at an angle α at the interface, $T(\alpha) = 4\alpha^2/\{[\alpha + \mathrm{Re}(U)]^2 + \mathrm{Im}(U)^2\}$ is the transmission coefficient of the electromagnetic beam through the interface, and $U = (\alpha^2 - 2\delta_1 + 2i\delta_2)^{1/2}$ (see Fig. 1). The x-ray fluorescence of an ion embedded in the material at a distance z from the surface will be proportional to $I(z,\alpha)$. If $\phi_f(z)$ is the concentration profile of the fluorescent probes, in a direction normal to the interface, then the total fluorescence is proportional to

$$I_f(\alpha) = \int \phi_f(z) I(z,\alpha)\, dz. \tag{2}$$

The fluorescence signal $I_f(\alpha)$ is dependent on the glancing angle α through $T(\alpha)$ and $\beta(\alpha)$. In principle, if $I_f(\alpha)$ is measured with sufficient resolution in

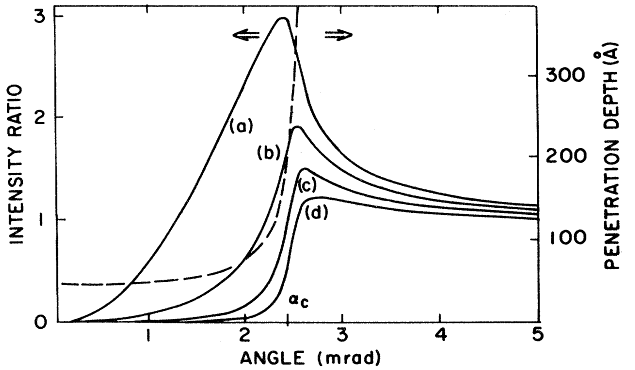

FIG. 1. The intensity ratio $I(\alpha,z)/I_0$ of the electric field inside the material as a function of the angle of incidence α of the beam at depth z from the interface following (1). Here $\delta_1 = 3\times10^{-6}$, $\delta_2 = 2\times10^{-7}$, and (curve *a*) $z = 0$, (curve *b*) $z = 100$ Å, (curve *c*) $z = 200$ Å, and (curve *d*) $z = 300$ Å. The corresponding penetration depth $1/\beta$ is shown with a dotted line.

the angle α then the concentration profile $\phi_f(z)$ can be reconvoluted from $I_f(\alpha)$. Alternatively if a model for such a concentration profile exists it can be substituted in (2) and a fit may check the validity of the predicted model, subsequently yielding the experimental parameters.

Recent mean-field[3] and scaling theories[2,4,11] provide specific predictions for the concentration profile of the adsorption and/or depletion layer. For dilute neutral-polymer solutions, the mean-field theory gives the concentration profile[6]

$$\phi/\phi_b = \coth^2[(z/R)+\sigma], \tag{3}$$

where ϕ_b is the bulk polymer volume fraction, R is the dilute-solution polymer radius of gyration, and σ is a dimensionless constant such that ϕ_b/σ^2 (for $\sigma << 1$) is the surface volume fraction. Scaling results for the profile dependence in the power-law region, $1 >> z/R >> \sigma$, give z/R^τ with $\tau = \frac{4}{3}$ in good solvents. For polyelectrolytes, i.e., charged polymers, in polar solvents the theory is much less developed. Scaling arguments[12,13] based on Debye screening suggest that $\tau = 2$, which coincidentally agrees with the mean-field result of Eq. (3) developed for a neutral polymer. The concentration profile at the air-liquid interface is not easily accessible by experiments. For instance, ellipsometry[14] measures an average layer thickness but assumes a uniform concentration in the absorbed layer. It is only recently that Allain, Aussere, and Rondelez[7] have demonstrated that optical evanescent waves can be used to give more detailed information. We will later discuss the difference between our method and the optical evanescent-wave approach. Becker, Golovchenko, and Patel[15] (in a different context) demonstrated that the total fluorescence yield off a bulk flat Ge crystal is consistent, in general, with that expected from the evanescent-wave equations. However, the depth dependence of the intensity inside the material was not studied earlier in the x-ray regime. We confirmed the dependence given by Eq. (1) in a preliminary study on fluorescent monolayers embedded at different depths from the interface.[16]

We report here the first direct measurement of the polymer concentration profile at the air-liquid interface and the experimental setup used to perform it. The profile length scale at a polymer-solution–air interface is expected to be of the order of tens to hundreds of angstroms. Under our experimental conditions the minimum penetration depth for $\alpha = 0$ is $(1/\beta)_{\min} = 1/[(8\delta_1)^{1/2}k] \approx 40$ Å while for $\alpha = \alpha_c$ the penetration depth in our case is about 400 Å (Fig. 1). With these values we should be able to get a reasonably sensitive reading of the polymer profile provided that the angular resolution of the instrument is a small fraction of the critical angle, α_c.

We designed the experiment to have an angular resolution better than $\frac{1}{20}\alpha_c$ around $\alpha_c \sim 2$ mrad. The specifications of the beam at the Stanford Synchrotron Radiation Laboratory on Station IV1 are compatible with this requirement within any one electron fill. It introduces an error of about 40 μrad in the angular definition of the incident beam. Our instrument (see inset of Fig. 2) consisted of an x-ray mirror (D) which tilts the horizontal synchrotron beam towards the surface of the liquid, and of a liquid trough. The beam was confined by means of slits (B and E) and its intensity monitored with detectors (C and F) before and after the reflection from the mirror, respectively. The platinum-coated mirror was defined for its slope flatness to be better than 50 μrad over its whole length and was designed to rotate in resolution of 50 μrad. The beam illuminated a spot (I) of 50×20 mm^2 of the liquid surface sample (H) at any desirable angle α. The sample was slightly sulfonated polystyrene dissolved in dimethylsulfoxide. The molecular weight of the polymer was 115 000 with approximately 10 mole% of the chain labeled with manganese sulfonate. The trough (J) height was adjusted for each tilting angle in

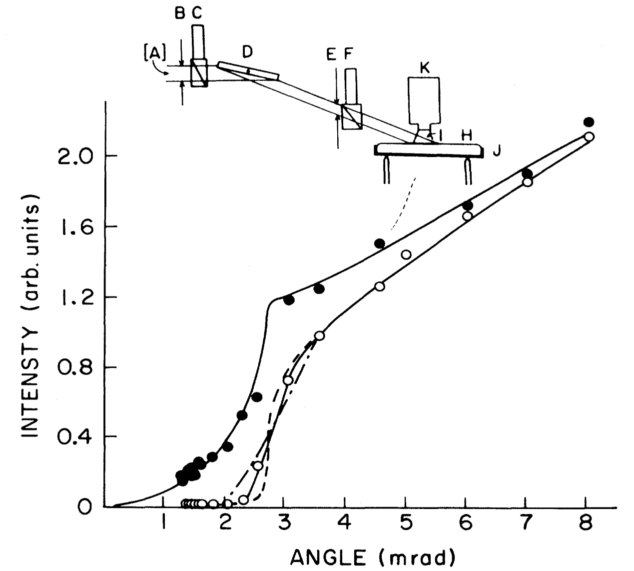

FIG. 2. Open circles, the $K\alpha$ fluorescence intensity from sulfur in a manganese-neutralized sulfonated-polystyrene (10 mole%)–dimethylsulfoxide solution sample, against the angle of incidence of the incoming beam. The fit was done using (2) and uniform profile, with no free parameters and convoluted with an error in the angular definition of (dashed line) 0.0 mrad; (solid line) 0.5 mrad; (dot-dashed line) 1 mrad. Solid circles, the $K\alpha$ fluoresence intensity from the manganese ion in sulfonated polystyrene (molecular weight 115 000) as a function of the angle of incident of the exciting x-ray beam. The fit was done by employment of the profile of Eq. (3) substituted in (2) (see details in the text). A schematic diagram of the liquid diffractometer is given in the inset. For details see text.

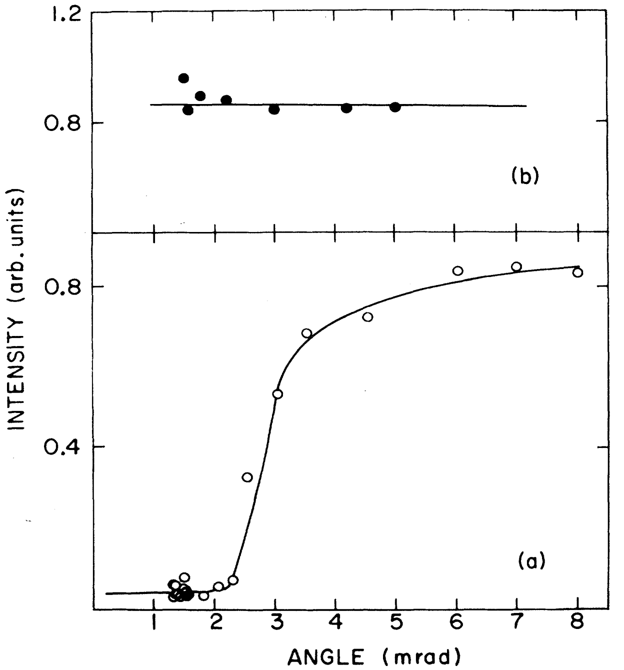

FIG. 3. (a) The intensity ratio of the fluorescence from the sulfur atom in the solvent to the manganese ion attached to the polymer. The sharp decrease of this ratio at about the critical angle indicates that the polymer is strongly attracted to the interface. (b) The same intensity ratio when a dilute manganese dichloride is evenly distributed in the same solvent (DMSO). Here the ratio is about constant as expected.

order for the deflected beam to hit the center of the trough. These adjustments and four alignment movements for the mirror and trough were stepper motor controlled. A full account of the design and construction of this instrument will be given elsewhere. The fluorescence radiation emitted from the excited ions in the liquid was collected with a Si-Li energy dispersive detector (K) which was placed directly above the trough. The illuminated spot was larger than the acceptance angle of the detector profile. Fluorescence from two types of atoms was monitored, the sulfur $K\alpha$ line from the solvent dimethylsulfoxide (DMSO) and the $K\alpha$ line of the Mn ion attached to the sulfonated polystyrene chain. In Fig. 2 the intensity of the fluorescence from sulfur is plotted against the angle of incidence of the incoming beam as open circles. The fit for this experiment was done with a uniform profile substituted in (2) broadened by a spread $\Delta\alpha$ in the angle α. The value of $\Delta\alpha$ was estimated from this fit to be 0.5 ± 0.1 mrad which is primarily due to ripple on the surface of the liquid. In the same figure the intensity of the fluorescence from the magnanese ion (collected simultaneously with the sulfur signal) is depicted as closed circles. Compared to the sulfur signal (Fig. 2, open circles), the intensity below α_c is higher, which indicates an enhanced manganese concentration in the interface region. A detailed analysis of this data utilizing the mean-field expression (3) and including angular divergence due mainly to liquid ripple (established from the normalization fits), as well as the normal absorption of the fluorescent beam exiting from the solution, yields a good fit to the data with $\sigma = 0.1 \pm 0.02$ and $R = 300 \pm 100$ Å.

This result clearly implies a strong attraction of the polymer to the interface with a concentration enhancement factor of about $1/\sigma^2 \sim 100$ over the bulk solution concentration value. This can also be demonstrated by observation of the ratio of the intensities from the sulfur and the manganese (Fig. 3). If the polymer chains were to be uniformly spread around the interface then this ratio would have been constant for different angles α. Obviously this is not the case and the sharp drop in this ratio around the critical angle α_c is a clear indication of the dramatically enhanced concentration of the polymer at the interface. In Fig. 3, the fit was performed with the same parameters as in Figs. 1 and 2. For the purpose of comparison, in Fig. 3(b) the ratio between manganese and sulfur fluorescence intensities is given for manganese dichloride dissolved in DMSO. Here the intensity ratio remains approximately constant, as is expected for two homogeneously dispersed ions. Attempts to fit the polymer profile with functional dependence other than in (2) (i.e., $\tau = 2$) confirmed that a slower decay $\tau \sim 1 \pm 0.2$ is inconsistent with the data, but a more rapid falloff, i.e., $\tau \sim 3$, cannot be excluded. If we were to adopt the calculations for a neutral polymer with the surface tension values measured for our sample[17] we would obtain a surface enhancement factor $1/\sigma^2 \approx 100 \pm 20$, in good agreement with our result, but the profile length, $R = 300$ Å, derived from our experiment is about 5 times larger than that expected from a neutral-polymer model.[6] This result implies a radius of gyration considerably larger than the one expected from a neutral polymer. Divergence of the specific viscosity and light scattering results for our sample at low concentrations[17] indeed indicate swelling of the polymer and a larger radius of gyration at low concentration. This polyelectrolyte character is consistent with the 10% sulfonation level. As mentioned earlier our profile is consistent with that expected from scaling arguments for a polyelectrolyte ($\tau \sim 2$–3). Further experiments are necessary to clarify the detailed ionomer conformational structure in a moderately polar solvent like DMSO ($\epsilon \approx 40$).

It is instructive to outline some basic differences between the optical method employed by Allain, Aussere, and Rondelez[7] and the method detailed in this work, because of their apparent similarity. The optical method employs the total *internal* reflection effect since in the optical regime the index of refraction

n is larger than unity. This restricts their experiments from being done on the air-liquid interface. Also, the optical method employs by its very nature a much larger wavelength (3500 Å in their case). This defines the lowest value for the penetration depth in their experiment to be an order of magnitude larger than in the x-ray regime (460 Å compared to 40 Å in this work). As a consequence they report a change in signal associated with the polymer profile to be of about 10% while we detect a 5000% effect. But a more subtle difference emerges from the difference in the normal absorption mechanism of the two methods. For optical light wavelengths the liquid is practically transparent for thousands of angstroms (i.e., $\delta_2 \sim 0$) so that the penetration depth above the critical angle is infinite as compared to typical profile lengths of a polymer molecule (hundreds of angstroms at most). This sets a particularly stringent requirement on the angular resolution of α at $\alpha \leqslant \alpha_c$ if one were to try to get information on the actual profile. In the x-ray case the absorption is not negligible, and therefore we encounter a crossover between two processes that limit the perturbation depth. At low angles $\alpha < \alpha_c$ it is given by the drastic attenuation as a result of the evanescent-wave cancellation effect. For $\alpha \geqslant \alpha_c$ the regular absorption takes over and the penetration depth is not suddenly infinite but proportional to α. This relaxes the requirement for the resolution in α around α_c to measurable values. It is noteworthy that Eq. (1) inherently contains the contribution of both processes (through δ_1 and δ_2) and is adequate to describe the perturbation depth for any small angle α around α_c.

In this first investigation, we have demonstrated that the near-total external fluorescence technique is able to provide detailed structural information at a polymer-solution–air interface. More work is underway to study the effects of parameters such as molecular weight, bulk solution concentration, level of substitution, etc. Together with other dynamic and hydrodynamic experiments, NTEF can provide sufficient experimental input to help clarify the nature of the physical mechanisms related to the formation of polymeric interfaces. Finally, it also demonstrates, in general, the effectiveness of the method for the study of liquid and solid interface structures on the scale of dozens to hundreds of angstroms in a nondestructive manner—a regime which is rather difficult to probe with other techniques.

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