A NEUTRON REFLECTION TEST OF THE 'REPTATION TIME'

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DEC 7 1988

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CONF-880715--11

DE89 003637

July 1988

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Manuscript submitted to the International Conference on Neutron Scattering,
July 12-15, 1988, Grenoble, France.

*Work supported by the U. S. Department of Energy, BES-Materials Sciences,
under contract W-31-109-ENG-38.

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ABSTRACT

Two chemically similar polymers in contact at a temperature above the glass transition interdiffuse with a concentration profile which, for times shorter than a "reptation time," is thought to remain discontinuous at the interface. It is shown how the size of the concentration gap can be systematically tested by neutron reflection from bilayers of deuterated/protonated polymers.

KEYWORDS

Neutron reflection, interdiffusion, reptation

In 1971 De Gennes proposed¹ a bold new concept to explain the motion of high polymers in a melt. In the most simple picture, each polymer chain is assumed linear (not branched) and has a total length L of N monomers. The melt is formed by molecules, which are deeply intertwined with each other. In the De Gennes description each molecule is wrapped in an ideal sheath which runs along its entire length: the molecule can move only within the sheath, with a worm-like wriggling along its length. The time it takes for a molecule to move by its contour length L is termed "reptation time"; in this time the polymer will completely wriggle out of its old sheath and generate a new one.

An immediate consequence of the introduction of the reptation time is the unusual form of the diffusion at the interface of two chemically similar polymer layers, heated above the glass transition. In the conventional diffusion process, a sharp initial interface becomes fuzzier at $t > 0$, since the gradient of concentration becomes finite. This is because, in the basic formulation of the diffusion equation,² the flow of material is taken as proportional to the gradient of concentration. Not so for the reptating polymers. At $t = 0$ only a few polymers have their head (or tail) in the plane of the interface, and only those are allowed to diffuse across the interface. Practically the interface is divided in two areas, one covering the regions for which interdiffusion is forbidden (and for this the initial gap in concentration remains) and the second where the polymer diffuse. As a result, a net gap in the concentration is present at the interface even at finite times. Gradually the heads of other

molecules find their way to the interface and the gap reduces until the concentration profile becomes continuous - at the reptation time.

We propose to monitor the density depth profile of a polymer bilayer during diffusion by neutron reflectivity, a technique capable of a depth resolution of ten Angstroms, and also capable of examining the interdiffusion of materials, distinguished only by different isotope composition, and thus with negligible chemical difference.

In neutron reflection a neutron beam of wavelength λ is sent upon the sample surface at glancing angle θ , and is partially reflected. The reflection process is fully described³ in terms of the component of the neutron momentum perpendicular to the surface k_z . This quantity, which in vacuum is defined as $k_{z0} = 2\pi \sin \theta / \lambda$, is modified in a medium characterized by a neutron scattering amplitude b per unit volume V as follows:

$$k_z = \sqrt{(k_{z0}^2 - 4\pi b/V)} \quad (1)$$

The variation of the b/V at an interface separating two media 1 and 2 gives rise to the reflectivity:

$$R = \left| \frac{k_{z1} - k_{z2}}{k_{z1} + k_{z2}} \right|^2 \quad (2)$$

The boundary between a deuterated material and the same material but with light hydrogen (protonated) causes a fair amount of reflection, and thus can be observed quite readily. For instance if

$b_1/V_1 = 1.4 \times 10^{-6} \text{ \AA}^{-2}$; and if medium 2 is made of deuterated polystyrene (d-PS), $b_2/V_2 = 6.5 \times 10^{-6} \text{ \AA}^{-2}$. In the limit of large k_{z0} the reflectivity, eq.(2), becomes:

$$R_{k_{z0} \rightarrow \infty} \approx \{ \pi [(b_2/V_2) - (b_1/V_1)] / k_{z0}^2 \}^2 \quad (3)$$

and thus is inversely proportional to the fourth power of the neutron momentum. In practice this limit is already fairly well achieved when k_{z0} has three times the value for total reflection.

The reflectivity given in eq.(2) is for a sharp interface and thus is hardly amenable to studying an interdiffusion process. However the reflectivity can be given in closed form even for a smoother variation of b/V at the interface. For instance, if b/V was to vary from b_1/V_1 to b_2/V_2 with a dependence⁴

$$b(z)/V(z) = (b_1/V_1) + [(b_2/V_2) - (b_1/V_1)] / (1 + \exp(-\alpha z)) \quad (4)$$

the reflectivity would become:

$$R = \left| \frac{\sinh[\pi(k_{z1} - k_{z2})/\alpha]}{\sinh[\pi(k_{z1} + k_{z2})/\alpha]} \right|^2 \quad (5)$$

$1/\alpha$ may be thought as a conventional diffusion length: for $1/\alpha = 0$ there is no diffusion and eq.(5) becomes eq. (2). Note that the profile given in eq.(4) is not the solution of a diffusion equation, but is one of the few analytical expressions for which the reflectivity is obtained in closed form (however a real potential might be approximated by a linear combination of a few terms of this kind). The profile is symmetric compared to the interface ($z=0$), which implies that the diffusion constants for the two polymers are equal as when they have equal molecular weights.

Perhaps the most visible difference between eq.(5) and eq.(2) is in the asymptotic values for R at large k_{z0} , which for eq.(5) is:

$$R_{k_{z0} \rightarrow \infty} = \left| \frac{2\pi^2 [(b_2/v_2) - (b_1/v_1)]}{\sinh(2\pi k_{z0}/\alpha)} \right|^2 \quad (6)$$

In this expression the reflectivity goes to zero much more rapidly than with a fourth-power-law; for instance at $k_{z0}=\alpha/2$, eq. (6) gives a reflectivity one order of magnitude smaller than that given by eq.(2). Numerically, at an interface PS/d-PS this situation occurs at $k_{z0}=0.024 \text{ \AA}^{-1}$ when the diffusion length, $1/\alpha$, is of the order of only 20 Angstroms. Even truncating the observations at this value of k_{z0} , where the reflectivity is still fairly high (almost 10^{-3}), the two cases can be distinguished without ambiguity. In conclusion neutron reflection makes possible a systematic study of the interdiffusion of layers of PS/d-PS: if at the interface the composition has a gap, Rk_{z0}^4 extrapolates to a non-zero constant which is proportional to this gap.

A neutron reflection test made on a bilayer of d-PS/PS has already confirmed the permanence of a gap during short-time interdiffusion, but for a specially prepared sample. To start with, the sample did not have a simple interface between two very thick layers, being made of a sequence air/d-PS/PS/fused silica. With fairly thin layers, reflections from three boundaries interfere with each other to yield a cumbersome expression for the reflectivity⁵. Fortunately the strongest reflections occur just at the front and the back of the d-PS layer, so that we can visualize the behaviour of this layer of thickness z_0 using the expression:

$$R = \frac{r_1^2 + r_2^2 + 2r_1 r_2 \cos 2k_{z1} z_0}{1 + r_1^2 + r_2^2 + 2r_1 r_2 \cos 2k_{z1} z_0} \quad (7)$$

$|r_1|^2$ and $|r_2|^2$ are the reflectivities of the front and back interfaces. Eq. (7) shows an interference function which allows to obtain z_0 from the period of k_z , to which it is inversely proportional.

The second peculiarity of the sample tested was the following: the molecular weight of the top d-PS layer was $M_w = 2 \times 10^5$, much smaller than that of PS, or $M_w = 10^7$. In view of this difference, the lighter material (d-PS) is expected to diffuse much more readily in the heavier one than viceversa. In this picture PS soaks d-PS and swells⁶: with a resulting density profile which is far from symmetric. This is exactly what does experimentally happen after a short annealing. As shown in Fig.1, after annealing the interference minimum has drastically shifted its position toward larger k_{z0} values indicating, in the light of eq.(7), a shrinking of the d-PS layer; the composition profiles for the reflectivity curves numerically fitted in Fig.1 are quantitatively shown in Fig.2.

One remarkable feature is that an interference pattern persists after annealing. This is even when the interference period has varied so much that the minimum is at the k_{z0} value where the maximum was before the annealing process. In any kind of continuous diffusion models, if the diffusion moves the position of the apparent interface, the interface should be smeared over the same distance⁶. As a result the reflectivity should be obtained by averaging contributions for a range of z_0 which, if large enough,

totally destroys the interference pattern. We can see that this should be our case just using the crude procedure of averaging the two reflectivities of Fig.1. What we do observe is that after annealing the interface remains much sharper than possible in a continuous diffusion model. There is a true gap in composition at the interface. The profile of fig.2 is fitted for an interface with finite thickness even at $t=0$; but quite likely this is an optical effect, due to the lack of planarity of the interface. The solution of this question will be part of the more systematic program, that now we have undertaken to unravel the short-time diffusion problem.

ACKNOWLEDGMENTS

Work at Argonne performed under the auspices of the U.S. Department of Energy, BES-Materials Sciences under contract W31-109-ENG-38.

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FIGURE CAPTIONS

- Fig.1.** Reflectivities of a bilayer sample of d-PS/PS before (dots) and after (squares) a short annealing. Continuous (before) and dotted (after) lines are for the fitted models, based on the real space profiles of Fig.2.
- Fig.2.** Evolution of the concentration profile of a bilayer d-PS/PS, in which PS has much larger molecular weight than d-PS, following a short-time anneal.

Fig 2