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Neutron reflectivity study of the kinetics of polymer-polymer interface formation

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We have investigated how the interface width between two thin polymer films approaches its equilibrium state. Neutron reflection for different polyolefin bilayers of various degrees of incompatibility as a function of the annealing time was measured. By tuning the interaction parameter, we have probed both an immiscible polymer couple and systems approaching criticality where the interface is wider. Since polymer chains have slow dynamics, we have observed the slow broadening of the interface connected to the growth at long times of the wavelength capillary-wave modes, which involve large-scale hydrodynamic flows.

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It is now clear that the equilibrium interface width in polymer systems is substantially broader than the mean-field prediction and that the origin of this broadening is related to thermally excited capillary waves [1–5]. Our previous experiments using neutron reflectivity on both strongly immiscible polymer pair and quasimiscible systems have shown that for high degrees of incompatibility—the product of the degree of polymerization, N, and the Flory-Huggins interaction parameter χ—the self-consistent-field (SCF) theory (strong segregation limit) with the additional contribution due to thermally excited capillary waves describes interfaces very well [3,6]. The total interfacial width $2w$ between two polymers can be written as [3,6]

$$2w = (4w_I^2 + 2\pi\sigma_\zeta^2)^{1/2}, \tag{1}$$

where w_I represents the intrinsic interfacial width, obtained with the self-consistent-field theory [7,8] and σ_ζ^2 is the capillary-wave mean dispersion term. In the case where confinement effects are not present, this term is given by [3,9–11]

$$\sigma_\zeta^2 = \frac{k_B T}{2\pi\gamma} \ln \frac{\lambda_{coh}}{\pi w_I}, \tag{2}$$

where γ is the interfacial tension, k_B the Boltzmann constant, T the temperature, and λ_{coh} the neutron coherent length. As the miscibility between the two phases is increased, the interface becomes broader: close to the critical point, defined by the condition $\chi N=2$, the interface diverges as the two phases start to merge into one and the mean-field approach of the SCF theory needs to be reconsidered [12,13]. However, two different regimes were found for the dependence of the interfacial width on the distance away from the critical point: for strongly immiscible polymer pairs, the width of the interface increases slowly when the degree of immiscibility is decreased, while closer to the critical point the dependence on the degree of miscibility becomes stronger and the way in which the interfacial width diverges, as criticality is approached, is related to the chain length and χ [9]. Our experiments found that the SCF theory numerical calculations, with the additional contribution due to capillary waves, provides a good description of the width of the interface between two polymer bulk phases in particular at higher and intermediate values of χN. The weak segregation limit—the square-gradient theory—approximates the experimental data, however, for the lowest values of degrees of immiscibility studied, where the interfacial width starts to diverge [6,9,14,15].

One current issue is concerned with how the interface approaches its equilibrium state. Polymer chains have slow dynamics, and it should be possible to distinguish between the initial broadening of the interface, which we expect to be controlled by single-chain mobility [5,16], from the growth at long times of the wavelength capillary-wave modes, which involve large-scale hydrodynamic flows. To investigate this process, we have performed then neutron reflection experiments to measure the interfacial width of polymer-polymer systems as a function of the annealing time for different polyolefin blends of various degrees of incompatibility.

As in our previous experiments [6,9,14,15] and in order to take full advantage of polymers as model systems for studying fluid interfaces and critical phenomena in confined geometries, we have synthesized highly controlled polymers with well-defined interactions. Random copolymers of ethylene and ethyl-ethylene were obtained by hydrogenating anionically polymerized polybutadiene with different chain microstructures [6,17]. By varying the solvent in which the polymerization takes place, random copolymers of microstructure $(C_4H_8)_{1-x}\,(C_2H_3(C_2H_5))_x$ with a controlled copolymer ratio have been produced. Pairs of these copolymers have an unfavorable interaction, expressed as the Flory-Huggins interaction parameter that depends in a relatively simple way on the copolymer ratios of the components [17]. The degrees of immiscibilities, χN, of the systems used in these experiments were 3.7, 6.8, and 18, while the molecular weight was about 150 000 g/mol. The neutron reflectivity experiments were performed on D17 at the ILL, Grenoble, and on Eros at Saclay (France). The resolution was around 4% and 6% for the experiments. A first layer of partially

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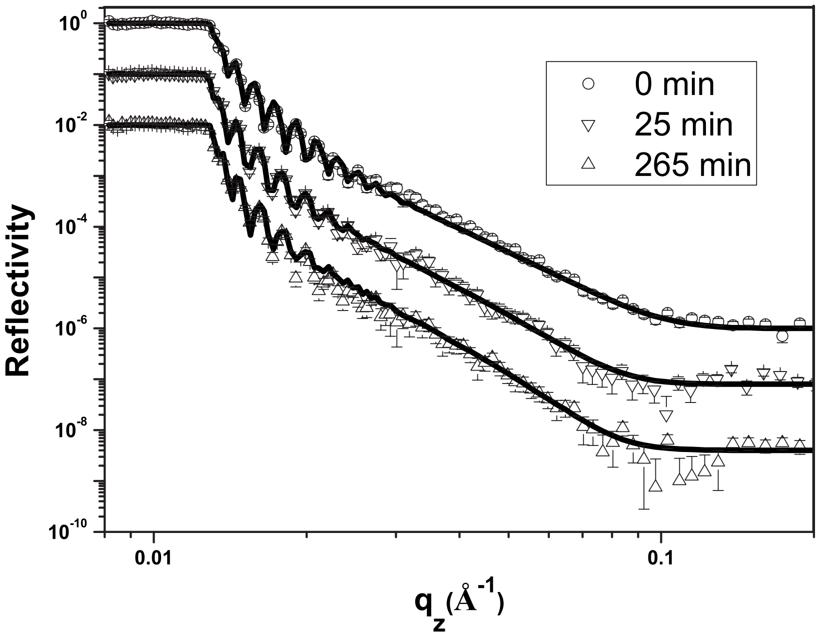

FIG. 1. Reflectivity profiles for the copolymer pair $\chi N=3.7$ for three different annealing times as an example. The solid lines are the fitted curves (see text for details). The curves are shifted of a factor of 10 on the y axis for clarity.

deuterated copolymer was spin-cast on a silicon wafer (110) of 5 cm diameter and 0.5 cm thick from toluene solution. The second layer was spin-cast on a glass slide and floated on top of the first layer. To avoid a confinement effect on the capillary-wave term [6], the thickness of each layer was between 2000 and 3000 Å [6,9,14,15]. A way to extend the range of sensitivity of neutron reflectivity to wider interfaces is to manipulate the neutron refractive index in order to match different phases and then to obtain contrast mainly from the polymer-polymer interface. Substitutions between hydrogen (H) and deuterium (D) can be used to change the neutron refractive index of the polymers in order to match different phases: in principle, for example, in a bilayer system, by matching the scattering length density of the top layer to the one of air and the scattering length density of the bottom layer to the one of silicon, we could get a reflection coming just from the polymer-polymer interface. As a result, the structure of the single interface that originates the reflectivity profile could be determined more reliably [18].

In the geometry used—silicon substrate/deuterated copolymer/hydrogenous copolymer/air—since the value of the scattering length density of the hydrogenated copolymer is very low (10^{-8}–10^{-7} Å^{-2}), there is a very small contrast at the top surface between the sample and the air. The scattering length density of the partially deuterated layer was around 3.3×10^{-6} Å^{-2}. The sensitivity of the measurement to the presence of a diffuse interface between the two polymers is therefore improved. Considering the difference in the scattering length density between the two polymer layers, the effect of an increased interfacial roughness is present in the low-q_z spectra of the reflectivity profile, between 0.014 and 0.021 Å^{-1}, as observed in our previous experiments [18].

After the deposition of the second layer, the sample was immediately quenched at a temperature of −80 °C. The reason for this is that the glass transition of the polymers is around −61 °C. To investigate how the interfacial width reaches equilibrium, for each degree of incompatibility, samples were then annealed for different lengths of time, from 5 min to 5 days, well above the T_g, 83 °C. After the annealing the samples were immediately quenched at a temperature of around −80 °C just before the neutron reflection measurements.

Figure 1 shows an example of the neutron reflectivity (NR) curves for the systems with $\chi N=3.7$ for various annealing times (just a few annealing times are shown for clarity). The top NR curve is for the unannealed system, while the bottom curve is for 4 h of annealing. The fringes observed are connected to the thickness of around 2000 Å of the top layer (the bottom layer is quite thick). A decay of the reflectivity intensity is observed: an indication of a wider interface for longer annealing time. For the $\chi N=18$ case, all reflectivity curves for the various annealing times are superimposed. These results already point out that for the system with the lowest χN, where the contribution to the total interfacial width due to the fluctuations is more important, the time needed to reach equilibrium is higher, while for the other systems, with a higher degree of immiscibility, the equilibrium width is reached quickly.

The solid lines in Fig. 1 represent fits obtained by a least-squares fit to a three-layer model (Si/SiO2/D-polymer/H-polymer) with Gaussian roughness at the surface and at the polymer-polymer interface. The scattering length densities of the copolymer layers were also determined with neutron reflectivity on single layers and then fixed during the fitting procedure, while the thicknesses of the silicon oxide layer and of the copolymer films were also measured previously with spectroscopic ellipsometry. The surface roughness was fixed at about 10 Å: due to the value of the scattering length density of the hydrogenated layer, the exact value of the roughness of the top layer is not relevant [6,18]. This value was the roughness of a single layer measured with neutron reflectivity and obtained also from atomic force microscopy (AFM) imaging of the surface of similar polymer-polymer samples, as previously done [6,18]. The interfacial roughness, as extracted by the reflectivity profiles, as a function of the annealing time is shown in Fig. 2 for the χN measured.

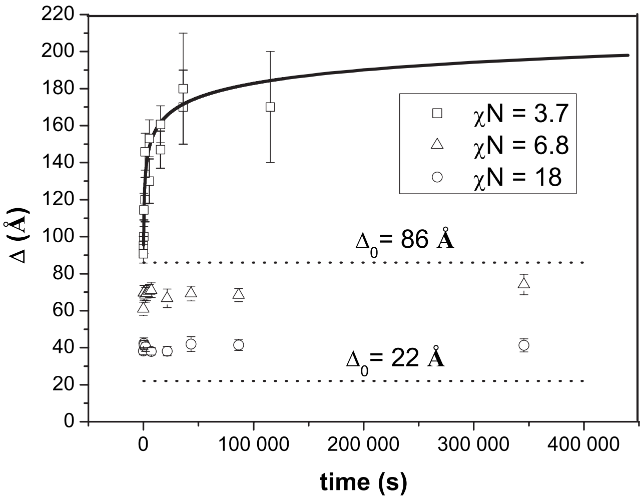

FIG. 2. Interfacial roughness as a function of the annealing time for three degrees of immisicibility χN (3.7, 6.8, and 18). The point line represents the theoretical prediction of the SCF theory in the strong-segregation limit (SSL) for $\chi N=18$ ($\Delta_0=22$ Å) and in the weak-segregation limit (WSL) for $\chi N=3.7$ ($\Delta_0=86$ Å). The solid line represents a fit using the equation for the capillary-wave term (see text for details).

We observe that for the lowest χN the roughness increases with the time up to a limit value—the equilibrium roughness. By comparing systems with different degrees of immiscibility, it can also be observed that for higher χN the interface roughness is already at the equilibrium value at the beginning (after the first measuring time). To understand the behavior of the roughness, since polymer chains have slow dynamics, we argue that there is a quick increase of the initial broadening of the interface that we expect to be controlled by single-chain mobility [4,16]. This is followed by the slow broadening of the interface connected to the growth at long times of wavelength capillary-wave modes, which involve large-scale hydrodynamic flows, as observed in Fig. 2 [4,5]. As reported in Eq. (1), the measured width is composed of an intrinsic width and a capillary-wave term. The w_I component, in the strong-segregation limit, is equal to $a/\sqrt{6\chi}$ [7], with a being the statistical chain length. For systems with finite relative molecular mass, Tang and Freed proposed w_I and γ to behave as the following interpolation formulas which have been shown to be in good agreement with numerical calculations of SCF theory [20,21]:

$$w_I=\frac{a}{\sqrt{6\chi}}\left[\frac{3}{4}\left(1-\frac{2}{\chi N}\right)+\frac{1}{4}\left(1-\frac{2}{\chi N}\right)^2\right]^{1/2}, \tag{3}$$

$$\gamma=k_BT\rho a\sqrt{\frac{\chi}{6}}\left(1-\frac{1.8}{\chi N}-\frac{0.4}{(\chi N)^2}\right)^{3/2}, \tag{4}$$

where ρ is the density of the polymer, k_B the Boltzmann constant, and T the temperature. The corrections depend only on the degree of immiscibility, χN, and become important close to criticality.

The intrinsic width w_I is connected to the roughness via the equation $\Delta_0=w_I\sqrt{2\pi}$ [3].

The dotted line shown in Fig. 2 for $\chi N=18$ represents Δ_0 calculated using relation (3): the fact that the equilibrium roughness is around 40 Å and constant clearly indicates that the capillary-wave term has already reached its equilibrium at the early time. A calculation of this term using Eq. (2) and considering an interfacial tension of 8×10^{-4} J/m [as in our previous work [6] and calculated from Eq. (4)] gives a value of 30 Å. The value extracted from the experimental data using the equation $\sigma_\zeta^2=\Delta_{mes}^2-\Delta_0^2$ gives a value of 33 Å, in very good agreement with the calculation. For the $\chi N=6.8$ case, the width reaches the equilibrium value very quickly (around 65 Å): this system is in a region of transition of validity between the SCF theory and the WSL regime, where both theories do not fit well the data, as observed in our previous analysis [6].

For the lowest-χN cases, the WSL has been used to estimate the intrinsic interfacial width and the interfacial tension [13]:

$$w=\frac{a\sqrt{N}}{3}\left(\frac{\chi}{\chi_{crit}}-1\right)^{-1/2}, \tag{5}$$

$$\gamma=\frac{2kT}{3a^2\sqrt{N}}\left(1-\frac{\chi_{crit}}{\chi}\right)^{3/2}, \tag{6}$$

where χ_{crit} represents the value of the interaction parameter at the critical point. We can observe the prediction of Δ_0 obtained using Eq. (5) in Fig. 2 as a dotted line.

For the case of $\chi N=3.7$ a different behavior is observed. The experimental initial roughness is of 91 Å, while the calculated width using Eq. (5) is 86 Å. An estimation considering the capillary-wave term gives a value of 30 Å for the first measurement (similar to the value obtained for the $\chi N=18$ case). The width then grows as a function of time, reaching an equilibrium value of around 180 Å. We observe the slow broadening of the interface connected to the growth at long times of the capillary-wave modes, which involve large-scale hydrodynamic flows. The time dependence of the capillary-wave term has been derived by considering the thermal motion of an interface between two immiscible fluids [19]. The derived expression in three dimensions gives a logarithmic dependence on the time t, $\ln(\omega t)$, where ω is the frequency of the length at which the hydrodynamics description breaks down.

In the case of the viscous regime, as for our polymer case, ω is given by $(\gamma/\eta)q_c$ where γ is the interfacial tension, η the viscosity of the polymers, and q_c the wave vector given by $q_c\sim1/w_I$. We can than obtain an expression for the time-dependent capillary-wave term:

$$\sigma_\zeta^2=\frac{k_BT}{\pi\gamma}\ln\frac{(\gamma/\eta)t}{w_I}. \tag{7}$$

In Fig. 2, a fit to the experimental data considering this equation and Eq. (1) is reported. The fitted parameters were the intrinsic width, the interfacial tension, and the viscosity. The results obtained gives $\Delta_0=86\pm3$ Å, $\gamma=(2.0\pm0.5)\times10^{-5}$ J m^{-2}, and $\eta=(3.0\pm0.5)\times10^5$ Pa s. The interfacial width is in good agreement with the calculated value using

Eq. (5). The interfacial tension obtained using Eq. (6) is 5×10^{-5} J m^{-2}, of the same order of magnitude and in line with our previous observation [6,9,14,15]. The obtained viscosity can be compared to the viscosity of polybutadiene polymers at the same temperature: an estimation using the WLF equation given a value of $\eta = 6 \times 10^4$ Pa s [22]. We could than argue that the analysis of the broadening of the interface in terms of the thermal fluctuations could be useful to obtain also viscoelastic information of the system. Recent works on the surface and interface dynamics of thin polymer films by x-ray photon correlation spectroscopy have shown that by analyzing the thermally driven in-plane dynamics at the interfaces, some insights into the rheology of thin polymer films can be obtained [23].

In conclusion, we have investigated the broadening of the interface between two polymers for systems with different degrees of immiscibility with neutron reflection. We observe that while for the higher degree of immiscibility the broadening is quick and the capillary term reaches its equilibrium value of around 30 Å very fast, for the system of a wider interface we have observed a slow broadening of the interface connected to the growth of capillary-wave modes, which involve large-scale hydrodynamic flows. The model that considers the growth of the capillary term as a function of the interfacial tension and the viscosity of the system gives a reasonable explanation of the results.

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