

# Interfacial width of novel polymers approaching the critical point

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*Neutron reflectivity profiles have been measured for thin bilayers of polyolefins, random copolymers of ethylene and butene, for two systems with different degrees of immiscibility:  $\chi N=23$  and  $\chi N=47$ . The interfacial width has also been measured as function of the thickness of the bottom layer, keeping the top layer thickness fixed at about 3000 Å, to investigate how confinement effects modify thermally excited interfacial fluctuations.*

The width of the interface between strongly immiscible polymers is well described by the self-consistent field theory with an additional contribution due to thermally excited fluctuations [1]. As the degree of immiscibility is decreased, self-consistent field theory becomes inaccurate as the interface starts to diverge. Approaching the critical point, square gradient theories can be used to predict the interfacial width, but the way the two approaches cross over is not well known [2].

To entangle this issue, neutron reflectivity experiments have been performed on bilayers of polyolefins, random copolymers of ethylene and butene, obtained by hydrogenating or deuterating anionically polymerised polybutadiene. In this system, by controlling the copolymer ratio between ethylene and butene, it is possible to obtain pairs of polymers with different Flory-Huggins interaction parameter  $\chi$ , and therefore to probe different situations, from strongly immiscible to quasi-miscible polymers [3].

The aim of the experiment was to study how the width of the interface depends on the degree of immiscibility ( $\chi$  multiplied by the degree of polymerisation  $N$ ), and to investigate how confinement effects in thin layers geometry modify interfacial fluctuations.

We prepared bilayers of deuterated and hydrogenated polyolefins of different copolymer ratios and molecular weight  $M_w \sim 100K$  on silicon substrates. The first layer was prepared by spin coating the deuterated polymer directly onto the silicon substrate, while the hydrogenous polymer was before spun onto a glass slide and then floated in water to deposit it on the top.

We investigated two different pairs of polymers with degree of immiscibility of  $\chi N=23$  and  $\chi N=47$ . For each pair we prepared a series of samples fixing the thickness of the top layer at about 2500 Å and varying the thickness of the bottom layer in the range 600-4000 Å.

The thickness of all the layers has also been measured before the experiment by ellipsometry.

All the samples have then been annealed for 5 days at 80°C, which is well above the glass transition temperature.

For each sample, we measured the specular reflectivity at the reflectometer AMOR. We then fitted the reflectivity profiles with a two-layer model to determine surface and interface roughness.

Our preliminary results show a dependence of the interfacial width on bottom film thickness: the interface roughness increases with the thickness up to a thickness of about 1500 Å, after which it reaches an equilibrium and it is constant (see Figure 1).

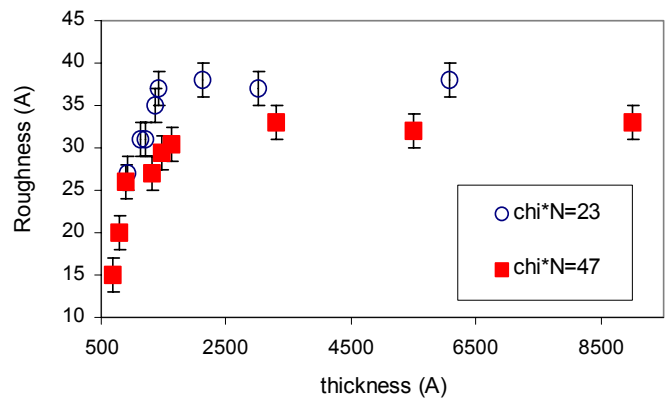
By comparing the two systems, as shown in Figure 1, we

observed that the interface roughness increases faster when the degree of immiscibility  $\chi N$  is smaller, and the value of the interfacial width at the equilibrium is in this case higher.

However the relative value of the roughness suggests that for both these values of  $\chi N$  we are still in the case of immiscible polymers, far from the criticality.

For our future experiments, we plan to investigate the structure of the interface closer to the critical point.

## Interface roughness vs thickness



**Figure 1:** Interface roughness as a function of the thickness for pairs of polymers with different  $\chi N$

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