Approaching criticality in polymer-polymer systems

C. Carelli,[1,*] R. A. L. Jones,[2] R. N. Young,[2] R. Cubitt,[3] R. Dalgliesh,[4] F. Schmid,[5] and M. Sferrazza[6,†]
[1]*Department of Physics, University of Surrey, Guildford, United Kingdom*
[2]*Department of Physics and Astronomy, University of Sheffield, Sheffield, United Kingdom*
[3]*ILL, Institute Max Von Laue Paul Langevin, Grenoble, France*
[4]*ISIS, Rutherford Appleton Laboratory, Chilton, United Kingdom*
[5]*Fakultät für Physik, Universität Bielefeld, Bielefeld, Germany*
[6]*Département de Physique, Université Libre de Bruxelles, Boulevard du Triomphe, CP223, Bruxelles, Belgique*
(Received 19 May 2005; published 19 September 2005)

The interfacial width of polyolefins blends has been probed as a function of distance away from the critical point by using neutron reflectivity. For strongly immiscible polymer pairs, the width of the interface increases slowly when the degree of immiscibility is decreased and the interfacial width varies with the interaction parameter χ of the polymers. 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 both the chain length and χ. The self-consistent field 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 intermediate values of the degree of immiscibility.

DOI: 10.1103/PhysRevE.72.031807 PACS number(s): 82.35.Rs, 68.08.−p, 68.55.−a

I. INTRODUCTION

The structure of the interface between two polymer phases is a topic of considerable interest in polymer physics. Polymers represent, in fact, model systems to address problems of statistical mechanics of fluids, and to test mean-field theories. Moreover, polymer/polymer interfaces play an important role in technology, because the structure of the interface between immiscible or quasi-immiscible polymers controls adhesion, wetting, mechanical, and optical properties of materials. One of the current issues concerns with the relative importance of the intrinsic interfacial width, of the type calculated from mean-field theories, and interfacial fluctuations in determining the overall structure of an interface [1,2]. These fluctuations of the local position of the interface broaden the interfacial width.

The width of the interfacial region between two immiscible polymer phases is described by the self-consistent field (SCF) theory, developed by Helfand and Tagami [3,4]. In this approach, a polymer chain is considered as a random walk under the effect of a mean-field potential, resulting from the interaction with all the other polymer chains. For strongly immiscible polymers, in the limit of chains with infinite lengths, an analytical solution for the self-consistent field equation is derived to calculate the width of the interface and the interfacial tension. Successively, Broseta *et al.* and Tang and Freed determined the corrections for finite molecular weights, showing the relative importance due to finite chain lengths [5,6].

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 [7–9]. Our previous experiments on the strongly immiscible polymer pair polysterene and poly(methyl-methacrylate) have shown that for high degrees of incompatibility—the product of the degree of polymerization N and the Flory-Huggins interaction parameter χ—the SCF theory with an additional contribution due to thermally excited capillary waves describes the interface quite well [9–11]. However, close to the critical point, defined by the condition $\chi N=2$, the interface should diverge and the mean-field approach of the SCF theory needs to be reconsidered.

Criticality can be achieved at low molecular weight with a larger segment-segment interaction parameter or at high molecular weight with a smaller segment-segment interaction parameter. At high molecular weights, we expect mean-field exponents for the divergence of the interfacial width approaching criticality, while in more strongly interactive systems whose critical point occurs for lower degrees of polymerization, we should cross over a nonclassical exponent. As the degree of incompatibility is increased, square gradient theories (the weak segregation limit) become inaccurate [12]. At high degrees of incompatibility, self-consistent field theory (the strong segregation limit) [3] should describe the situation at the mean-field level, but the way the two approaches cross over is not well characterized. Recently, numerical methods and Monte Carlo simulations have also been developed to solve exactly systems of SCF differential equations and to calculate a composition profile across the interface [13]. The existing experimental data are limited to demonstrating the divergence near the critical point qualitatively [14].

In this work, we studied systematically the dependence of the interfacial width on the distance away from criticality with the aim to characterize the crossover from strongly immiscible to weakly immiscible polymers. We then compared

*Present address: Ecole Supérieure de Physique et Chimie Industrielles (ESPCI) Paris, France.
†Author to whom correspondence should be addressed; electronic address: msferraz@ulb.ac.be

our results with SCF numerical calculations to make a quantitative test of the theory.

II. EXPERIMENTS

To make full advantage of polymer systems to investigate fluid interfaces, we have synthesized highly controlled polymers with well-defined interactions. To probe different conditions of miscibility, our work has been focused on a particular class of materials, model monodisperse polyolefins prepared by the catalytic hydrogenation (or deuteration) of polybutadienes. By controlling the architecture of the precursor polybutadiene we were able to synthesize random copolymers of ethylene and ethyl-ethylene of microstructure $[(C_4H_8)_{1-x}(C_2H_3(C_2H_5))_x]$, whose copolymer ratio x can be precisely controlled. Mixtures of these copolymers have an unfavorable interaction, expressed as the Flory-Huggins parameter χ, which can be calculated from the in copolymer ratios of the two components using the relation [15] $\chi=(a_0+a_1\bar{x}+a_2\bar{x}^2)(x_1-x_2)^2$. In the previous expression x_1 and x_2 are the two copolymer ratios, $\bar{x}$ is the mean copolymer ratio, and the coefficients a_0, a_1, and a_2 are linear combinations of the homopolymers interaction parameter $\chi_{A/B}$ and of the interactions between homopolymer and copolymer $\chi_{A/A-B}$ and $\chi_{B/A-B}$. The values of these coefficients at 83 °C are respectively 0.062, −0.114, and 0.220. Thus, tuning the interaction χ and varying the degree of polymerization N via the molecular weight, we were able to explore the full continuum of situations, from near criticality to strongly immiscible pairs. The combinations of copolymer ratios investigated with the respective interaction parameter are reported in Table I.

We have performed neutron reflectivity experiments on bilayers of 50%-deuterated and hydrogenated random copolymers. In order to understand the relative importance of energetic interactions and entropic effects in determining the interfacial profile, two different sets of experiments have been performed. In the first set, the molecular weight has been fixed, and different conditions of miscibility have been probed by changing the combinations of copolymer ratios, and thus the interaction parameter χ. The values of χ varied between 0.0008 and 0.016, while the molecular weight was fixed at ~150 000 g/mol corresponding to a degree of polymerization N of ~2500. To avoid the effect on the capillary waves due to confinement, the thickness of each layer was between 3000 and 6000 Å.

In another series of samples we determined the interfacial width as a function of the molecular weight for five fixed values of the interaction parameter in the range 0.0009–0.0022, varying the average value of N between 2400 and 16 000. Moreover, criticality was approached by varying the molecular weight of the polymers between 100 000 and 900 000 g/mol for fixed values of the interaction parameter in the range 0.0009–0.0022.

For the experiments, the structure of the samples was silicon substrate/deuterated copolymer/hydrogenous copolymer/air (D/H). In this geometry, since the value of the scattering length density of the hydrogenated copolymer is close to 0, there is a small contrast at the top surface between the sample and the air. The sensitivity of the measurement to the presence of a diffuse interface between the two polymers is therefore improved. The bottom deuterated layer of the copolymer has been spun-cast onto silicon substrate from toluene solutions, while the top hydrogenated layer was first spun onto a glass slide and then floated in water and deposited onto the substrate. The samples were then annealed in a vacuum oven for five days at temperature of around 83 °C, well above the glass transition temperature of the polymers to allow the interfacial width to reach an equilibrium value [16].

TABLE I. The table reports the combinations of copolymer ratios x_1 and x_2 investigated with the respective interaction parameter χ. See text for details.

x_1	x_2	χ
0.69	0.78	0.0008
0.685	0.78	0.0009
0.685	0.79	0.0011
0.68	0.79	0.0012
0.66	0.78	0.0014
0.59	0.72	0.0014
0.65	0.78	0.0016
0.66	0.79	0.0016
0.68	0.81	0.0017
0.7	0.83	0.0018
0.68	0.83	0.0022
0.66	0.82	0.0025
0.7	0.86	0.0027
0.66	0.83	0.0029
0.68	0.85	0.0030
0.59	0.78	0.0031
0.65	0.83	0.0032
0.67	0.85	0.0033
0.66	0.85	0.0037
0.65	0.86	0.0045
0.59	0.83	0.0053
0.59	0.86	0.0069
0.5	0.86	0.0112
0.5	0.87	0.0119
0.5	0.90	0.0144
0.5	0.92	0.0162

III. RESULTS

The neutron reflectivity profiles were measured using two different reflectometers: D17B at the Institut Max Von Lau-Paul Langevin (Grenoble), and CRISP at the Rutherford Appleton Laboratory (UK). The resolution used varied between 3% and 5%.

Figure 1 shows examples of neutron reflectivity profiles measured from bilayers D/H with degree of polymerization $N\sim2500$ for three different values of χ: 0.0112, 0.0033, and 0.0018. All the curves present total reflection up to q_c

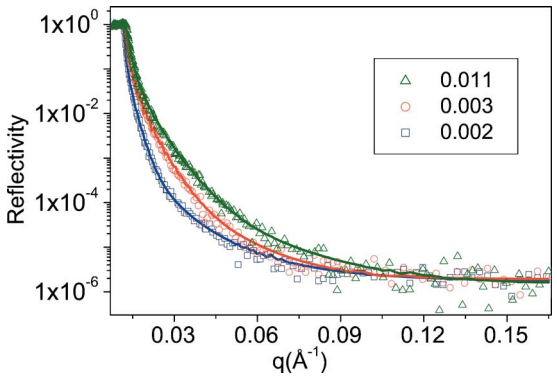

FIG. 1. (Color online) Reflectivity profiles for copolymer pairs with different interaction parameter χ and degree of polymerization $N \sim 2500$. The solid lines are the fitted curves (see text for details).

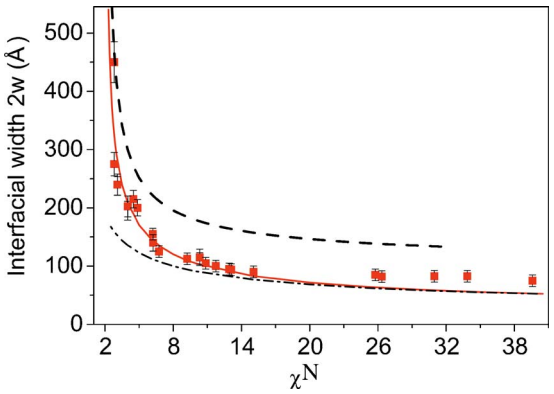

FIG. 2. (Color online) Interfacial width as a function of the degree of immisicibility χN for polymer pairs with changing interaction parameter χ and degree of polymerization $N \sim 2500$. The solid line represents the SCF numerical calculation, the point-dashed line the theoretical prediction of the SCF theory in the strong segregation limit, while the dashed line is obtained by using the squared gradient theory in the weak segregation limit.

~ 0.0125 Å^{-1} due to the presence of approximately the same amount of deuterium in the bottom layer. However, after the critical edge, the reflectivity profiles fall off more rapidly as the degree of immiscibility χN is decreased. This behavior, characteristic of a rough interface, is more pronounced when the interaction parameter χ is decreased from 0.0033 to 0.0018.

The reflectivity profiles obtained from the bilayers were then fitted using a three-layer model on a silicon substrate composed of a thin silicon oxide layer, the deuterated copolymer, and on top the hydrogenated copolymer, with Gaussian roughness at the surface and at the polymer/polymer interface. In this configuration, since the hydrogenated film has a very low scattering length density, there is not much contrast between the air and the top surface of the sample. Thus, the reflectivity measurement is not very sensitive to the value of the surface roughness. The thicknesses of both the silicon oxide layer and the copolymer films were also previously measured with spectroscopic ellipsometry. The roughness of the SiO_2 layer was fixed to 5 Å, as measured previously in similar silicon crystals [9]. The scattering length density and the surface roughness of the polymers were also determined with neutron reflectivity experiments on single layers and then fixed during the fitting. For deuterated copolymers, the value of the scattering length density was around 3×10^{-6} Å^{-2}, while for hydrogenated blends it was found to be between 2×10^{-7} and -3×10^{-7} Å^{-2}. The surface roughness was around 8 Å for all the copolymers, as measured also from atomic force microscope experiments. From the values found for the interfacial roughness σ_{int}, obtained considering an error function (erf) to describe the interfacial profile, the total width of the interface $2w$ has then been determined with the relation $2w = \sqrt{2\pi}\sigma_{int}$ [9].

Figure 2 shows the results obtained for polymer pairs with degree of polymerization $N \sim 2500$ and different interaction parameters as a function of the degree of immiscibility χN. The dependence of the interfacial width on the distance from the critical point presents two different behaviors: for degrees of immiscibility higher than 8, the interfacial region increases very gradually as the interaction parameter is decreased, while for more miscible polymer pairs the width of the interface starts to diverge.

IV. DISCUSSION

To verify the validity of the analytical expressions for the interfacial width and the interfacial tension in the approximations of strong and weak segregation, the experimental data obtained for polymer pairs with $N \sim 2500$ have also been compared with the predictions of the theory in these limits. We should note that considering the Ginzburg criterion to estimate how close to the critical point one needs to be to consider increasingly large concentration fluctuations, we are not near enough to the critical point for these fluctuation effects to be relevant.

The self-consistent field theory, in the strong segregation limit, with the additional correction for interfacial fluctuations, should describe the behavior of the interfacial width for highly immiscible polymers, but when approaching the critical point, the predictions of square gradient theory, in the weak segregation limit, should be more accurate.

As mentioned above, in order to compare the experimental results to the theoretical predictions the contribution of capillary waves needs to be taken into account. The experimental interfacial profile is broadened by thermally excited lateral fluctuations, which give rise to a dependence of the apparent interfacial width on the lateral resolution. Hence, the total interfacial width $2w$ can be written such as [9,13]

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

where w_I represents the intrinsic interfacial width, and σ_ζ is the capillary waves' contribution to the total width. The w_I component, in the strong segregation limit, is equal to $a/\sqrt{6\chi}$ for the self-consistent field theory [3] with the statistical chain length a. In general, to consider finite molecular mass, Tang and Freed suggested the following formulae for w_I and the interfacial tension γ, which have been shown to be in good agreement with the numerical calculations of the SCF theory [6]:

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

$$\gamma = k_B T \rho a \sqrt{\frac{\chi}{6}}\left[1-\frac{1.8}{\chi N}-\frac{0.4}{(\chi N)^2}\right]^{3/2}, \quad (3)$$

where ρ is the density of the polymer, k_B the Boltzmann constant, and T the temperature.

In the weak segregation limit, values for w_I and for γ are given by the theoretical predictions for the critical interfacial width w and the critical interfacial tension γ [17,18]:

$$w = \frac{a\sqrt{N}}{3}\left[\frac{\chi}{\chi_{crit}}-1\right]^{-1/2}, \quad (4)$$

$$\gamma = \frac{2kT}{3a^2\sqrt{N}}\left[1-\frac{\chi_{crit}}{\chi}\right]^{3/2}, \quad (5)$$

where χ_{crit} represents the value of the interaction parameter at the critical point.

To make a more quantitative analysis, the results have also been compared with the predictions of SCF numerical calculations for incompressible blends [3,4]. Since the density is taken to be constant, the only model parameter is χN and no knowledge on the equation of state is required [4,20]. The statistical chain length a is taken to be equal for all copolymers; $a=6$ Å [19]. The interfacial tension can also be determined if the density of the polymers is known. In the SCF numerical calculations, the width was determined from the order parameter profile $m(z)=\Phi_A(z)-\Phi_B(z)$ following the second-moment definition, dm/dz, appropriate for erf profiles:

$$w_m^2 = \int dz\left(\frac{dm}{dz}\right)z^2 \Big/ \int dz\left(\frac{dm}{dz}\right). \quad (6)$$

It should be pointed out that in the limit $\chi N \to \infty$ (strong segregation limit), the exact solution of the SCF theory is a tanh profile [3]. Even close to the critical point, our SCF profiles are better approximated by tanh profiles than by erf profiles. However, this difference does not affect significantly our results, with the difference being less than 5%. Moreover, the second-moment definition w_m [Eq. (6)] for the interfacial width differs somewhat from the usual definition of w_I in the theoretical literature, $w_I=|m(\infty)|/(dm/dz)_0$, which are, e.g., used in Eqs. (2) and (4). For tanh profiles, the relation is $w_m=\pi/2\sqrt{3}w_I \approx 0.9w_I$, and for erf profiles, $w_m=\sqrt{2/\pi}w_I \approx 0.79w_I$.

In a system with linear dimension L, the effect of capillary waves on the width broadens the width according to [9]

$$(2w_L)^2 = (2w_m)^2 + \frac{2}{\pi}\frac{k_B T}{\gamma}\ln\left(\frac{L}{B}\right), \quad (7)$$

where B is a microscopic coarse-graining length.

In the experiments performed, the lower cutoff L for capillary wave vectors is related to the lateral coherence length of the neutron beam, that we took as 20 μm [9]. The product πw_I has been used as a cutoff for short wavelengths B, as suggested by Semenov [8,21].

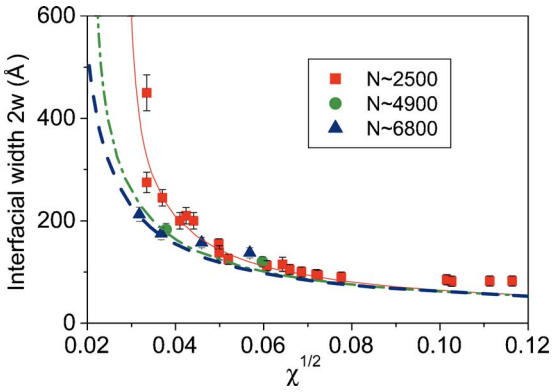

FIG. 3. (Color online) Interfacial width as a function of the square root of the interaction parameter χ for different values of the degree of polymerization N. The lines represent the SCF numerical calculations for the different cases (see text for details).

As we can observe in Fig. 2, for $N \sim 2500$ the SCF numerical calculation predicts well the behavior of the experimental data at low values of χ, from $\chi N < 20$ and lower to around 8, while the square gradient theory approximates the experimental data for the lowest values of degrees of immiscibility studied, where the interfacial width starts to diverge. For degrees of immiscibility higher than 20, and thus $\chi > 0.005$, the results show discrepancies between experimental data and theoretical calculations. The measured interface is broader than the prediction. However, if the values of the interfacial tension are reduced by approximately 40%, and thus a higher contribution to the interface due to capillary waves is considered, the theoretical predictions describe well the interfacial width also for more immiscible systems. Lower values of interfacial tension were observed by other authors [22] and were confirmed by our experiments on the effect of the confinement approaching criticality [23], where systematically we observed a 40% reduced interfacial tension from the predicted SCF values. A qualitative similar behavior is observed for higher degrees of polymerization, where the divergence from the theoretical predictions at

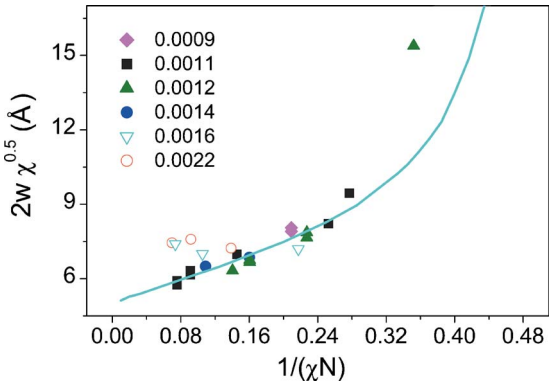

FIG. 4. (Color online) Interfacial width multiplied by $\chi^{1/2}$ as a function of the inverse of the degree of immiscibility for series of polymer pairs with different degrees of polymerization N and fixed interaction parameters (χ are reported in the figure). The solid lines are obtained from numerical calculations of SCF theory for $\chi = 0.0012$.

higher values of χ becomes more important. To understand better the effect of the degree of polymerization N on the interfacial width as criticality is approached, in Fig. 3 the data obtained for the the interfacial width for series of polymer pairs with different degrees of polymerization is plotted as a function of the square root of the interaction parameter χ.

As can be observed in Fig. 3, at higher values of the interaction parameter χ ($\sqrt{\chi} \geqslant 0.05$) the experimental data collapse. Thus, in this case, the degree of polymerization does not affect the interfacial width and the approximation of infinite relative molecular masses is valid. This behavior suggests also that the discrepancy observed between experimental data and theoretical predictions at higher degrees of immiscibility is not influenced by the molecular weight, but depends only on the interaction parameter χ. For less interacting systems, polymer pairs with higher degree of polymerization show a narrower interface, in agreement with the theoretical predictions. Thus, as criticality is approached, the length of the polymer chains becomes an important factor in determining the divergence of the interface.

For polymer pairs with fixed interaction parameter and varying molecular weights, the dependence of the interfacial width on the degree of polymerization N has been also determined. For these systems, at higher values of χN, as the distance from the critical point is reduced, the interfacial width is almost constant. However, for more miscible polymer pairs, the dependence of the width $2w$ on the molecular weight becomes stronger. Comparing the results obtained for different values of χ, systems with a lower interaction parameter present a wider interface. In particular, for values of χ lower than 0.0014 we observe a good agreement between the experimental data and the SCF theory predictions over a wide range of miscibilities. However, for higher values of χ (0.0016 and 0.0022) there is a divergence with the theory at higher molecular weights and the measured interface is broader. This behavior could be explained again considering a lower interfacial tension, and thus a higher contribution to the interface due to capillary waves, at higher χN. A discrepancy is also observed close to the critical point, for χN lower than 3.

These deviations from the theoretical predictions are clear in Fig. 4, where the product of the interfacial width and the square root of the interaction parameter has been plotted as a function of the inverse of the degree of immiscibility for all the sets of data. In the legend, the values of χ used are reported. Since the interfacial width, for fixed values of χN depends principally on $\chi^{1/2}$, the theoretical curves representing $2w\chi^{1/2}$ as a function of $1/\chi N$ collapse onto a single line. It should be pointed out that the contribution of capillary waves to the interfacial width varies with $\chi^{1/4}$ and not with $\chi^{1/2}$ as the intrinsic width. However, the corrections due to this dependence are very small, as shown when the theoretical curves calculated for different values of χ were calculated. Differences between theory and experimental results are observed only for $\chi > 0.0016$ and at very low degrees of immiscibility.

V. CONCLUSIONS

To summarize, the dependence of the interfacial width on the distance away from the critical point has been studied with neutron reflectivity. The experimental values of the interfacial width, measured for polymers with degree of polymerization $N \sim 2500$ and a changing interaction parameter, have been compared with the analytical solutions derived from mean-field theories in the strong and weak segregation limits. At high degrees of immiscibility, the SCF theory, in the approximation of infinite relative molecular masses, follows well the width of the interfacial region for degrees of immiscibility higher than 8. For lower χN, a crossover is observed to a region of miscibility where the square gradient theory in the weak segregation limit better approximates the interfacial width close to criticality. The results are well predicted when compared with numerical calculations of the self-consistent field theory at intermediate values of the interaction parameter, although a bigger value for the interfacial tension and thus a higher contribution due to capillary waves needs to be considered for strongly immiscible systems.

[1] A. Werner *et al.*, J. Chem. Phys. **110**, 1225 (1999).
[2] K. Binder *et al.*, J. Stat. Phys. **95**, 1045 (1999).
[3] E. Helfand and Y. Tagami, J. Chem. Phys. **56**, 3592 (1971).
[4] F. Schmid, J. Phys.: Condens. Matter **10**, 8105 (1998).
[5] D. Broseta *et al.*, Macromolecules **23**, 132 (1990).
[6] H. Tang and K. Freed, J. Chem. Phys. **94**, 6307 (1991).
[7] K. Shull *et al.*, Macromolecules **26**, 3929 (1993).
[8] A. N. Semenov, Macromolecules **27**, 2732 (1994).
[9] M. Sferrazza, C. Xiao, R. A. L. Jones, D. G. Bucknall, J. Webster, and J. Penfold, Phys. Rev. Lett. **78**, 3693 (1997).
[10] M. Sferrazza *et al.*, J. Phys.: Condens. Matter **13**, 10269 (2001).
[11] M. Sferrazza *et al.*, Philos. Mag. Lett. **80**, 561 (2000).
[12] J. W. Cahn and J. E. Hilliard, J. Chem. Phys. **28**, 258 (1958).
[13] A. Werner *et al.*, J. Chem. Phys. **107**, 8175 (1997).
[14] U. K. Chaturvedi, U. Steiner, O. Zak, G. Krausch, and J. Klein, Phys. Rev. Lett. **63**, 616 (1989).
[15] W. W. Graessley *et al.*, Macromolecules **27**, 3896 (1994).
[16] A. Losch *et al.*, J. Polym. Sci., Part B: Polym. Phys. **33**, 1821 (1995).
[17] R. A. L. Jones and R. W. Richards, *Polymers at Surfaces and Interfaces* (Cambridge University Press, Cambridge, 1999).
[18] J. F. Joanny and L. Leibler, J. Phys. (Paris) **39**, 951 (1978).
[19] T. Kerle, J. Klein, and K. Binder, Phys. Rev. Lett. **77**, 1318 (1996).
[20] F. Schmid, J. Chem. Phys. **104**, 9191 (1996).
[21] A. N. Semenov, Macromolecules **26**, 6617 (1993).
[22] J. Genzer and R. J. Composto, Polymer **40**, 4223 (1999).
[23] C. Carelli *et al.*, Europhys. Lett. **71**, 763 (2005).