PHYSICAL REVIEW E VOLUME 62, NUMBER 1 JULY 2000

Wetting in a phase separating polymer blend film: Quench depth dependence

Mark Geoghegan,[1,2,*] Hubert Ermer,[1] Gerald Jüngst,[1] Georg Krausch,[2,3] and Rüdiger Brenn[1,4]
[1]*Fakultät für Physik, Universität Freiburg, Hermann-Herder-Straße 3, D-79104 Freiburg im Breisgau, Germany*
[2]*Lehrstuhl für Physikalische Chemie II, Universität Bayreuth, D-95440 Bayreuth, Germany*
[3]*Bayreuther Zentrum für Kolloide und Grenzflächen (BZKG), Universität Bayreuth, D-95540 Bayreuth, Germany*
[4]*Freiburger Materialforschungszentrum (FMF), Stefan-Meier-Straße 21, D-79104 Freiburg im Breisgau, Germany*
(Received 19 October 1999; revised manuscript received 10 April 2000)

We have used ^{3}He nuclear reaction analysis to measure the growth of the wetting layer as a function of immiscibility (quench depth) in blends of deuterated polystyrene and poly(α-methylstyrene) undergoing surface-directed spinodal decomposition. We are able to identify three different laws for the surface layer growth with time t. For the deepest quenches, the forces driving phase separation dominate (high thermal noise) and the surface layer grows with a $t^{1/3}$ coarsening behavior. For shallower quenches, a logarithmic behavior is observed, indicative of a low noise system. The crossover from logarithmic growth to $t^{1/3}$ behavior is close to where a wetting transition should occur. We also discuss the possibility of a ‘‘plating transition’’ extending complete wetting to deeper quenches by comparing the surface field with thermal noise. For the shallowest quench, a critical blend exhibits a $t^{1/2}$ behavior. We believe this surface layer growth is driven by the curvature of domains at the surface and shows how the wetting layer forms in the absence of thermal noise. This suggestion is reinforced by a slower growth at later times, indicating that the surface domains have coalesced. Atomic force microscopy measurements in each of the different regimes further support the above. The surface in the region of $t^{1/3}$ growth is initially somewhat rougher than that in the regime of logarithmic growth, indicating the existence of droplets at the surface.

PACS number(s): 68.45.Gd, 68.10.Jy, 68.15.+e, 82.65.Dp

I. INTRODUCTION

The ubiquity of wetting and the simplicity of the general concept hide many problems in fundamental physics [1]. It has long been accepted that polymer blends present an ideal means to study wetting because the length of polymer chains slows their motion to experimentally accessible time scales. The formation and growth of wetting layers is a case in point and has received a great deal of attention, both experimentally [2–10] and theoretically [11–20].

We consider the growth of the wetting layer in a phase separating system undergoing surface-directed spinodal decomposition [9]. Theoretically, it has been shown to be possible to form a layered structure parallel to the interface. Normally, however, Ostwald ripening of domains at the surfaces tends to drive the phase separation without layering [13–18]. In order to study wetting from a mixture without such domain growth, it is desirable to have a surface energy difference between the components (which drives the wetting) dominating over bulk phase separation. This can only be achieved in low noise systems or close to the critical point.

In most phase separating polymer systems the wetting layer grows with a $t^{1/3}$ growth law, but previous measurements on a blend of deuterated polystyrene (d-PS) and poly(α-methylstyrene) (PαMS) [7] revealed a surface layer that grew logarithmically with time. This system has been suggested as a good candidate for a polymer blend exhibiting low noise behavior [11]. There has been an attempt to experimentally simulate low noise, but this was limited to late stage coarsening [10]. In the present work, we consider the growth of the wetting layer in d-PS/PαMS blends as a function of the quench depth ε. This enables us to vary the strength of the surface field with respect to thermal noise. We observe three different growth laws and shall discuss the results in terms of the wetting transition. We also suggest that a plating transition at the surface [13] might also contribute.

In a phase separating mixture, as in any binary mixture, the surface is enriched by the component of lower surface energy. For shallow quenches, a homogeneous wetting layer will grow into the bulk of the film. Complete wetting is determined by the sign of the spreading coefficient S given by Young's equation,

$$S=\gamma_B-(\gamma_{AB}+\gamma_A), \tag{1}$$

where γ is the interfacial tension of a particular component. The subscripts A, B, and AB indicate the different components and the interface, respectively. When S is positive, the A component will form a wetting layer at the surface. At the critical point the interfacial energy will be zero (because the two components will be at the limit of miscibility) and wetting will proceed. Such critical point wetting, and the transition to partial wetting, has been developed theoretically [21]. It has been noted that polymer mixtures are particularly interesting as the interfacial tensions are usually low, and the transition from partial to complete wetting (hereafter the wetting transition) can occur some distance from the critical point [22].

For quenches deeper than that corresponding to the wetting transition, partial wetting corresponds to the energy

---

[*] Author to whom correspondence should be addressed (Bayreuth).

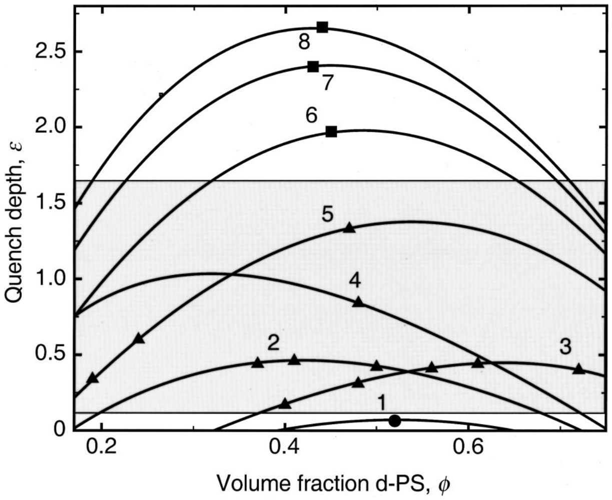

FIG. 1. Quench depth ε for mixtures of d-PS and PαMS with different molecular weights and compositions. M_w(d-PS)/M_w(PαMS) (1) 35 000/41 700, (2) 80 000/41 700, (3) 35 000/108 000, (4) 80 000/108 000, (5) 190 000/41 700, (6) 123 000/108 000, (7) 163 000/108 000, (8) 190 000/108 000. Squares, triangles and the circle denote regions where best fits to the data give approximate growth laws of $t^{1/3}$, log(t), and $t^{1/2}$, respectively. The shaded area marks the region of log(t) growth.

minimum. That is, droplets of one phase will exist at the surface in coexistence with a minority phase. It has been shown theoretically, however, that a wetting layer may exist even when partial wetting would be expected. Using cell dynamical simulations, Marko [13] demonstrated that, in phase separating systems, it is possible to have a uniform domain at the surface (''plating''), even when the equilibrium surface energies would predict two different phases at the surface. This can only be the case when thermal noise is small compared to the effective surface field. However, when thermal noise is increased, this uniform layer can no longer be supported and the surface consists of nucleated ''surface droplets.'' The transition from surface droplets to plating is known as the ''plating transition.'' In polymer systems, the low noise criterion can only be achieved in higher molecular weight (M_w) systems, and then usually only for very shallow quenches. The higher the molecular weight, the easier it will be to observe plating. Low molecular weight polymer blends are not expected to display plating at all, even for the shallowest quenches.

II. EXPERIMENT

Films of blends of deuterated polystyrene and poly(α-methylstyrene) were created by spin casting from toluene solution. All polymers were monodisperse (polydispersity less than 1.10) and were purchased from Polymer Standards Service (Mainz). In previous studies of these blends the stability of the PαMS was tested at high temperature [8]. PαMS is intrinsically unstable, but, by using an appropriate termination, the polymer will withstand the elevated temperatures needed for the experiments described below. Eight such blends were made, using different combinations of molecular weights, shown in Fig. 1. The films were about 1 μm thick, in order that finite size effects caused by the formation of the wetting layer could be ignored (although for the deepest quenches this proved not to be the case). All samples were annealed in vacuum ($<10^{-2}$ mbar) at 185 °C for a range of annealing times from a minimum of 20 min to a maximum of eight days. The oven temperature was considered stable to ±1 °C and the accuracy of the thermocouple was tested by observing an indium wire melt at 156 °C. We therefore attribute a systematic error of 1 °C and a random error of 1 °C to our results.

All measurements were made using the ion beam profiling technique of ^{3}He nuclear reaction analysis (NRA) [23] at the 8 MV Van de Graaff accelerator facility of the University of Freiburg. This technique enables a concentration-depth profile of a deuterated component to be measured. Monoenergetic (1 MeV) ^{3}He ions incident on the sample react with deuterium, creating protons and α particles. The energy of these particles is dependent upon the energy of the ^{3}He ions, which in turn is dependent on the depth z in the sample that the reaction took place. The depth dependence is due to the ^{3}He ions (and α particles) losing energy in traversing the sample. Either the α particles or protons can be detected. Since we are measuring the profile at the surface we mainly detect α particles [24].

III. RESULTS

A. Phase diagram

The phase diagram for blends of polystyrene and PαMS is well known (several references are listed elsewhere [8]). We use the measurements of Lin and Roe [25] as the basis of our phase diagram. They calculated an interaction parameter given by

$$\chi=\frac{A}{T}[0.0626-0.0018\phi-(5.6\times10^{-5})T], \qquad (2)$$

where T is the absolute temperature, ϕ is the volume fraction of d-PS, and A is a constant (53 K). The lattice parameter is 0.56 nm Å. We found that the value $A=53$ K was too low for our measurements; surface-directed spinodal decomposition was observed in films that should have been miscible with this interaction parameter. We were able to measure χ and so to scale the value of A by observing the value of ϕ in the depletion layer at the coexistence value behind a wetting layer for a metastable mixture [8]. This value remained constant with time, so any effect of phase separation in the metastable region of the phase diagram could be neglected. Another determination of coexistence was made by measuring the equilibrium surface excess z^* as a function of bulk d-PS concentration (the adsorption isotherm) [8]. In this case the measured surface excess should diverge logarithmically at the binodal:

$$z^{\star}=-Z\ln\left(\frac{\phi_\infty-\phi_\alpha}{\phi_\infty}\right), \qquad (3)$$

where Z is a constant and ϕ_∞ and ϕ_α are the respective bulk and binodal volume fractions. The adsorption isotherm for this blend is shown in Fig. 2.

We therefore use $A=84$ K for the least immiscible blend (35 000/41 700) and $A=77$ K for all others (it was measured

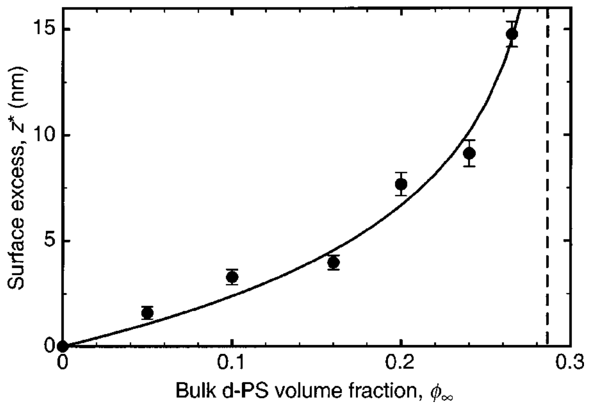

FIG. 2. Adsorption isotherm for the 35 000/41 700 blend at 185 °C. The surface excess diverges at $\phi = 0.28$, which we take for the binodal at this temperature.

for the 35 000/108 000 blend). For more immiscible systems it is more difficult to obtain this value accurately, because the depletion layer becomes smaller. In these cases, however, errors in the value of A are much less important. The reason for the discrepancy in the values of A and the difference of our χ value from that of Lin and Roe [25] is not clear but is likely to be due to slight differences in the synthesis of the PαMS. We note, for example, that the glass transition temperatures of the different PαMS samples have been measured by differential scanning calorimetry and are 169 °C ($M_w = 41\,700$) and 173 °C ($M_w = 108\,000$). This may be one reason why the values of χ are different, and there are likely to be others, an example of which might be the effect of different polydispersities in the different polymers. Since we measure all samples after heating at 185 °C (458 K), we are using our own measurement of χ in the present work. The Lin and Roe value [25] is used in its scaled form to calculate the location of the critical temperature, which is important for the calculation of the quench depths. Deeper quench depths may well be slightly in error if the temperature dependence of the value of χ is different from that measured in Lin and Roe's work. However, such an effect should be small and will not alter the conclusions of the present work.

B. NRA measurements of growth laws

We have measured samples for a variety of quench depths, from $\varepsilon = (\chi - \chi_s)/\chi_s = 0.06$ to $\varepsilon = 2.6$, where χ_s is the value of χ on the spinodal. Sample data are shown in Fig. 3. The surface excess was determined as the integrated amount of polystyrene

$$z^\star = \int_0^{z_0} \phi(z)dz, \tag{4}$$

where z_0 is the depth at which ϕ is a minimum (i.e., we measure the surface excess with respect to the height of the depletion layer and not the bulk volume fraction). At early times, we cannot tell whether or not the surface layer or surface phases have reached coexistence due to the limited resolution of the experiment. However, this uncertainty is present in very few samples and certainly will not affect the results that we present. Incidentally, we should point out that we are not using the local equilibrium approximation of Lipowsky and Huse [19] in our analysis. Since we are in the two-phase region of the phase diagram, it is very likely that, for deeper quenches, the depletion layer itself contains two phases.

In Fig. 4 we plot the measured surface excess as a function of annealing time. We show the growth laws as both double-and single-logarithmic plots, with the linear fit contained in the main plot. For the deepest quenches ($\varepsilon = 2.6$, 2.4, and 2.0) we found a surface excess $z^\star(t)$ growth close to $t^{1/3}$, with growth exponents of 0.34, 0.37 [Fig. 4(a)], and 0.35, respectively. The error in each exponent is about 0.02. For shallower quenches, which were at critical and off-critical compositions, the surface layer growth was logarithmic [Fig. 4(b)]. Finally, for the shallowest quench [$\varepsilon = 0.06$, Fig. 4(c)] we see that a rapid initial $t^{0.47}$ growth law eventually crosses over to a smaller growth exponent ($t^{0.13}$).

C. Atomic force microscopy measurements

Given the different growth regimes that we observed using NRA, it would clearly be desirable to acquire a three-dimensional image of the near-surface region. However, distinguishing between d-PS and PαMS proves to be a very difficult task given that the polymers are chemically quite similar. In spite of these limitations, we measured one set of films from each of the above growth regimes using atomic force microscopy (AFM). Sample images are shown in Fig. 5. For films that display a $t^{1/3}$ growth law for the surface wetting layer, the surface is initially rough, with a rms roughness of 3.6 nm after annealing for 270 min [Fig. 5(a)]. We see here small holes in the surface. These holes disappear at later times, when the surface is completely covered with d-PS. This is shown in Fig. 5(b) for a sample annealed for 10 945 min. The surface also becomes flatter, as befits a sample with a uniform surface layer; the roughness in this figure is measured at 1.9 nm. In the logarithmic growth regime, the surface does not display any evidence of roughness. Samples measured for 31, 1325, and 6532 min have a roughness of less than 0.6 nm. We show one example in Fig. 5(c) for the 6532 min sample. The behavior for the shallowest quench is quite striking. In Figs. 5(d) and 5(e) we show images for samples annealed for 752 and 10 945 min. The sample annealed for 752 min has a roughness of 4.0 nm. However, holes develop in these samples and grow. In the 10 945 min sample they are clearly visible. The area around the holes in this sample has a roughness of around 1 nm, indicating that the film has become more homogeneous. In the insets to Fig. 5, we show line scans of part of each image to clarify these height variations. The roughnesses quoted above were *not* calculated from these line scans, but from the complete images [the holes in Fig. 5(e) were excluded from the roughness calculations, however].

D. NRA measurements of single-chain diffusion

We shall see in the discussion below that it is useful to assess whether or not phase separation occurs in the bulk of the mixture with the shallowest quench. If phase separation were occurring, there would be two different entropic (reptation) diffusion coefficients, one corresponding to each phase. To measure these diffusion coefficients, a blend ($\phi = 0.518$, of the least immiscible 35 000/41 700 blend) was

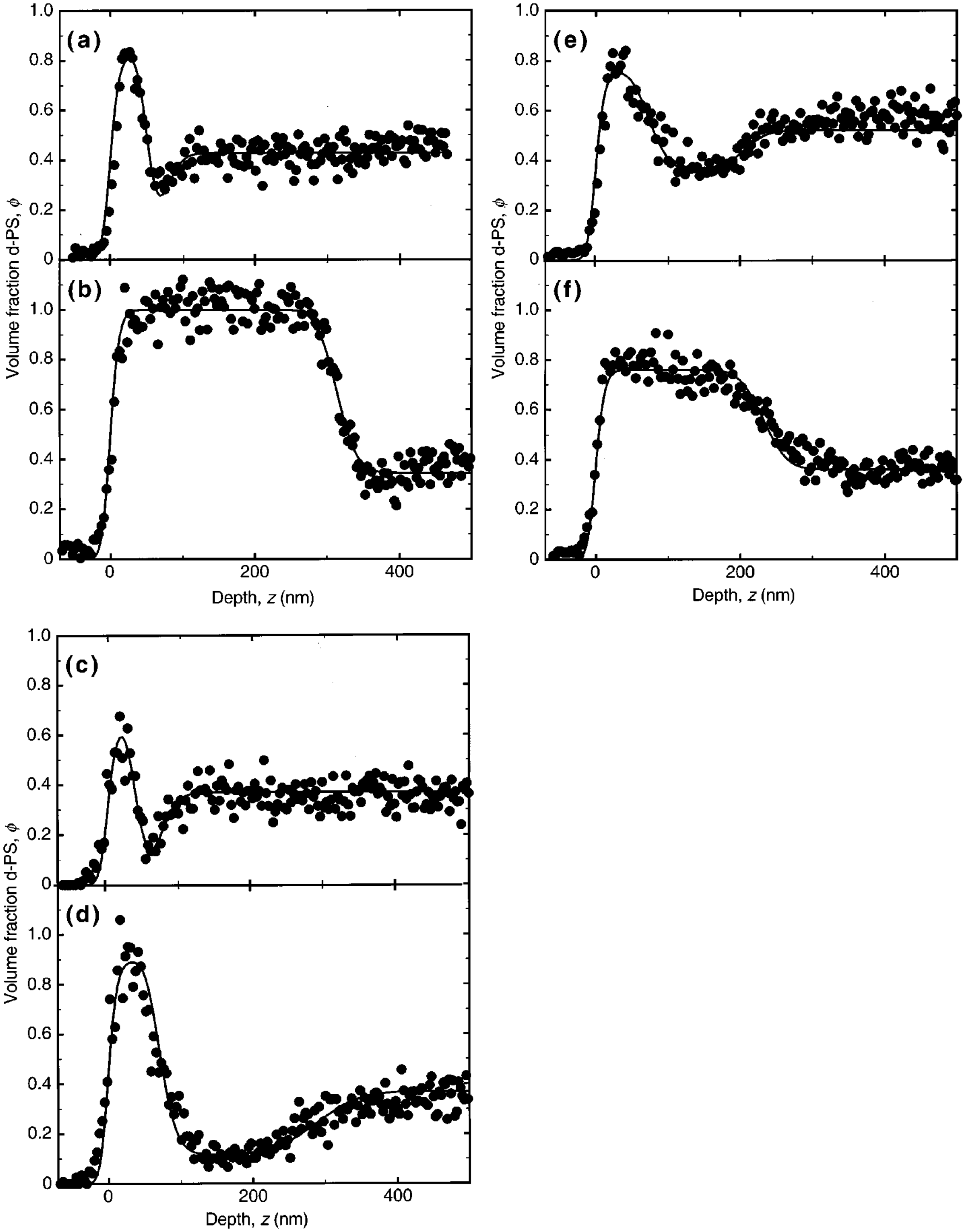

FIG. 3. NRA data for different annealing times for three different blends. In (a) and (b) we present data for the 163 000/108 000 blend after annealing for 270 and 8125 min, respectively. In (c) and (d) we present data for the 80 000/41 700 blend after 270 and 6000 min annealing, respectively ($\phi_\infty = 0.37$). In (e) and (f) we present data for samples from the 35 000/41 700 blend after respective annealing times of 270 and 2883 min.

floated off a glass microslide onto water. This was picked up on a silicon wafer onto which a similar film had already been spin coated to make a two-layer film (bilayer). The only difference between the two layers is that the bottom layer contained normal (nondeuterated) polystyrene (h-PS) with $M_w = 34\,000$ and $\phi = 0.515$. Given the similarity of the two layers there should be no thermodynamic barrier to diffusion across the two films. One can therefore measure the diffusion coefficient of the polystyrene in the mixture. Shown in Fig. 6 are the data for an unannealed bilayer, and bilayers annealed for 15 and 30 min at 187 °C. The diffusion coefficient in each film is $4.8 \times 10^{-13}\,\mathrm{cm}^2\,\mathrm{s}^{-1}$. It was not possible to obtain a diffusion coefficient in a similar experiment with $M_w = 108\,000$ PαMS in place of the 41 700 used here due to phase separation and nucleation in the as cast film.

IV. DISCUSSION

A. Deepest quenches

All evidence, both theoretical and experimental, suggests that for deep quenches the growth exponent should be $\frac{1}{3}$ [4,5,13–18]. Indeed, this is what we observe. The growth of the surface layer can be either through droplets of one phase forming and coalescing on the surface or via a uniform wetting layer. In our case, the roughness of the surface would indicate that a wetting layer did not initially form. However, at later times, when a pure d-PS layer was present at the surface, the roughness did significantly decrease to that for a homogeneous film.

The wetting layer in these samples consisted of d-PS with a volume fraction of very close to unity. In the 163 000/108 000 blend we saw the wetting layer grow to a thickness of some 500 nm. In this case finite size effects are significant. Here the surface layer probably formed from droplets rich in one phase. Since coexistence in these films is near unity, droplets rich in d-PS will expel PαMS-rich phases from the surface as these domains coarsen.

B. Logarithmic growth

The logarithmic growth has also been predicted theoretically [13,15], where a strong surface field orders the phases parallel to the surface. The slowing down is due to the fact that polymer motion must be cooperative if ordering is to persist into the film. It is hard to conceive of a mechanism whereby this surface growth is due to the formation of surface droplets and not to a wetting layer. Our AFM measurements support the existence of a uniform wetting layer because the surface remained relatively flat with roughnesses remaining less than 6 Å.

We are also able to make conclusions about the surface interaction in this system. In a numerical study of the kinetics of wetting in an unstable system, a logarithmic thickening of the surface layer was obtained for a short-ranged surface potential [15,16]. A Lifshitz-Slyozov-like power law of $t^{0.28}$ (the Ostwald ripening regime) was obtained only for a very long-range surface field [16]. In another numerical study [18] it was proposed that a polymer blend always exhibited a Lifshitz-Slyozov growth law when the system was undergoing bulk spinodal decomposition. Puri, Binder, and Frisch [16] argued that this would be so only if there were droplets at the surface. Our results support this conclusion [16]. Lipowsky and Huse [19] also report a slower growth of the wetting layer. They demonstrated that even in the metastable region the dynamics of the further growth of an initial thin wetting layer is proportional to $t^{1/8}$, $t^{1/10}$, and log(t) for nonretarded and retarded van der Waals forces, and short-range forces, respectively. All the available theoretical evidence leads us to conclude that the surface interaction is short range.

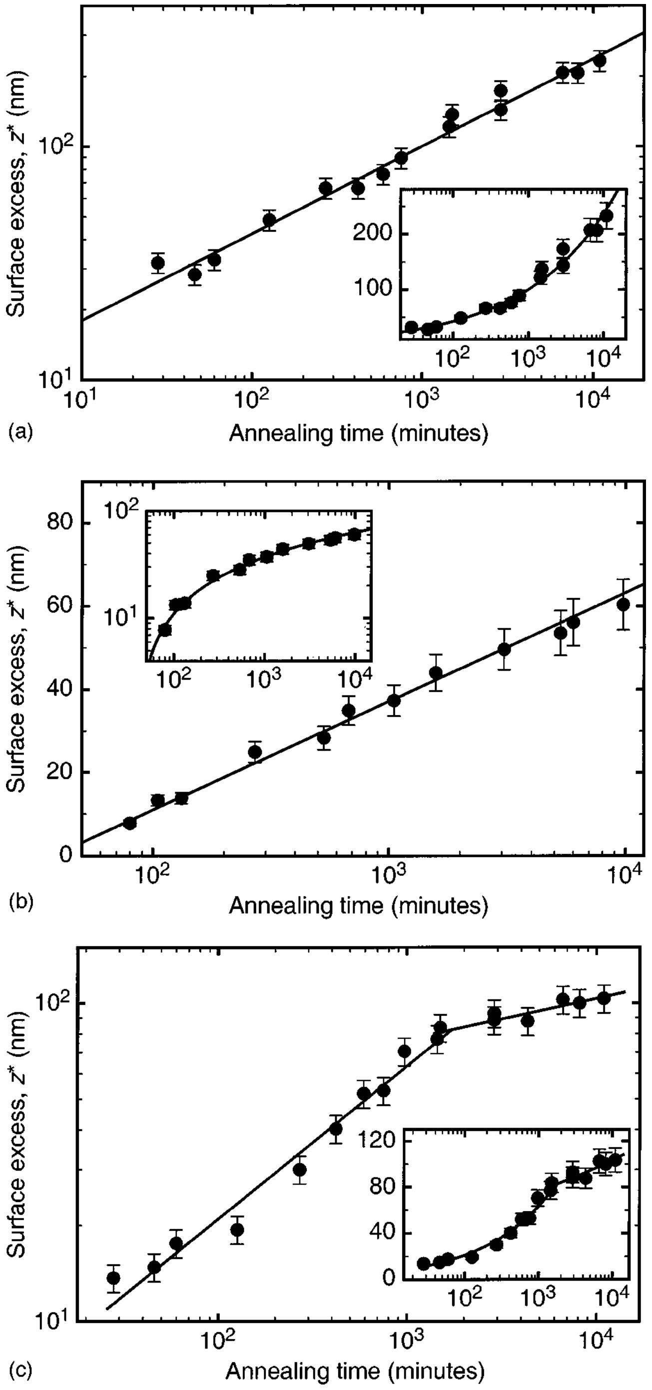

FIG. 4. The evolution of the surface excess z^* as a function of annealing time for quench depths of (a) $\varepsilon = 2.4$ (163 000/108 000), (b) $\varepsilon = 0.44$ (80 000/41 700, $\phi_\infty = 0.37$), and (c) $\varepsilon = 0.06$ (35 000/41 700). The best fit in (a) is to $t^{0.37 \pm 0.01}$. Most quenches, for example those in (b), have best fits to a logarithmic wetting layer growth. The shallowest quench (c) shows a crossover from $t^{0.47}$ scaling to a slower $t^{0.13}$ wetting layer growth. For comparison, the insets to (a) and (c) show the surface excess on a linear scale and the inset to (b) shows a double-logarithmic plot.

It has been suggested that the data presented in the earlier publication demonstrating surface-directed spinodal decomposition in a d-PS/PαMS blend [7] could be a very good realization of a low noise system on account of the logarithmic growth of the surface layer [11]. These authors argued that previous studies, specifically those on the isotopic poly(ethylenepropylene) (PEP/d-PEP) blend [5], corresponded to a high noise, low surface field regime. The suggestion was that the wetting layer in the PEP/d-PEP film was formed

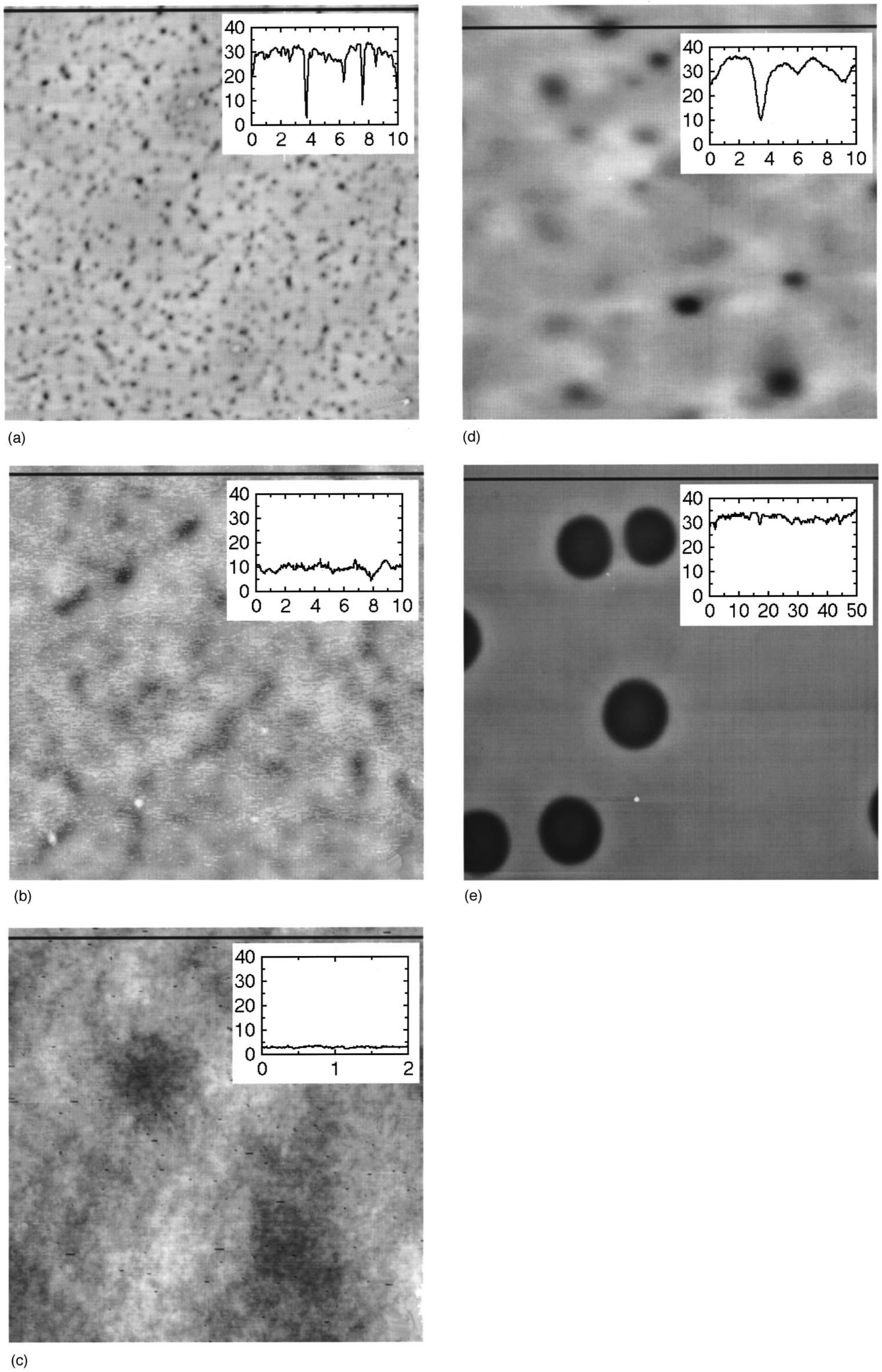

FIG. 5. AFM data, showing the topography of the surface of samples from each different growth regime. In (a) and (b) we show samples for the molecular weight pair 163 000/108 000 after annealing for 270 and 10 945 min, respectively. In (c) we show the surface of the molecular weight pair 35 000/108 000 ($\phi_\infty = 0.37$) after annealing for 6532 min. In (d) and (e) we show samples from the shallowest quench (35 000/41 700) after annealing at 185 °C for 752 and 10 945 min, respectively. The lighter regions of the figures represent higher areas and the relevant length scales are [length (μm) × width (μm) × height (nm)] (a) 10×10×50, (b) 10×10×20, (c) 2×2×5, (d) 10×10×50, and (e) 50×50×150. In the inset to each figure we show a line scan, to illustrate the roughness in the film (abscissas are in μm and the ordinates in nm). The lines used for these scans are shown in each image. In (a) and (e) we applied an offset to the height in the line scans to enable the use of the samescale in each plot.

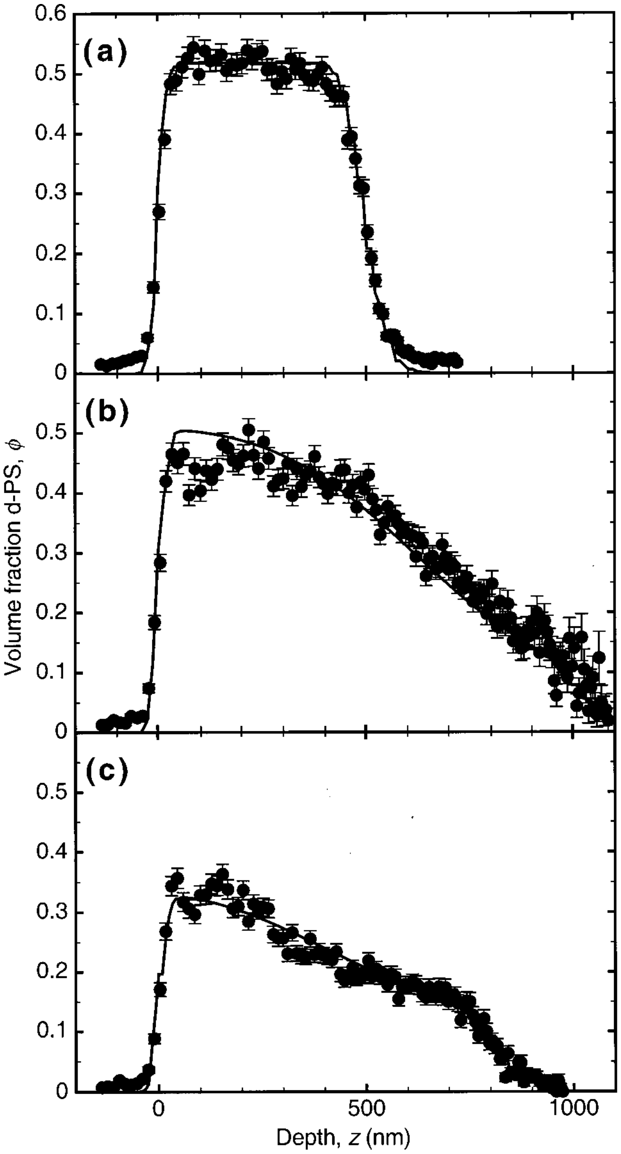

FIG. 6. NRA data for a diffusion couple in which the top and bottom layers have similar amounts of polystyrene ($\phi = 0.518$ and 0.515, respectively). The top layer contains the 35 000/41 700 blend, while in the bottom layer the $M_w = 35\,000$ d-PS is replaced by $M_w = 34\,000$ h-PS. In (a) we present data for the unannealed sample and in (b) and (c) the samples have been annealed at 187 ±1 °C for 15 and 30 min, respectively. The thickness of the upper layer varies considerably between bilayers (500, 670, and 370 nm, respectively). By measuring the diffusion across the boundary we show that a diffusion coefficient of $4.8 \times 10^{-13}\,\mathrm{cm^2\,s^{-1}}$ is appropriate in both cases.

from droplets on the surface. In fact, the greater ordering that occurs in the PEP/d-PEP blends (a second d-PEP-rich layer is visible behind the surface layer) may suggest that this blend is a better realization of the low noise system than the d-PS/PαMS blend studied here. We discuss this in more detail below when we consider the plating transition.

Incidentally, our measurements are not the first when a logarithmic growth law is replaced by $t^{1/3}$ for deeper quenches. This change in kinetics as a result of different quench depths has also been reported for AlZn alloys [26], where the growth law is $t^{1/3}$ at room temperature and log(t) at elevated temperatures.

C. Shallowest quench

The fast growth of $t^{1/2}$ for $\varepsilon = 0.06$ is probably driven by the curvature of domains at the surface, as would be expected for an Ising system [27]. We suggest that for this earlier stage of phase separation the surface layer growth can be described similarly to that with a nonconserved order parameter (Ising system) with the bulk acting as a reservoir for both components as given in the treatment of Sagui *et al.* [17]. In order for this to be possible, it is necessary that there be little or no phase separation in the bulk of the film. Should phase separation occur, the flux of material from the surface would be reduced, lowering the growth exponent. At later times we do see a slowing down of the surface layer growth. We assume that, at later times, when sufficiently large domains have formed at the surface, coalescence occurs, forming a wetting layer. After this ordering the further growth is slowed down by the thickening of a wetting layer. We estimated the growth exponent to be $\alpha = 0.13 \pm 0.02$, although we suspect that this growth is logarithmic. Once a wetting layer has formed, Ising-like behavior can no longer be observed due to the presence of a fully formed depletion layer. It seems reasonable to suppose that there is limited growth in the bulk of the film because the films are close to the spinodal. Bulk spinodal decomposition is controlled by interdiffusion. Interdiffusion is inhibited both inside and outside the spinodal by thermodynamic slowing down, a phenomenon already observed in d-PS/PαMS blends [28].

The speculation that phase separation in the bulk is slow is confirmed by the single-chain diffusion coefficient measurements (Fig. 6). Because the data for the two annealing times can be fitted using the same diffusion coefficient, we can assume that phase separation in the bulk is extremely slow. Furthermore, the value of the diffusion coefficient that we measured ($4.8 \times 10^{-13}\,\mathrm{cm^2\,s^{-1}}$) is in relatively good agreement with measurements of these diffusion coefficients for smaller values of ϕ (in the one-phase and metastable regions), the extrapolated value being $2.9 \times 10^{-13}\,\mathrm{cm^2\,s^{-1}}$ [29]. We conclude therefore that in the shallowest quench fluctuations can be neglected and the mixture is an extremely good example of a low noise system.

Neutron reflectometry data from a similar blend close to the spinodal also revealed a similar growth law [8] although in this case there were only four annealing times. In this paper it was suggested that nucleation affected the different growth laws in the metastable regime. We know now that this is not the case, with the two deeper metastable quenches probably being just inside the spinodal (their behavior is similar to the shallowest quench described above). Although there has been another observation of this growth law [30], it is for a small molecule mixture with the formation of the wetting layer already accomplished. In this case capillary flow due to hydrodynamic effects is responsible. This should not be the case for our polymer blend, particularly since we see a dropping off of the exponent at later times. Wiltzius and Cumming [3] observed even faster dynamics ($t^{3/2}$) for a polymer system. Although this result has not yet been satisfactorily explained, it is also likely to involve hydrodynamic effects.

The AFM data do not contradict our suggestion of curvature driven growth. The presence of holes at the surface demonstrates that there is no homogeneous wetting layer forming

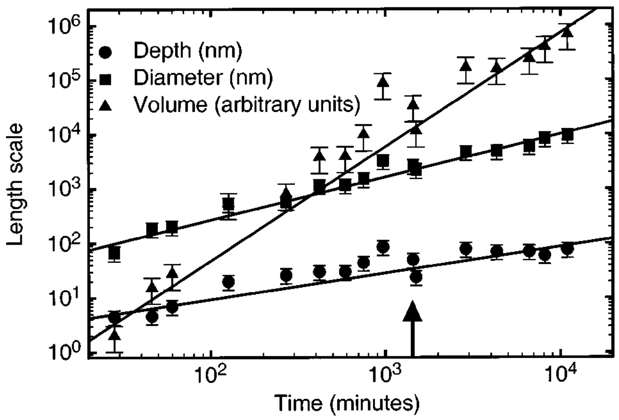

FIG. 7. The depth, diameter, and volume of the holes in the surface layer of the films for the shallowest quench as a function of annealing time. The volume is proportional to the product of the square of the diameter of the holes and their depth; the exact volume itself is not plotted. The volumes given are considered accurate to ~50%. The error bars on the depth and diameter are ±30%. The power law fits show that the depth, diameter, and volume of the holes grow as $t^{0.48}$, $t^{0.79}$, and $t^{2.1}$, respectively. The arrow signifies the point at which we observe a crossover in the growth of the surface layer from $t^{0.47}$ to $t^{0.13}$.

there; there must be two different phases at the surface. The crossover from the $t^{1/2}$ to $t^{0.13}$ growth laws corresponds to a flattening of the surface. In the $t^{0.13}$ growth regime the area around the holes is quite flat (~1 nm), whereas, when $t^{1/2}$ growth is observed, the surface has a greater roughness as measured by AFM (~4 nm). This fits in with the idea that in the slower growth regime a wetting layer has formed because the regions of the lower surface energy phase have coalesced to form a homogeneous wetting layer. The remaining questions are as to how and why these holes form, and whether or not they are relevant to our understanding of the wetting phenomena, or are just particular to the system we describe here.

The question as to how these holes form must remain open but we do propose possible explanations. The immediate suggestion is that dewetting has taken place. The holes have cross sections similar to that of a polymer dewetting from a more viscous substrate [31]. Could a d-PS-rich surface layer be dewetting from a PαMS-rich depletion layer? Since more immiscible blends did not display such behavior, this possibility is highly unlikely.

A more plausible explanation for the holes may be that as the two separate phases form at the surface, the region near the surface will shrink in volume. A d-PS-rich phase will not significantly cause a change in volume, but a PαMS-rich phase will contract rather more strongly, as it comes closer to its glass transition. The film then ruptures at the surface. If the polymer cannot move rapidly enough, the film will rupture. That we also see similar (albeit smaller) holes in the $t^{1/3}$ system [Fig. 5(a)] also supports this argument. Here, we also believe that there are two different phases at the surface. This means that here, as in the shallow quench, there is initially no uniform wetting layer. As PαMS-rich phases form at the surface, the film ruptures.

In Fig. 7 we show the growth of the volume of the holes (the product of the radius squared and the depth) as a function of time. The straight line shows the best fit, revealing that the volume of the holes grows as $t^{2.1}$. We note that there is no significant change in the growth of these holes at the same time as the growth rate of the wetting layer changes from $t^{1/2}$ to $t^{0.13}$ (the crossover from $t^{1/2}$ to $t^{0.13}$ is marked in Fig. 7). We conclude that the holes form when two separate phases form on the surface. This is due to the rupture of the films caused by the change in the volume of the two separate phases.

D. Wetting transition

Jones [22] argued that polymer mixtures are ideal systems to observe the wetting transition. This is because wetting can occur some distance away from the critical point in polymer mixtures. In our experiments, as we increase the quench depth, the growth laws governing the behavior of the wetting layer change from logarithmic growth to $t^{1/3}$. Such behavior is accompanied by a change in the roughness of the interface. When wetting is occurring, we should expect, and observe with AFM measurements, a flat surface. In the partial wetting regime, the film surface is rougher, consistent with nucleated droplets at the surface. We shall predict the location of the wetting transition using such simple arguments. The wetting transition occurs when the energy required to support two separate phases of a mixture is equal to the reduction in energy caused by having the lower surface energy phase at the surface [21].

To quantify such energy costs and gains more directly we consider that the free energy of this system is given by three contributions. It is energetically beneficial for the component of the lower surface energy to be situated at the surface. Against this, one needs to consider the energy cost in supporting two different phases. Finally, the interface between the two phases has its own contribution. We write the free energy per unit area as [32]

$$\frac{F}{k_BT}=f_s(\phi)+\int_0^\infty\left[G(\phi)-\phi\Delta\mu_\infty+\frac{a^2}{24\phi(1-\phi)}\left(\frac{d\phi}{dz}\right)^2\right]dz, \tag{5}$$

where a is the Kuhn segment length (0.67 nm for polystyrene), $f_s(\phi)$ represents the surface energy, $G(\phi)$ is the Gibbs free energy, and $\Delta\mu_\infty$ is the chemical potential evaluated in the bulk system. Both $G(\phi)$ and $\Delta\mu_\infty$ can be evaluated using Flory-Huggins lattice theory. The last term in the integral is the free energy cost of a gradient in composition and is evaluated in the strong segregation limit of the random phase approximation. The strong segregation limit is used because, in our blends, the crossover from logarithmic to $t^{1/3}$ growth occurs when $N\chi\approx 6\gg 1$ [33], where N is the chain length for an equivalent symmetric system. In the weak segregation limit the prefactor 24 would be replaced by 36. One minimizes the free energy using Euler's equation to obtain

$$-\mu_s=a\left(\frac{G(\phi)-G(\phi_\infty)-(\phi-\phi_\infty)\Delta\mu_\infty}{6\phi(1-\phi)}\right)^{0.5}, \tag{6}$$

where $-\mu_s$ can be considered as a surface chemical potential and is given by [22]

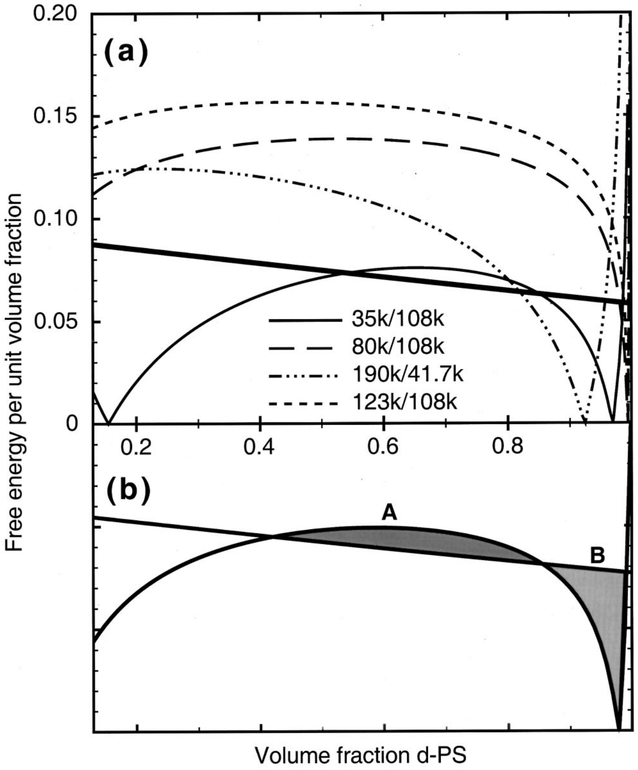

FIG. 8. (a) Phase portraits (Cahn plots) at 458 K for four of the blends used in this study. The blends correspond to 3, 4, 5, and 6 in Fig. 1. Of these, only the 35 000/108 000 blend displays complete wetting at equilibrium. The thick solid line represents the surface chemical potential [Eq. (7)]. (b) Idealized phase portrait. The wetting transition occurs when the shaded areas A and B are equal. When the area under B is greater than that under A, there is complete wetting, otherwise partial wetting represents the energy minimum.

$$-\mu_s = \frac{b^3 \Delta \gamma}{k_B T} - b\chi(\phi - \tfrac{1}{2}). \tag{7}$$

Here b is the lattice parameter (0.56 nm) and $\Delta\gamma$ is the surface energy difference between the two components (0.27 mJ m^{-2} [8]). We plot Eq. (6) and the right hand side of Eq. (7) for some of the polymer mixtures measured here at the calculated coexistence values [Fig. 8(a)]. In Fig. 8(b) we show the conditions necessary for a wetting transition. Only the 35 000/108 000 blend displays complete wetting at equilibrium, and this is well inside the region of logarithmic growth (Fig. 1).

Below we consider how a plating transition can extend wetting to regions where the minimum in energy corresponds to partial wetting. Before we draw such conclusions, it is important to note the limits of our calculations. If we used a surface energy difference between the two polymers of some 30% greater than that used in the calculations of the location of the wetting transition, the plating transition would not be needed to explain the observed behavior. The value used here is quoted from earlier measurements [8], and because of the different miscibilities and T_g's of the different PαMS samples used in these experiments, this is certainly possible, if unlikely.

E. Plating transition

Marko [13] postulated the existence of a plating transition for low noise systems. He defined low noise by introducing the inequality $\sqrt{g} < 1$, where

$$g = \frac{1}{\sqrt{N\varepsilon}} \tag{8}$$

and N is a chain length and we have replaced $1 - T/T_c$ by ε. When this noise is smaller than the surface field, ''plating'' occurs at the surface, and when the noise is greater, droplets form at the surface. This surface field is somewhat difficult to calculate but Marko points out that a reasonable estimate would be

$$s_B = \frac{\sqrt{N}}{k_B T \varepsilon} \sigma^2, \tag{9}$$

where k_B is Boltzmann's constant, b is the Kuhn segment length, and σ is of the order of the surface energy difference between the two polymers. Using 0.27 mJ m^{-2} for σ [8] and $N = 291$ (d-PS has a monomer molecular weight of 120.4 on our lattice), we obtain a surface field of 5.4. This we can compare with $g = 0.24$ ($\sqrt{g}/s_B \approx 0.09$). Using such an estimate we therefore should be well inside the plating regime of Marko, which is borne out by our results. For the smallest quench displaying $t^{1/3}$ kinetics (123 000/108 000) we obtain $\sqrt{g}/s_B \approx 0.49$ and for the deepest quench we measured (190 000/108 000), this was ~ 0.43. Although the ratio of thermal noise to surface field is less than unity, our results could still provide a demonstration of Marko's plating transition [13]. The reason why we observe surface droplets when $\sqrt{g}/s_B < 1$ is probably due to the approximations that we have made. The main approximation is that the parameter σ is equal to the difference in surface tensions of the two components. Marko pointed out that this parameter is of the *order* of the difference in the surface tensions of the two components. A better approximation would be to use the surface energy difference of the two phases. This will be lower than the surface energy difference of the two components, and will slightly lower s_B, increasing the ratio $\sqrt{g}/s_B$. Even this improvement is rather simplistic and we cannot take our estimated values of $\sqrt{g}/s_B$ as anything more than a first approximation. Also, since we estimated the quench depth from one value of coexistence at one temperature, any error in ε will also be translated through to our result. We suspect, however, that the approximations in σ are the main explanation of why $\sqrt{g}/s_B < 1$ in the surface droplet regime.

Marko's analysis of the isotopic PEP data of Jones *et al.* [9] is consistent with our results. He suggests that Jones *et al.* have $\sqrt{g}/s_B \approx 0.15$ and 0.13 in their mixture, which would correspond to plating. In our data, $\sqrt{g}/s_B \approx 0.15$ would correspond to the logarithmic regime, indicative of a wetting layer (i.e., plating). We note, however, that Marko's analysis contradicts the suggestion of Puri and Frisch [11] that the wetting in this system is driven by the formation of droplets at the surface.

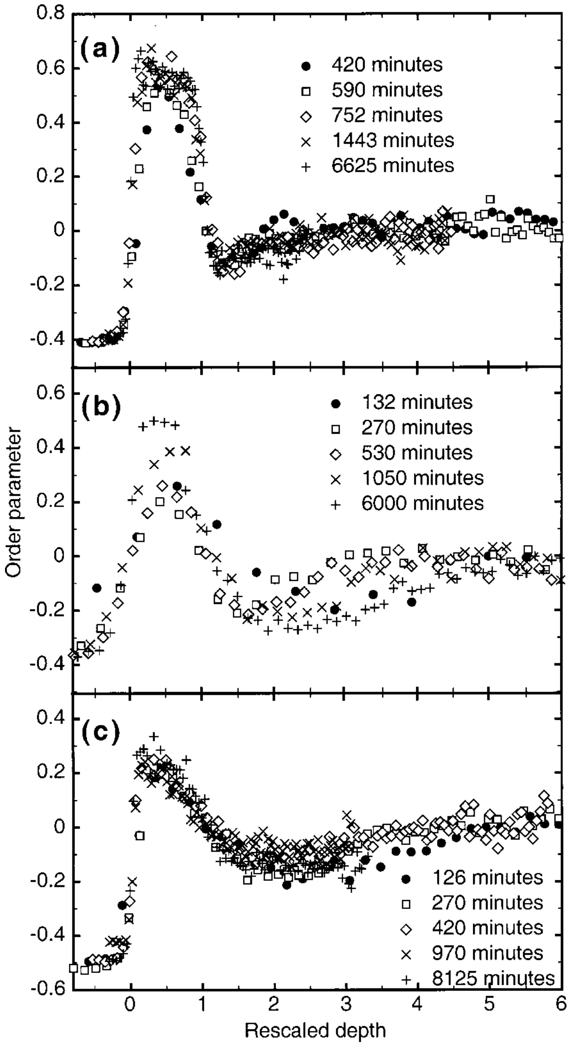

FIG. 9. Dynamic scaling tests for a blend in each of the observed growth regimes. The molecular weight pairs are as follows: (a) 163 000/108 000, (b) 80 000/41 700 ($\phi_\infty = 0.37$), (c) 35 000/41 700. The annealing times are shown on the figures. To reduce scatter and improve clarity, the data have been rebinned in groups of three points.

F. Dynamic scaling

It has been demonstrated theoretically [14] and experimentally [5] that when there is only one relevant length scale present, or when all length scales have the same growth law, dynamic scaling should occur. This means that the volume-fraction–depth profiles, when the depth is divided by the relevant length scale (the thickness of the surface layer, for example), should overlap each other. In Fig. 9 we show such data for one blend in each of the different growth regimes.

For the deepest quenches ($t^{1/3}$ growth law), as in the experiment of Krausch *et al.* [5], we observed dynamical scaling. For such deep quenches, all relevant length scales are expected to grow with such a scaling law; domains in the bulk as well as the surface layer. However, for shallower quenches when the surface layer grows logarithmically with time, it is not at all clear that any bulk phases in the vicinity of the surface should grow logarithmically. This is confirmed by the numerical simulations of Puri and Binder [15], in which the growth behavior parallel to the surface was different from that perpendicular to the surface. If the surface is growing logarithmically, and bulk domains are growing as $t^{1/3}$, dynamic scaling will not be possible simply because the depletion layer has a different growth law from the surface layer. Earlier measurements on this system [7] demonstrated that there could be two different growth laws occurring simultaneously. In these earlier measurements a growth close to the Lifshitz-Slyozov value was observed in a layer close the substrate, while the surface layer exhibited logarithmic growth.

Dynamic scaling provides an interesting test of our postulation that the surface layer growth is curvature driven. We have suggested that the work of Sagui *et al.* [17] provides the best explanation for the growth law at the shallow quench. If the surface layer growth is curvature driven at early times, with the bulk providing a reservoir, we need to assume that there is little or no phase separation in the bulk, otherwise the flux of material to the surface is depleted. In such circumstances, there should be only one length scale, that of the wetting layer, and therefore dynamic scaling should hold. We see in Fig. 9(c) that this is indeed the case. However, at late times, the depletion layer becomes so large that the only length available is the thickness of the wetting layer. In such circumstances dynamic scaling is not testable.

V. SUMMARY

In conclusion, we have experimentally demonstrated that, by changing the quench depth of a system, we can change the growth law of the surface wetting layer. In the chosen blend of d-PS and PαMS, a d-PS-rich surface layer is always observed after annealing at 185 °C. AFM measurements showed that the deepest quench samples were initially considerably rougher than for shallower quenches. This indicates that for these quenches droplets formed at the surface. In the films for the deepest quench a $t^{1/3}$ growth law was observed. For shallower quenches the growth of the surface layer was logarithmic in time. The small roughness for a film exhibiting logarithmic growth at the surface indicated a uniform wetting layer at the surface, in agreement with theoretical predictions. By estimating the surface field and noise, we have been able to show that our results are consistent with a wetting transition extended by a plating transition of the type predicted by Marko [13].

For the shallowest quench made we also observed, via AFM measurements, a rough surface. The rapid growth law ($t^{1/2}$) measured with NRA for the surface layer suggests a curvature driven growth of the coexisting phase with the lower surface energy (the d-PS-rich phase). This is supported by theory, providing there is no phase separation in the bulk [17]. Measurements of single-chain diffusion coefficients supported this suggestion that bulk phase separation is extremely slow. This growth law decays to a slower $t^{0.13}$ (possibly logarithmic) growth at later times, which tends to indicate coalescence of the regions of the lower surface energy phase and the formation of a wetting layer. Such a conclusion is supported by the flattening of the surface, as measured by AFM.

Dynamic scaling measurements support all of our conclusions. The observation of dynamic scaling for the deepest quench ($t^{1/3}$ growth) is not new [5]. The absence of dynamic scaling in the logarithmic region can be explained by bulk phase separation having a different growth law from that at the surface. If we suppose that for the shallowest quench there is little or no phase separation in the bulk, then we have only one length scale, and so dynamic scaling should be observed, which it is.

As a final remark, we note that the polymer blend studied here consists of two polymers with differing glass transitions. By measuring samples annealed at temperatures only ~15 °C above the higher of the two glass transition temperatures, concentration fluctuations may be minimized because they lead to significant variations in density. As such it may be that such blends will generally display low noise behavior and therefore act as ideal systems for testing mean-field behavior.

Note added in proof. We have become aware of experiments carried out at the same time as those in the present work, which have also identified the wetting transition in a polymer blend film: J. Rysz, A. Budkowski, A. Bernasik, J. Klein, K. Kowalski, J. Jedliński, and L. J. Fetters, Europhys. Lett. 50, 35 (2000).

ACKNOWLEDGMENTS

We thank Dr. R. Magerle for help with the AFM measurements and Dr. M. Müller for very useful discussions. M.G. thanks the Alexander von Humboldt Stiftung for financial support. G.K. and M.G. also acknowledge financial support through the Deutsche Forschungsgemeinschaft (SFB 481).

---

[1] J. S. Rowlinson and B. Widom, *Molecular Theory of Capillarity* (Oxford University Press, Oxford, 1982).
[2] G. Krausch, Mater. Sci. Eng., R. **14**, 1 (1995).
[3] P. Wiltzius and A. Cumming, Phys. Rev. Lett. **66**, 3000 (1991).
[4] W. Straub, F. Bruder, R. Brenn, G. Krausch, H. Bielefeldt, A. Kirsch, O. Marti, J. Mlynek, and J. F. Marko, Europhys. Lett. **29**, 353 (1995).
[5] G. Krausch, C.-A. Dai, E. J. Kramer, and F. S. Bates, Phys. Rev. Lett. **71**, 3669 (1993).
[6] U. Steiner and J. Klein, Phys. Rev. Lett. **77**, 2526 (1996).
[7] M. Geoghegan, R. A. L. Jones, and A. S. Clough, J. Chem. Phys. **103**, 2719 (1995).
[8] M. Geoghegan, R. A. L. Jones, D. S. Sivia, J. Penfold, and A. S. Clough, Phys. Rev. E **53**, 825 (1996).
[9] R. A. L. Jones, L. J. Norton, E. J. Kramer, F. Bates, and P. Wiltzius, Phys. Rev. Lett. **66**, 1326 (1991).
[10] G. Krausch, J. Mlynek, W. Straub, R. Brenn, and J. F. Marko, Europhys. Lett. **28**, 323 (1994).
[11] S. Puri and H. L. Frisch, J. Phys.: Condens. Matter **9**, 2109 (1997).
[12] R. C. Ball and R. L. H. Essery, J. Phys.: Condens. Matter **2**, 10 303 (1990).
[13] J. F. Marko, Phys. Rev. E **48**, 2861 (1993).
[14] G. Brown and A. Chakrabarti, Phys. Rev. A **46**, 4829 (1992).
[15] S. Puri and K. Binder, Phys. Rev. E **49**, 5359 (1994).
[16] S. Puri, K. Binder, and H. L. Frisch, Phys. Rev. E **56**, 6991 (1997).
[17] C. Sagui, A. M. Somoza, C. Roland, and R. C. Desai, J. Phys. A **26**, L1163 (1993). The $t^{1/2}$ kinetics is expected to be valid only in the limit of small surface fields.
[18] Z. Jiang and C. Ebner, Phys. Rev. B **39**, 2501 (1989).
[19] R. Lipowsky and D. A. Huse, Phys. Rev. Lett. **57**, 353 (1986).
[20] S. M. Troian, Phys. Rev. Lett. **71**, 1399 (1993).
[21] J. W. Cahn, J. Chem. Phys. **66**, 3667 (1977).
[22] R. A. L. Jones, Polymer **35**, 2160 (1994).
[23] For a review, see M. Geoghegan, *in Polymer Surfaces and Interfaces III*, edited by R. W. Richards and S. K. Peace (Wiley, Chichester, 1999), p. 43.
[24] U. K. Chaturvedi, U. Steiner, O. Zak, G. Krausch, G. Schatz, and J. Klein Appl. Phys. Lett. **56**, 1228 (1990).
[25] J.-L. Lin and R.-J. Roe, Macromolecules **20**, 2168 (1987).
[26] M. Hennion, D. Ronzaud, and P. Guyot, Acta Metall. **30**, 599 (1982).
[27] G. F. Mazenko, O. T. Valls, and F. C. Zhang, Phys. Rev. B **32**, 5807 (1985).
[28] M. Geoghegan, R. A. L. Jones, M. G. D. van der Grinten, and A. S. Clough, Polymer **40**, 2323 (1999).
[29] M. Geoghegan, T. Russ, and R. Brenn, report (unpublished).
[30] P. Guenoun, D. Beysens, and M. Robert, Phys. Rev. Lett. **65**, 2406 (1990).
[31] S. Qu, C. J. Clarke, Y. Liu, M. H. Rafailovich, J. Sokolov, K. C. Phelan, and G. Krausch, Macromolecules **30**, 3640 (1997).
[32] I. Schmidt and K. Binder, J. Phys. (Paris) **46**, 1631 (1985).
[33] For a review, see G. H. Fredrickson, in *Physics of Polymer Surfaces and Interfaces*, edited by I. C. Sanchez (Butterworth-Heinemann, Boston, 1992), p. 1.