Spinodal-Decomposition-Like Patterns via Metastable State Relaxation

M. Maaloum,(1),(2) D. Ausserre,(1) D. Chatenay,(2) and Y. Gallot(3)
(1)*Laboratoire de Physique Statistique des Polymères et des Interfaces, Université du Maine, BP 535, 72017 Le Mans CEDEX, France*
(2)*Laboratoire de Physico-Chimie des Surfaces et Interfaces, Université Pierre et Marie Curie and Institut Curie, Section de Physique et Chimie, 11 rue Pierre et Marie Curie, 75231 Paris CEDEX 05, France*
(3)*Institut Charles Sadron (Centre de Recherche Macromoléculaire-Ecole d'Application des Hauts Polymères), 6 rue Boussingault, 67083 Strasbourg CEDEX, France*

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The slow demixing of block copolymer thin films in relief domains is interpreted as a two-dimensional phase transition kinetics following a quench into a biphasic region of a phase diagram. The associated scalar parameter Ψ is a linear function of the local thickness of film. Two samples with critical Ψ's have been experimentally studied by atomic force microscopy. At long times, the two stable phases draw spinodal-decomposition-like patterns. At shorter times, the existence of an additional metastable phase is demonstrated and explained.

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Thin liquid films of symmetric A-B diblock copolymers have been observed in two different states: disordered or ordered (Ref. [1]). In the first one, their thickness can take any value. In the second one, the thickness is quantized and belongs to a discrete spectrum $d_p = pL/2$, where p is an integer which is either odd or even, depending on interfacial energies for the two blocks at the free surface of the film and at the solid/polymer interface.

The disordered state can be obtained in principle by increasing the temperature above the microphase separation temperature T_c. Actually, this equilibrium disordered state is often impossible to reach because of the chemical degradation of the polymer at high temperatures. A solid disordered state can also be obtained below the glass transition temperature of both polymers by spin coating from a solution. At macroscopic scales ($>1\ \mu$m along the surface) these two disordered states correspond to a homogeneous distribution of the two species, A and B. In terms of density distributions and within that resolution, the two states are equivalent. In both cases, a transition from a disordered state to an ordered state can be obtained by a temperature jump into the interval $T_g < T < T_c$. Note that T_g and T_c are expected to depend on the film thickness (Refs. [2,3]). The disorder-order transition corresponds to the formation of the lamellar stacking (microdomains) at a molecular scale. The lamellar structure imposes a quantized thickness of the film which in general is not compatible with its initial thickness in the disordered state. As a consequence, a demixing of the film into regions of two thicknesses d_p and d_{p+2} belonging to the spectrum of allowed values is observed (Ref. [4]). The resulting thickness domains have a minimum lateral extension of order 1 μm, much larger than the bulk microdomain dimensions. The local thickness $d(x,y)$ of the film is a function only of the x and y coordinates along the surface. The formation of the domains can therefore be viewed globally as a two-dimensional process. One can define a local order parameter as $\Psi(x,y) = [2d(x,y) - (d_p + d_{p+2})]/L$. In the equilibrium ordered, $\Psi(x,y) = +1$ or -1. Within the hypothesis of incompressibility of the polymeric material, the average order parameter $\langle \Psi(x,y) \rangle$ over the sample surface is conserved. In terms of phase transitions, the two coexisting thicknesses correspond to two different surface densities of the single component material (the ordered copolymer). The formation of the domains from the single phase state therefore modelizes a phase separation process during a quenching experiment in a two-dimensional system.

The expected variation of the free energy of such a system with the order parameter for $T < T_c$ is drawn schematically in Fig. 1 (full line). The energy of the *ordered* homogeneous state at $\langle \Psi \rangle$ corresponds to point I, while

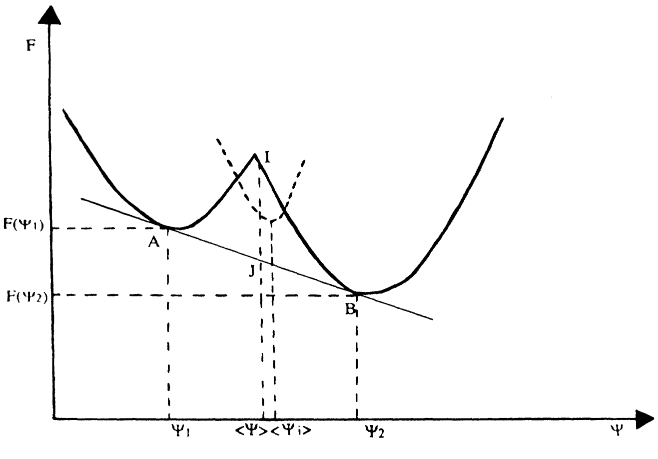


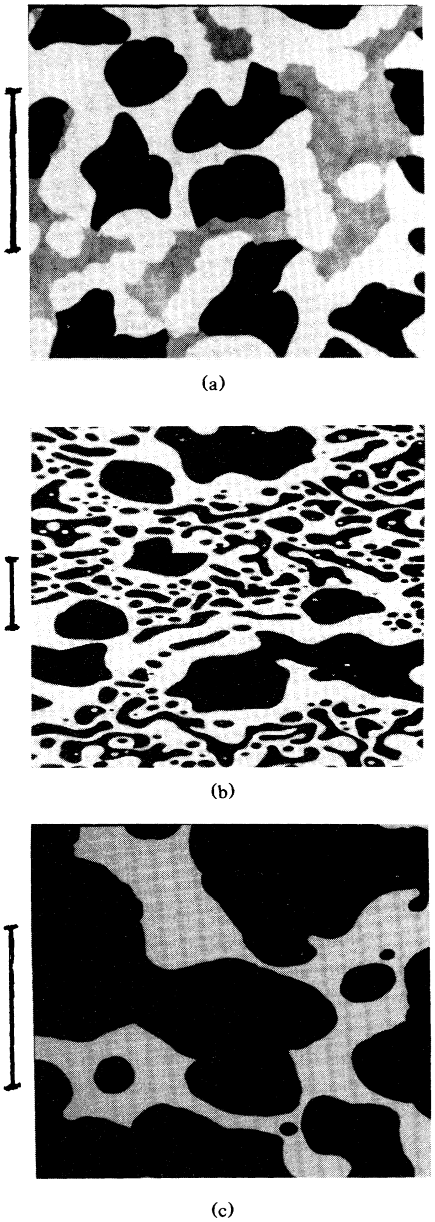
FIG. 1. Variations of the coarse-grained free energy of an ordered copolymer film with the order parameter Ψ. The full line curve with the two minima is the shape expected for a system with two stable phases. The dotted line curve illustrates the presence of a third minimum in $F(\Psi)$ leading to the formation of an additional metastable state.

the energy of the final (demixed) state at the same $\langle\Psi\rangle$, neglecting line tension, corresponds to the crossing at point J of the vertical line at $\langle\Psi\rangle$ and the straight line joining the two minima. According to the lever rule, the final surface fractions occupied by regions at $\Psi_1=-1$ and $\Psi_2=+1$ depend only on $\langle\Psi\rangle$. It is in particular independent of the relative height of the two minima $F(\Psi_1)$ and $F(\Psi_2)$. The energy of the initial disordered copolymer film is unknown but the latter is assumed to be unstable, although this is not essential for our task. Within this assumption, the whole relaxation mechanism should be viewed as a spinodal decomposition (Ref. [5]).

Let us now suppose that a third (relative) minimum is introduced in F at some critical $\langle\Psi_i\rangle$, intermediate between Ψ_1 and Ψ_2, as shown with dotted lines in Fig. 1. It corresponds to a new (metastable) state in which the system can be found at intermediate times. A new degree of freedom is therefore injected in the system which can now divide itself in three different states prior to complete demixing. The presence of this additional minimum is expected to affect the relaxation process for close-critical values of the order parameter $\langle\Psi\rangle$ and could influence the shape of the domains after complete demixing (Ref. [5]).

The present paper experimentally demonstrates the existence of such relaxation mechanisms.

The film is made of polystyrene-polymethymetacrylate (PS-PMMA) copolymer for which p is odd (Ref. [6]). The molecular mass of the two blocks are, respectively, $M_{\rm wPMMA}=26\,300$ and $M_{\rm wPS}=30\,700$ with very low polydispersity indices: $I_{\rm PS}=1.06$ and $I_{\rm COP}=1.05$, synthetized using anionic copolymerization. The copolymer was deposited on an oxydized silicon wafer by spin coating from a toluene solution. The initial close-critical thicknesses of the disordered films were of order 600 Å and 300 Å (close to $2L$ and L, respectively). The free surface topology was explored using a Nanoscope commercial atomic force microscope (digital, U.S.A.) in the constant force mode at 2×10^{-8} N after freezing the samples at room temperature.


(a)

(b)

(c)

FIG. 2. (a) Atomic force microscopy images of a sample with an average thickness $d\simeq 2L$. The length bar is 10 μm. The Z scale has been enlarged for the sake of simplifying image reproduction. It is not significant to the actual variations in Z, given in the text. (a) After annealing for 10 h; (b) after annealing for 24 h; and (c) after annealing for 240 h.

Figure 2 presents atomic force microscopy (AFM) images of a film of initial thickness $d\simeq 2L$ after annealing at 170 °C for 10 h [Fig. 2(a)], 24 h [Fig. 2(b)], and 240 h [Fig. 2(c)]. The long time pattern [Fig. 2(c)] is made of two stable coexisting thicknesses at $3L/2$ (black) and $5L/2$ (white). It is a typical structure of a spinodal decomposition (characterized by a single correlation length) (Ref. [5]). At intermediate times [Fig. 2(b)], a different pattern is obtained, made of the same two thicknesses, but not characterized by a single correlation length. At shorter times [Fig. 2(a)], one gets three coexisting thicknesses: $3L/2$ (black), $2L$ (grey), and $5L/2$ (white). Regions at $2L$ could be either (i) parts of a disordered film which has not yet demixed, (ii) semiordered domains with a well-defined lamellar stacking close to the solid surface covered by a mixed layer of PS/PMMA (Ref. [7]), (iii) partially ordered domains with a well-defined lamellar stacking close to the free surface covering a mixed layer of PS and PMMA, or (iv) and (v) ordered domains blocked into a metastable state at $2L$. The latter should be understood as a film with a correct L period but some defect in the piling order of the two species. Assuming that the differences $\gamma^{LV}_{\rm PMMA}-\gamma^{LV}_{\rm PS}$ at the free surface and $\gamma_{\rm PS/PMMA}$ at the polymer-polymer interface are close to the values measured in melts (Ref. [8]), respectively, 0.1 dyn/cm and 1.2 dyn/cm, one deduces that the defect in the piling is located at one boundary rather than inside the film. Hence, the wrong polymer species has to be present either at the free surface or at the solid wall. The two possible metastable states are therefore (iv) PMMA at the free surface instead of PS and (v) PS against the solid wall instead of PMMA. It leads finally to five possibilities, referred to as (i), (ii), (iii), (iv), and (v). Each of them corresponds to a given composition of the polymeric material at the free surface, respectively: (i) mixed PS and PMMA, (ii) mixed PS and PMMA, (iii) PS, (iv) PMMA, and (v) PS. A chemical analysis of this composition would be of great interest. More simply, one can use breath figures to demonstrate that the free surface of regions of intermediate thickness is not PS by contrast with their aspect on the $3L/2$ and $5L/2$ domains. This is shown in Fig. 3, obtained using a reflection microscope (Polyvar Reichert) after blowing over the surface of a three phase sample at $2L$. The size and density of the water droplets appear as identical everywhere over the stable domains and very different over regions of intermediate thickness. The only remaining possibilities therefore correspond to cases (i), (ii), and (iv).

Figure 4 shows the time evolution of a film with an initial thickness $d=0.8L$. It presents the same quantitative features as Fig. 2. This second example illuminates the previous discussion. Indeed, the average or initial thickness d of the film is now significantly different from the intermediate thickness L. Were the intermediate film disordered, it would have no constraint on its thickness and would remain at d, which is not the case. We therefore conclude the existence of a metastable ordered film at L, with PMMA at the free surface. The same conclusion is extended to the $2L$ sample. It corresponds to case (iv).

The shape of the patterns obtained at intermediate times [Fig. 4(b)] will not be discussed extensively here. We just underline presently that local matter conservation confines the exchanges between areas of different thicknesses in the vicinity of "triple points," i.e., contact points of the three phases. The small dark circular spots in the intermediate film [Fig. 4(a)] are interpreted as the result of the initial demixing of the unstable film at $d \simeq L$ in two domains at $L/2$ (stable) and L (metastable).

Coming back to Fig. 2(b), the patterns observed sup-

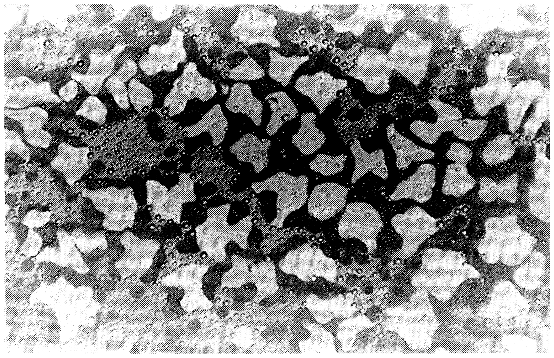
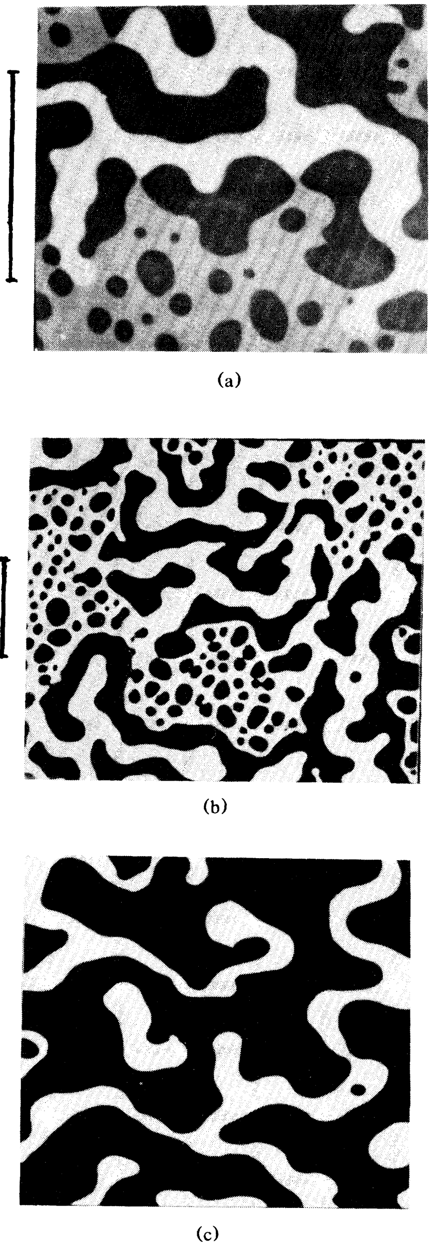


FIG. 3. Optical micrography (in reflection) of a breath figure on a three phase sample at $d \simeq 2L$. Full horizontal scale: 300 mm. The shape, density, and size of droplets are different on metastable and stable regions. The brightness of the droplets is directly related to their shape, since they act as optical lenses.



(a)

(b)

(c)

FIG. 4. AFM images of a sample with thickness $d \simeq L$, after annealing for (a) 10 h, (b) 24 h, and (c) 240 h. The length bar is 25 μm.

port the same qualitative conclusions for the $2L$ films, namely: (i) matter exchanges localized in the vicinity of the triple points and (ii) islands at $3L/2$ into areas at $2L$ resulting from the early stage demixing of the initial film at $d \gtrsim 2L$. Note that we have $\langle \Psi \rangle < \langle \Psi_i \rangle$ for the $2L$ film, and $\langle \Psi \rangle > \langle \Psi_i \rangle$ for the L film.

On the whole, the demixing of the film can be viewed as a three stage process: (1) demixing of the unstable film into one stable and one metastable state; (2) demixing of the metastable state into the two stable ones; and (3) growth of the pattern made of the two stable thicknesses, with asymptotic shapes characterized by a single correlation length. Using the classical partition between nucleation versus spinodal decomposition processes, the first stage is assimilated to a spinodal decomposition (assuming the disordered film to be unstable), while the second stage unambiguously belongs to nucleation phenomena, since it corresponds to the relaxation of a metastable state. The final structure, however, is a typical spinodal decomposition pattern. This illustrates the possibility of obtaining such structures via the relaxation of metastable states. More generally, the present study points out the importance of possible metastable states in phase transition kinetics. Hopefully, it also illustrates the potentialities of copolymer thin films as model systems for experimental investigations on two-dimensional phase transitions.

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Laboratoire de Physique Statistique des Polymères et des Interface is Unité associée au CNRS No. 807. Laboratoire de Physico-Chimie des Surfaces et Interfaces is Unité associée au CNRS No. 1379.

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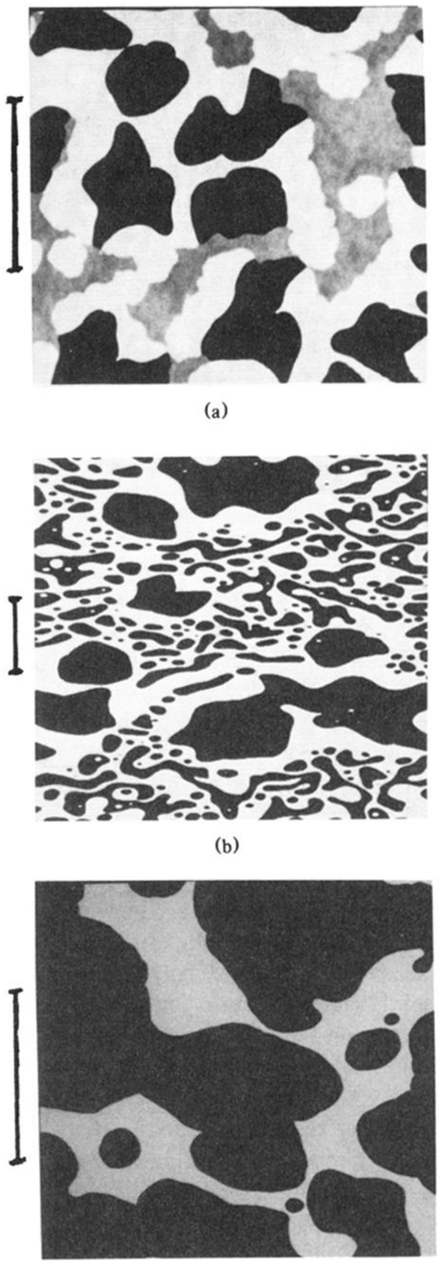

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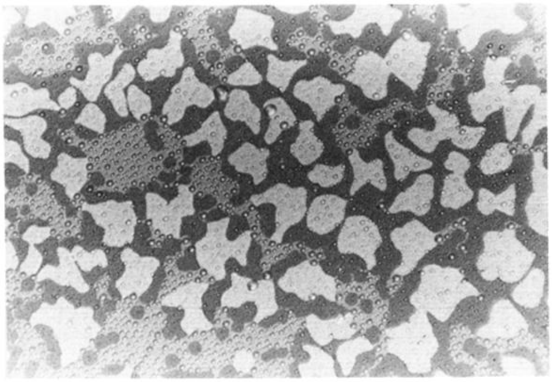

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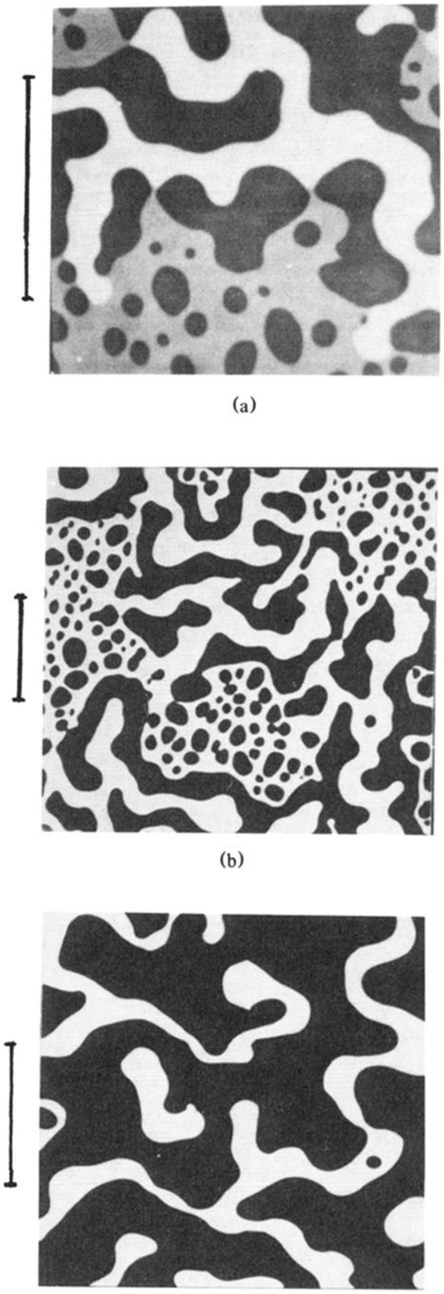

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