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Classification

Physics Abstracts

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Kinetics of growth of islands and holes on the free surface of thin diblock copolymer films

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Abstract. — When prepared on a silicon wafer and annealed above the glass transition temperature T_g , symmetric, diblock copolymers of poly(styrene-*b*-butylmethacrylate), P(S-*b*-BMA), exhibit a multilayer structure parallel to the substrate and islands (or holes) are formed on the free surface of the films. *In situ* interference microscopy has been used to follow the kinetics of growth of these islands or holes. It is shown that the kinetics of growth depends on the initial density of islands (or holes) : at 140 °C, for intermediate annealing times, there is no time-evolution of the free surface for dilute systems while for more concentrated ones, the size distribution function of islands or holes verifies a scaling law *versus* time. For longer annealing times at 170 °C, the ultimate behavior of the copolymer film is to eliminate islands or holes by allowing the permeation of the copolymer molecules into the inner layers of the film.

Introduction.

The behavior of diblock copolymers AB at surfaces and interfaces has received widespread attention in recent years [1-21]. Most studies have focused on the influence of external surfaces on the ordering in thin films [4-10, 13, 16, 17, 20]. More generally, the effect of symmetry breaking at interfaces on the microstructure and the transitions of systems that exhibit order-order and order-disorder transitions (including liquid crystals [22-24], polymer blends [25] and metallic alloys [26, 27]) has attracted considerable interest.

In the bulk, diblock copolymers undergo a phase transition from a disordered melt existing at high temperatures to various ordered mesophases that appear as the temperature is lowered. Such mesophases result from both the incompatibility between the two blocks and the connectivity constraints that hinder this phase separation. The morphologies of the various mesophases range from ordered spheres of one block embedded in a matrix of the other to

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alternating lamellar structures, depending on the relative length of the blocks [6, 28-33]. Lamellar microdomains are encountered in the case of symmetric diblock copolymers, i.e. when the volume fraction of the blocks A and B is equal.

Among the variety of different possible mesophases, it is the behavior of symmetric diblock copolymers in thin films which has been the most investigated. For such thin films, the interactions of the blocks with the interfaces have been shown to induce a nearly perfect orientation of the lamellar microdomains parallel to the film surface producing a multilayered structure [4, 6, 8-10, 13, 20]; as a consequence, the film thickness e_{ord} in the ordered state is quantized [8-10, 12, 13]:

$$\begin{aligned} e_{\text{ord}} &= (n + 1) L && \text{if the same block is present at both interfaces} \\ e_{\text{ord}} &= (n + 1/2) L && \text{if it is not} \end{aligned}$$

where n is an integer ≥ 0 and L is the lamellar period.

In the particular case of symmetric diblock copolymer of poly(styrene-*b*-*n*-butylmethacrylate), P(S-*b*-BMA), the copolymer of interest here, interference microscopy measurements [8, 12] have shown that, for thin films prepared on a silicon wafer, their thickness in the ordered state is given by: $e_{\text{ord}} = (n + 1) L$. Since the surface energy of PBMA is lower than that of PS [34], PBMA is expected to be located at the air/polymer interface; thus, the thickness quantization, $e_{\text{ord}} = (n + 1) L$, imposes that PBMA lies also at the substrate/polymer interface (Fig. 1).

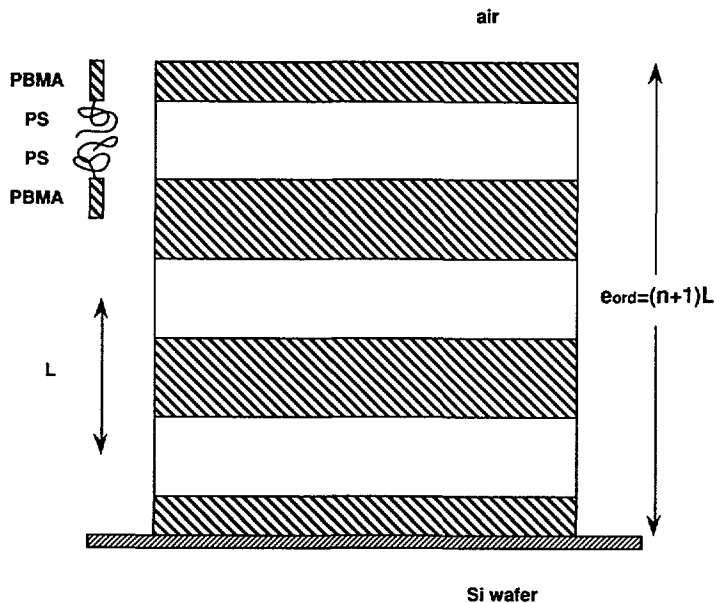


Fig. 1. — Schematic of the lamellar stacking in P(S-*b*-BMA) copolymer thin films deposited on silicon substrate. Each lamella is a bilayer of one component either PS or PBMA.

In general, the free surface of such thin films is not flat and smooth. Recent optical microscopic studies have reported the presence of islands or holes on their free surface [12, 14]. Indeed, when prepared by spin coating a copolymer solution onto a substrate at

temperatures T below the glass transition temperature T_g of the two blocks, as-cast thin films are in a disordered state, their surface is rough ($\sim 5 \text{ \AA}$) [35] and their thickness e_{ac} is determined by the amount of copolymer deposited on the substrate. The lamellar ordering can be induced by annealing these films at temperatures T between T_g and the microphase-separation temperature (ODT) [8-10, 12-14]. It is very unlikely that e_{ac} corresponds exactly to $e_{ord} = (n + 1)L$ and it has been shown that the morphology of the free surface of the ordered film depends on its initial thickness e_{ac} . If e_{ac} is equal to $(e_{ord} + \delta e)$ with $0 < \delta e < L$, the free surface is covered either with islands ($0 < \delta e < L/2$) or holes ($L/2 < \delta e < L$) of height L [12, 14]. This behavior allows the minimization of the interfacial energy at the air/polymer interface by putting the block component which has the lowest surface energy at the free surface, but creates a line free energy excess [8-10, 12-16]. It should be pointed out that another scenario could have been expected : a homogeneous copolymer layer of thickness δe lying on top of a lamellar stacking of thickness e_{ord} ; this situation would prevent the formation of islands or holes, but would not minimize the interfacial energy at the air/polymer interface. Obviously, both the lamellar ordering process and the formation of islands or holes are governed by the minimization of the interfacial energies. Indeed, we have shown in a previous paper [18], that the formation of islands or holes, of height L , on the free surface of copolymer films reflects the inner lamellar ordering process.

In this study, *in situ* interference microscopy has been used to follow the kinetics of growth of such islands and holes formed on the free surface of thin films of symmetric diblock P(S-b-BMA) copolymer and to investigate the ultimate morphology of the free surface as well. It has to be pointed out that islands and holes grow once the inner lamellar stacking is built up and that, in contrast with the formation stage, the growth stage is not related with the lamellar ordering mechanism. In the light of previous experiments on the kinetics of formation of islands and holes [18], systems with various surface coverages of islands or holes have been studied. Indeed, in terms of kinetics of formation, systems of islands and holes can be divided in two classes : the concentrated one (high surface coverage) where the kinetics of formation is fast, collective and characterized by isotropic spatial correlations and, in contrast, the dilute one (low surface coverage) where the kinetics of formation is slow, individual and without spatial correlations.

In this report, it is shown that dilute and concentrated systems of islands or holes do not exhibit the same kinetics of growth and that the ultimate behavior of the copolymer film is to eliminate as much as possible the incomplete top layer at the free surface.

Experimental.

The symmetric diblock copolymer of poly(styrene-*b*-butylmethacrylate) P(S-*b*-BMA), used in this study, was synthesized by anionic polymerization at the Institute Charles Sadron, Strasbourg (France). The average molecular weight M_w of the copolymer was 82,000 with a total number of segments, N , of 680 and a PS fraction f_{PS} of 0.59. The weight to number average molecular weight ratio M_w/M_n was 1.05. All these characteristics have been determined at the Institut Charles Sadron from size-exclusion chromatography coupled with light scattering measurements and viscosimetry. The glass transition temperatures of the blocks were measured by differential scanning calorimetry (D.S.C.) :

$$T_g(\text{PS}) = 102 \pm 2 \text{ }^\circ\text{C} \quad \text{and} \quad T_g(\text{PBMA}) = 30 \pm 2 \text{ }^\circ\text{C} .$$

Films of the copolymer were prepared with thicknesses ranging from 600 Å to 900 Å by spin coating a solution of the copolymer in toluene onto silicon substrates (2.5 cm in diameter, 300 μm in thickness), previously cleaned by oxidation of the surface impurities by U.V. irradiation under oxygen flow [36]. Specimens were then dried under vacuum overnight to

remove residual solvent. By varying both the concentration of the solution and the spinning speed, the film thicknesses e_{ac} were chosen in order to obtain, after annealing, either islands or holes, located in the incomplete top layer lying between $2L$ and $3L$, with different area coverages : both dilute and concentrated systems as well as intermediate situations have been investigated. The different systems of islands will be denoted in the following : CI (concentrated islands), SCI (semi-concentrated ones), DI (dilute ones) and CH, SCH, DH will refer to systems of holes as well.

Due to the spin coating process, the perimeter of the specimen exhibits a « bump » with thickness variations that can be large (up to $6\,000\text{ \AA}$) [8, 12]. Since this bump of material could act as a « reservoir » during the annealing procedure, it has been removed in order to avoid any flow of the copolymer molecules from the perimeter to the central part of the film. For each film thickness, kinetic experiments have been performed on circular films of two different diameters Φ in order to detect any influence of the film size on the growth laws [15] : $\Phi = 24\text{ mm}$ and $\Phi = 0.8\text{ mm}$; the latter value corresponds to the smallest film size allowing a reliable statistical analysis of the kinetics of growth for all the different systems of holes and islands (i.e. such that the total number of islands or holes is always greater than 100 even after long annealing times).

The examination of the film surface was made by *in situ* interference microscopy [8, 12, 14]. The copolymer films were annealed at $140\text{ }^\circ\text{C}$, under nitrogen atmosphere, for the desired period in a Mettler hot stage fixed onto the stage of the optical microscope. The study of the kinetics of growth of islands (or holes) on the free surface of the copolymer films consists mainly in measuring the time-dependence of the mean radius of the islands (or holes). To obtain an accurate expression of the growth laws, it is necessary to perform the kinetics of growth over two decades in time at least. On the other hand, in order to avoid any degradation of the copolymer molecules, the duration of the annealing procedure could not be longer than two weeks (about $22,000\text{ min.}$) ; thus, it was imperative to choose an annealing temperature such that the stage of formation of islands (or holes) of height L would be as short as possible. The choice of the annealing temperature has been made by investigating the time-variation of the height of the islands at different temperatures by Atomic Force Microscopy [18]. In the case of concentrated systems of islands (CI) or holes (CH), $T = 140\text{ }^\circ\text{C}$ was found to be the right value of the annealing temperature ; indeed, for such a temperature, the formation stage of the islands or holes lasts less than 100 min allowing a reliable analysis of the growth stage over a sufficiently long time.

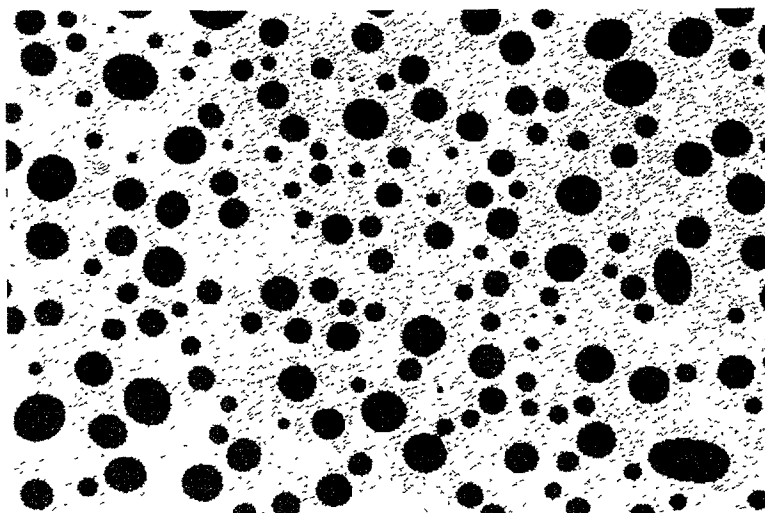
A Reichert Polyvar-Met microscope was used under reflection conditions to obtain interference colors from the white light source. The aperture diaphragm was closed down to ensure a parallel beam of light. The use of interference microscopy to investigate the free surface morphology of thin copolymer films has been previously presented [8, 12, 14] ; however, it has to be pointed out that, since each interference color corresponds to a specific film thickness, this technique is very suitable for detecting the existence of steps, islands or holes on the free surface. Furthermore, in previous works [8, 12], it has been shown that interference microscopy was very appropriate to measure the mean period L of a lamellar stacking. For the copolymer under study, the $2L$ and $3L$ thicknesses appear respectively as light-brown and violet interference colors and the mean lamellar period L was found to be equal to : $L = 300 \pm 10\text{ \AA}$.

The optical microscope was equipped with a high resolution CCD camera (COHU 4710). The image analysis has been performed by means of a Visilog 3.6 software (Noesis, France) ; most operations were carried out by a Compaq Deskpro 386/20 MHz microcomputer. Parameters such as the individual area of islands (or holes), the percentage of area occupied by the islands (or holes), their total number and their size distribution function were extracted in order to establish the growth laws of islands (or holes).

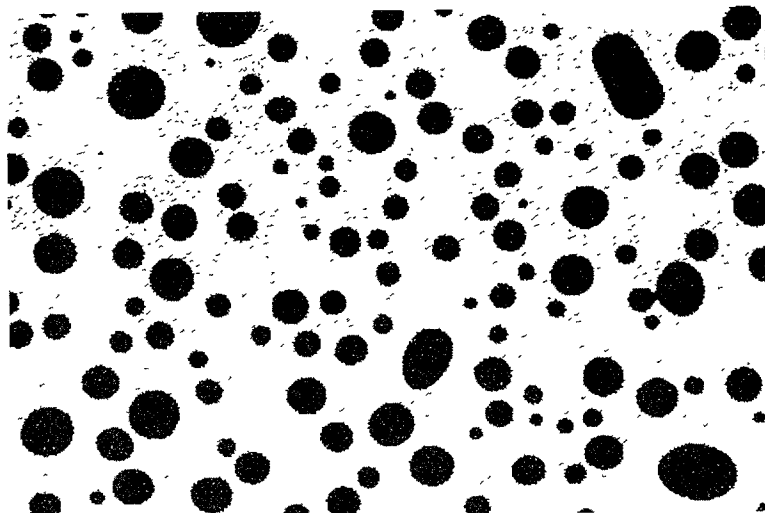
Results and discussion.

From a close examination of the images obtained during the kinetics of growth of all the different systems of islands or holes, several qualitative remarks can be made :

i) the centers of mass of islands or holes are fixed, i.e. there is no diffusive motion of either islands or holes in the plane of the free surface (Fig. 2) ;



a)



b)

Fig. 2. — Digitized images of optical micrographs of a P(S-b-BMA) copolymer thin film annealed at 140 °C : evolution of islands (black patches) with the annealing time : a) 12,000 min, b) 21,000 min, c) 25,000 min. The size of the images is $(150 \times 100) \mu\text{m}^2$.

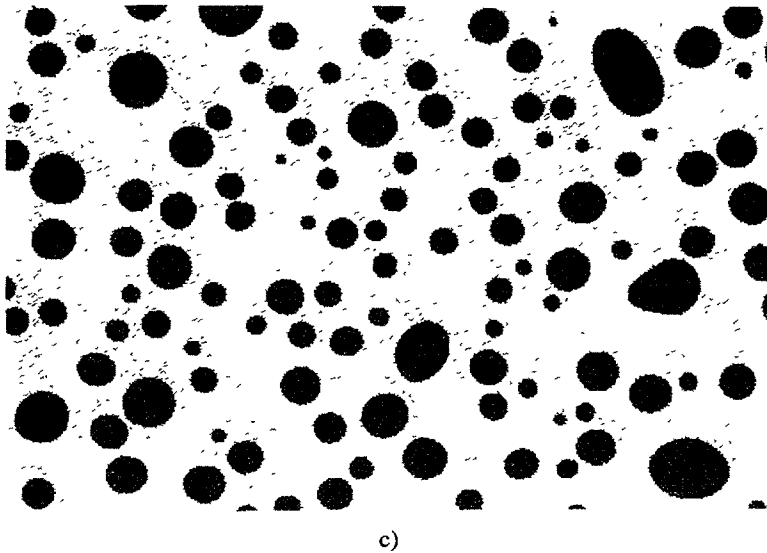


Fig. 2 (continued).

ii) three mechanisms are observed : growth of individual island (or hole), coalescence of neighbouring islands (or holes) and disappearance of the smallest islands (or holes) to the benefit of the neighbouring largest ones (Fig. 2) ;

iii) the existence of a line free energy : in the case of dilute systems, islands or holes exhibit a perfect round shape. Besides, after coalescence, the « new » island or hole tends to go back to a circular shape as the annealing time progresses (Fig. 2). All these qualitative features were previously identified in the specific case of concentrated systems of islands or holes [14].

Concerning the possible dependence of the kinetics of growth on the sample size, it has been pointed out that, whatever the system of islands or holes, no influence of the specimen size has been detectable ; as a consequence, only the data corresponding to the largest samples will be reported in the following.

As it has been mentioned in previous studies [12, 18], the patterns observed on the free surface are reminiscent of those observed in systems which exhibit first-order phase transition with conserved order parameter. For such systems, in the asymptotic time-range, the growth of clusters obey to power laws *versus* time [37]. Thus, our data have been intentionally analysed in terms of power laws ; however, the choice of this kind of analysis has not to be viewed as a way to anticipate the results.

If we focus first on the concentrated systems of islands (CI) and holes (CH), figures 3 and 4 show clearly that, from the beginning of the growth stage ($t \geq 100$ min), the number of islands (or holes) per unit area, D , obeys to a power law *versus* the annealing time : $D \sim t^{-\alpha}$ with $\alpha = 0.47 \pm 0.02$ for both islands and holes. The digitized images taken during the whole growth stage reveal that the three above-mentioned mechanisms are active.

For all the less concentrated systems, the growth stage starts later (the beginning of the growth stage, i.e. the end of the formation stage, has been defined as the time when the nucleation rate of islands or holes becomes equal to zero).

For dilute systems of islands (DI) and holes (DH), the end of the formation stage was found to occur at $t \sim 600$ min and $t \sim 300$ min, respectively. As shown in figure 3, for longer times, the total number of islands per unit area is constant (there are no coalescences and no dissolutions) while, for holes (Fig. 4), due to occasional coalescences, a very slight decrease

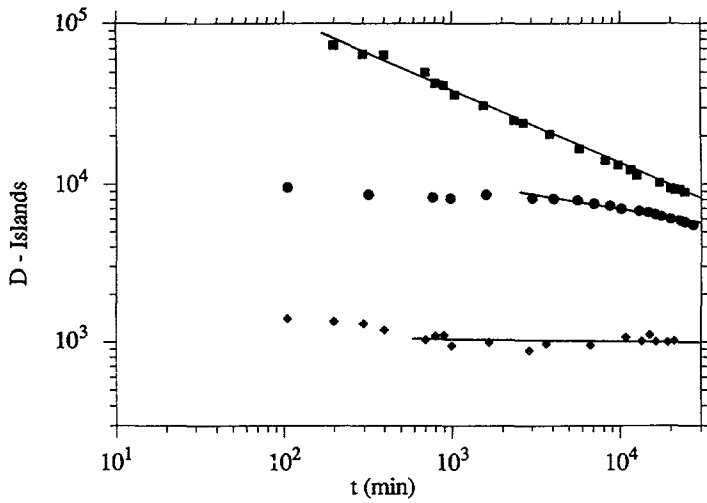


Fig. 3. — Time evolution of the number of islands per mm², D , (■: CI, ●: SCI, ◆: DI). D has been calculated from the (512 × 512) pixels digitized images. The solid lines refer to the growth stage. The observation by optical microscopy of the DI system has been made at low magnification (× 5); as a result, the resolving power was poor and the data are more scattered than those obtained for the DH system (Fig. 14) where the resolving power was better.

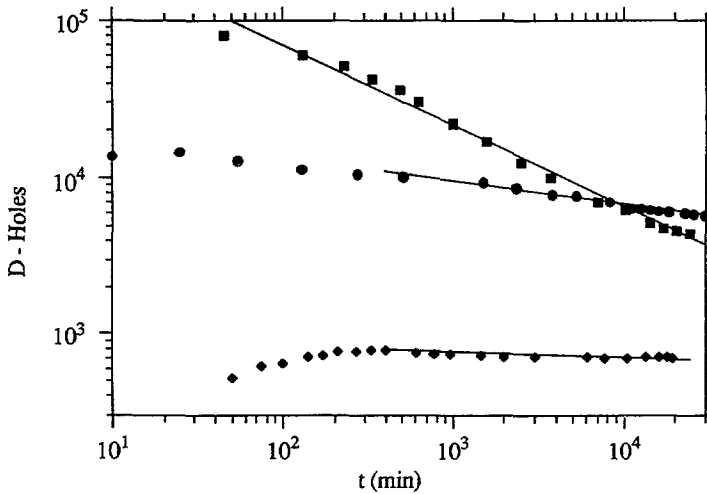


Fig. 4. — Time-evolution of the number of holes per mm², D , (■: CH, ●: SCH, ◆: DH). D has been calculated from the (512 × 512) pixels digitized images. The solid lines refer to the growth stage.

of D is observed (however, this variation ($\alpha \sim 0.02$) is within the error bars). In terms of power laws, the dilute systems correspond to an exponent $\alpha \sim 0$.

Finally, in the case of the semi-concentrated systems, the formation stage stops for $t \sim 2,000$ min (SCI) and $t \sim 300$ min (SCH). At longer times, in the case of holes, both the

coalescence and dissolution mechanisms are active while, for islands, only the dissolution mechanism is observed. The total number of holes per unit area, D , obeys a power law with $\alpha = 0.14 \pm 0.02$ (Fig. 4). Only one decade in time of the growth stage of islands is accessible through our experiment ; over this restricted time-range, D verifies a power law *versus* time with $\alpha = 0.20 \pm 0.04$ (Fig. 3).

All these observations show clearly that, during the growth regime, the decrease of the number of islands (or holes) per unit area is even faster that the system is concentrated. Indeed, the drop in the density of islands (or holes) is directly related to the coalescence and dissolution rates and the activity of these mechanisms is much higher for concentrated systems than for dilute ones.

The kinetics of growth of clusters is generally described by the time-dependence of the average cluster radius [37]. Since the parameter, which was directly accessible from our image analysis software, was the individual area S_i of each island (or hole), it is the time-dependence of the average island (or hole) area S_N which has been followed here. S_N has been defined as a number-weighted average :

$$S_N = \frac{\sum n_i S_i}{\sum n_i} = \frac{\sum n_i S_i}{N} \quad (1)$$

where n_i is the number of islands (or holes) whose area is equal to S_i and N is the total number of islands (or holes). The choice of the average is not particularly important because for all the systems except the SCH one the polydispersity in size, defined as $P = S_w$ (area-weighted average)/ S_N , was found to be constant during the growth stage. Typically, the P value lies between ~ 1.2 (dilute systems) and ~ 2 (concentrated ones). Figures 5 and 6 show unambiguously that $S_N(t)$ verifies a power law $S_N \sim t^\beta$ for both concentrated systems of islands and holes with $\beta = 0.46 \pm 0.02$ in the case of islands and $\beta = 0.56 \pm 0.02$ for holes.

When dilute, islands or holes do not grow once they are formed : over 2 decades in time, S_N is constant ($\beta = 0$) as shown in figures 5 and 6 ; only a slight increase of S_N ($\beta = 0.08 \pm 0.02$) is noticeable in the case of holes.

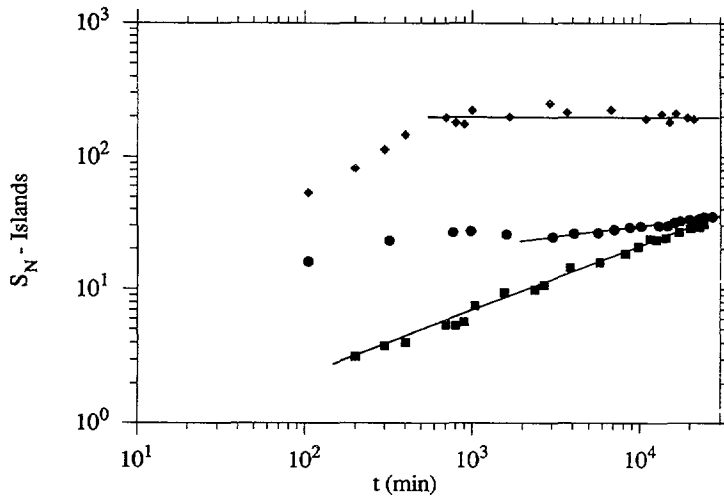


Fig. 5. — Time-evolution of the number-weighted average area of islands, S_N , (\blacksquare : CI, \bullet : SCI, \blacklozenge : DI). S_N has been calculated from the (512×512) pixels digitized images and is given in μm^2 . The solid lines refer to the growth stage.

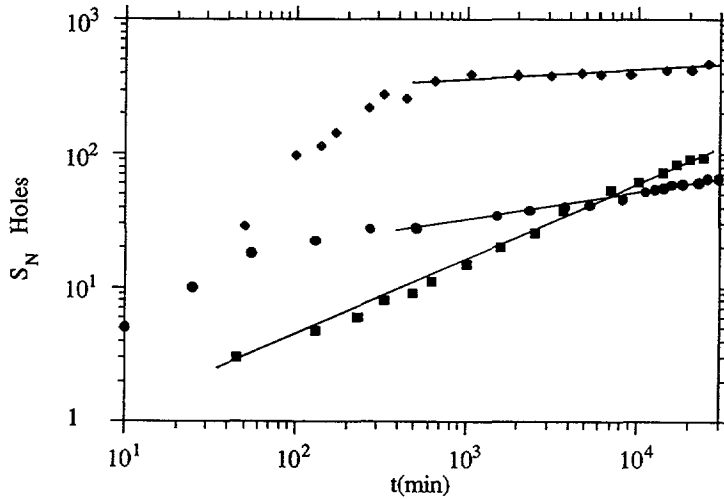


Fig. 6. — Time-evolution of the number-weighted average area of holes, S_N , (■ : CH, ● : SCH, ◆ : DH). S_N has been calculated from the (512×512) pixels digitized images and is given in μm^2 . The solid lines refer to the growth stage.

In the case of the semi-concentrated system of islands (SCI), S_N varies as $t^{0.20 \pm 0.04}$ during one decade of the growth stage while, for the semi-concentrated system of holes (SCH), the time-dependence of S_N is given by $t^{0.21 \pm 0.02}$ for $t \geq 300$ min.

The main conclusion, which can be drawn from all these data, is that the growth rate of islands or holes increases with the concentration of the system. However, it has to be pointed out that, for both dilute systems of islands and holes, at the end of the formation stage, the average size of the islands and holes is about 2 orders of magnitude greater than that in concentrated systems after the same annealing time. The previous results bring up several other remarks. First, for all the systems of islands, the exponents α and β , which describe the power law dependence of the density D of islands and their average area S_N , respectively, are equal. This behavior was expected since, as shown in figure 7, the surface coverage $\%S$ of islands is constant during the growth stage and by definition, D and S_N verifies : $D \times S_N = \%S$. $\%S$ is related to the initial thickness e_{ac} of the copolymer film, i.e. to the amount of copolymer deposited on the silicon substrate : $\%S = (e_{ac} - 2L)/L$. Thus, if e_{ac} and L are constant, $\%S$ should not vary with time. On the contrary, in the case of holes, $\beta \neq \alpha$ with $\beta > \alpha$. This is not very surprising ; indeed, the curves $\%S = f(t)$ do not exhibit a plateau during the growth stage (Fig. 8). The slight increase of $\%S$ with the annealing time can be described by a power law : $\%S \sim t^\gamma$ with $\gamma = 0.09 \pm 0.02$ (CH), 0.07 ± 0.02 (SCH) and 0.06 ± 0.02 (DH). Within the error bars, γ verifies : $\gamma = \beta - \alpha$. Since the amount of copolymer deposited on the substrate is constant, the variation of the surface coverage of holes is not, *a priori*, understandable. We will go back to this particular point later on and we will propose an explanation.

For the concentrated systems, the average size S_N of islands or holes follows a power law. The next step in the analysis of the kinetics of growth of such systems is to check if the size distribution function of islands or holes, $n(S_i, t)$, satisfies a scaling law *versus* the annealing time [38]. The time-evolution of the size distribution of both islands and holes is given in figures 9a and 10a. It is clear that, as time progresses, the maximum of the peak shifts towards larger values of S_i and the value of the maximum decreases. The data do superimpose onto a

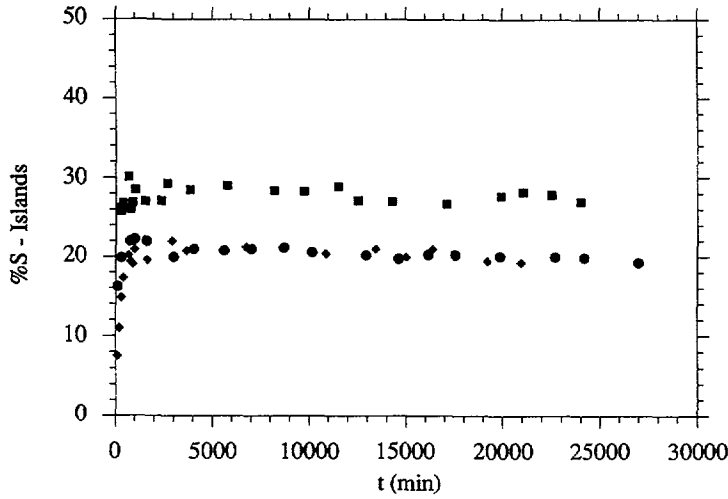


Fig. 7. — Time-evolution of the surface coverage $\%S$ of islands (■: CI, ●: SCI, ◆: DI). $\%S$ has been calculated from the (512×512) pixels digitized images. It should be noted that, for both the semi-concentrated (SCI) and dilute (DI) systems of islands, the curves $\%S = f(t)$ exhibit surprisingly the same plateau. In fact, the observation of the islands by optical microscopy has been performed at two different magnifications : $(\times 5)$ for the (DI) system and $(\times 20)$ for the (SCI) one. As a consequence, the value of the plateau level measured for the (DI) system is overestimated of about 4 %.

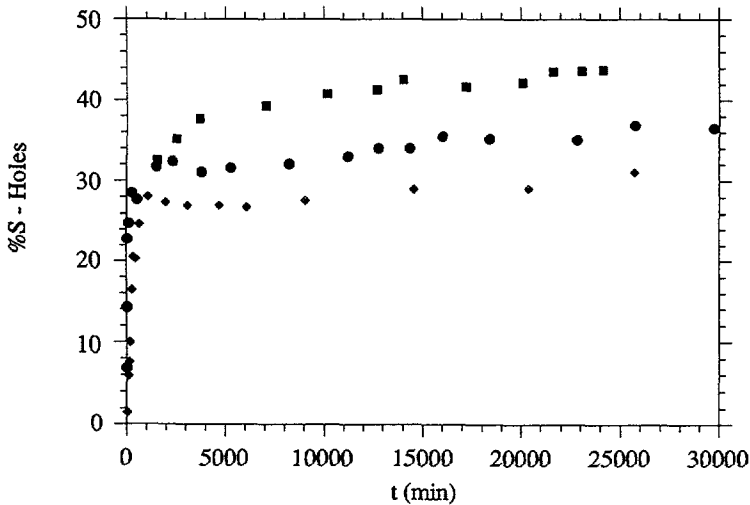


Fig. 8. — Time-evolution of the surface coverage $\%S$ of holes (■: CH, ●: SCH, ◆: DH). $\%S$ has been calculated from the (512×512) pixels digitized images.

single master curve (Figs. 9b and 10b) when plotted as the reduced quantities :

$$x = S_i/S_N \quad (2)$$

$$\tilde{n}(x) = n(S_i, t) S_N(t)/S_0 = n(S_i, t)/N(t)$$

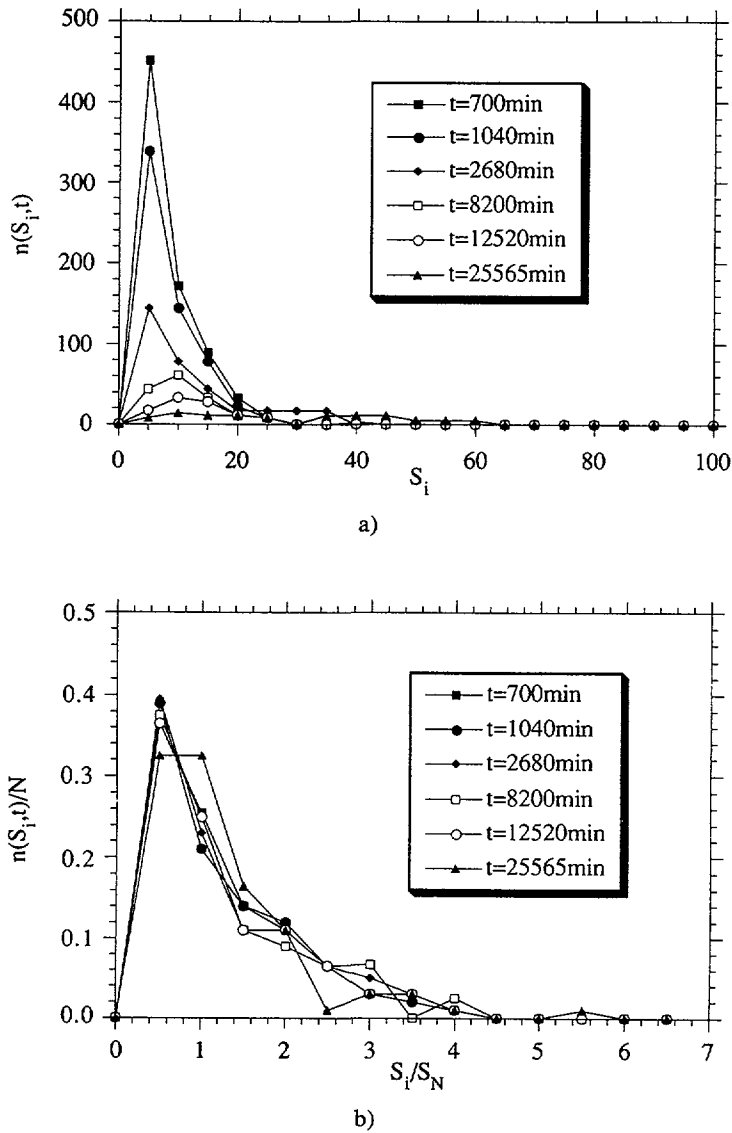


Fig. 9. — Concentrated islands (CI) : a) the size distribution function of islands $n(S_i, t)$ for different annealing times during the growth stage. S_i is the island area in μm^2 and $n(S_i, t)$ is the number of islands whose area is equal to S_i at a given annealing time t ; b) the renormalized size distribution function of islands $n(S_i, t)/N$. N and S_N are respectively the total number and the number-weighted average area of islands at a given annealing time t .

where $N(t)$ is the total number of islands or holes and S_0 the area of the film surface they occupy. S_0 is given by :

$$S_0 = \int n(S_i, t) dS_i(t). \tag{3}$$

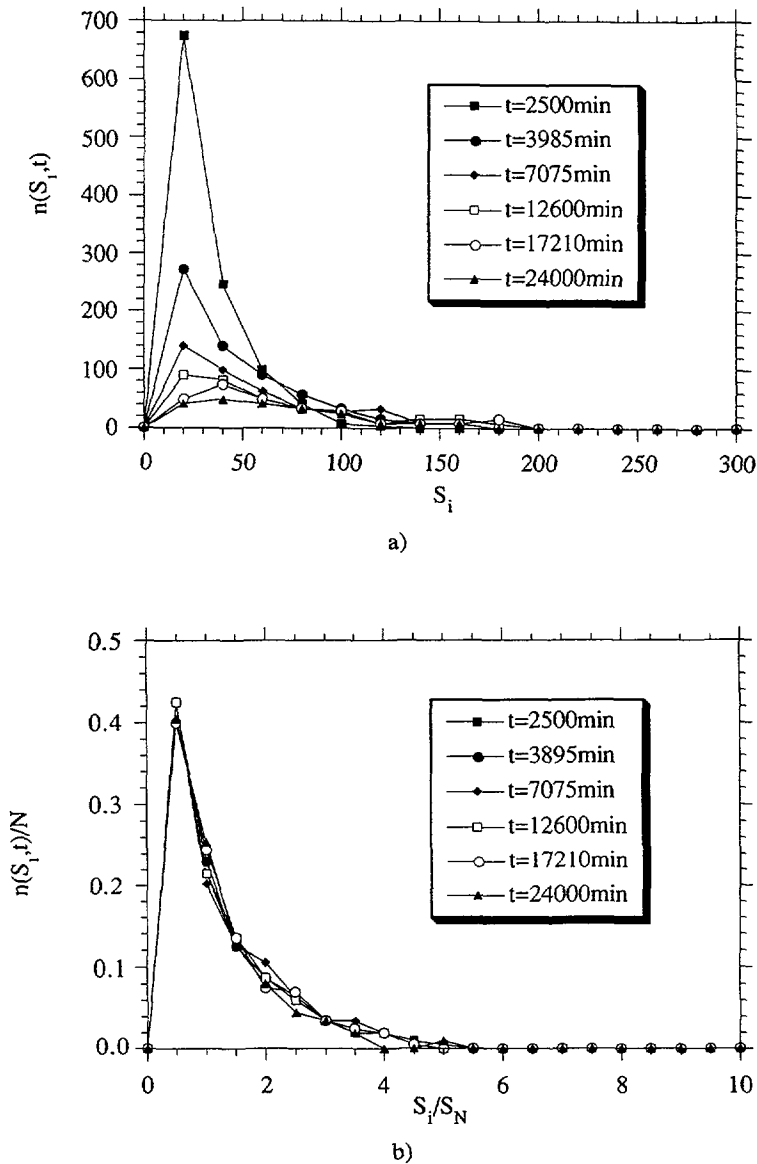


Fig. 10. — Concentrated holes (CH) : a) the size distribution function of islands $n(S_i, t)$ for different annealing times during the growth stage. S_i is the hole area in μm^2 and $n(S_i, t)$ is the number of holes whose area is equal to S_i at a given annealing time t ; b) the renormalized size distribution function of holes $n(S_i, t)/N$. N and S_N are respectively the total number and the number-weighted average area of holes at a given annealing time t .

Thus, the size distribution function obeys a universal scaling law and the kinetics of growth is dominated by a single length (the 2-dimensional Fourier transform exhibits an isotropic ring [14]). The scaling functions can be written in a usual way [38] : $\tilde{n}(t^{-0.46} S_i) \sim t^{0.46} n(S_i, t)$ for islands and $\tilde{n}(t^{-0.56} S_i) \sim t^{0.46} n(S_i, t)$ for holes. The latter relation shows clearly that the surface coverage of holes is not constant with time.

The growth regime of semi-concentrated systems is also described by power laws. If the size distribution function of islands verifies a scaling law, it is not the case for the distribution function of holes. Indeed, as we mentioned it above, the polydispersity in size, $P = S_w/S_N$, varies with the annealing time for the SCH sample. Thus, the semi-concentrated system of holes is not characterized by a unique length (Fig. 11) : $S_N \sim t^{0.20}$ and $S_w \sim t^{0.27}$. At the present time, we do not have any explanation for this specific behavior.

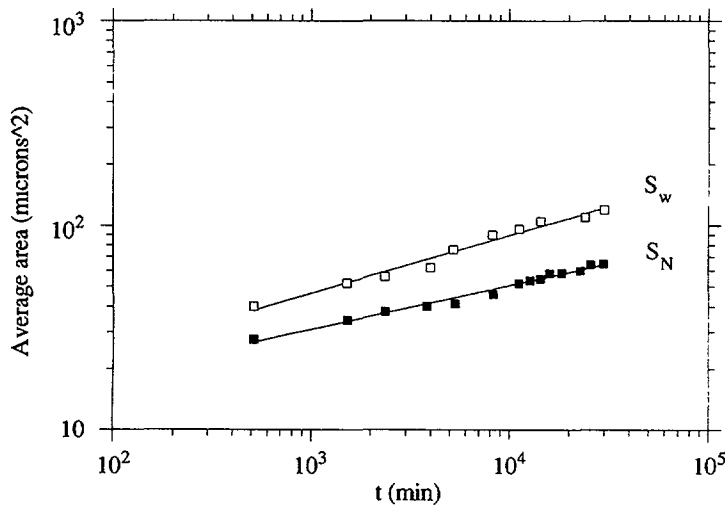


Fig. 11. — Semi-concentrated holes (SCH) : time-evolution of both the number-weighted average size, S_N , and the area-weighted average size, S_w . Both S_N and S_w and S_w/S_N ($S_w = \sum n_i S_i^2 / \sum n_i S_i$) are given in μm^2 and have been calculated from the (512×512) pixels digitized images.

The dependence of the growth law with the density of islands (or holes) is quite surprising. Indeed, the kinetics of droplet (or cluster) growth in binary solids [39, 40] or in polymer mixtures [41] have been extensively studied, particularly with respect to kinetics of unmixing (nucleation-growth and spinodal decomposition). For such systems which are controlled by cluster diffusion, the late stage of growth, known as Ostwald ripening [37], is dominated by a condensation-evaporation mechanism, also called the Lifshitz-Slyosov mechanism [42], and the theory [42-45] predicts a power law time-dependence for the mean droplet radius with an asymptotic growth exponent β of $1/3$. This value has been found for critical binary mixtures as well as for off-critical ones and is independent of the dimensionality of the system. In accordance with the asymptotic behavior of the mean droplet radius, the density of droplets decays as $t^{-3\beta}$ (3 dimensions) or $t^{-2\beta}$ (2 dimensions) and the droplet size distribution function satisfies dynamical scaling.

In general, an experimental value of β smaller than $1/3$ is seen as the signature of an intermediate, transient stage of growth. Binder [43] has pointed out that the coalescence (or coagulation) mechanism, which is active for intermediate times, induces a slowing down of the growth rate. Furthermore, in the case of binary metallic alloys, the typical size of clusters obeys a power law but the exponent depends on the dimensionality of the system, on the temperature difference, $T - T_c$, and on the concentration difference, $c - c_c$, where T_c and c_c are the critical temperature and concentration, respectively.

Our results indicate that, even after 2 decades in time, the asymptotic behavior of the growth stage has not been reached : for concentrated systems, the mean radius of islands and holes (defined as $R_N = (S_N/\pi)^{0.5}$) follows a power law whose exponent is smaller than $1/3$ and the coalescence mechanism is still very active. Furthermore, the growth exponent, as mentioned above, varies with the density D of islands (or holes). Obviously, the growth laws deduced from our experiments do not reflect the asymptotic behavior of the time-evolution of the free surface of the copolymer film. To reach the late stage of growth at $T = 140^\circ\text{C}$ would need to study the kinetics of growth over 1 or 2 more decades in time, i.e. for annealing times t such as : 2 months $< t < 2$ years. Due to the risk of degradation of the copolymer, it was not possible to extend the duration of the annealing procedure. Since our aim was to investigate the latter stages of growth, we chose to make a temperature jump of 30°C in order to speed up the kinetics. Another question to clear up was the increase of the surface coverage $\%S$ of holes during the kinetics of growth ; this increase could express the thinning of the copolymer film and could thus be attributed to a spreading of the copolymer over the silicon substrate at the perimeter of the film upon annealing. Consequently, the investigation of the late stage of the kinetics of growth has been performed on smaller copolymer films (diameter of about 0.4 mm) ; indeed, such small films are entirely visible in the field of view of the optical microscope and the analysis of both the central part and the perimeter of the film is possible. The annealing procedure was the following : 25,000 min at 140°C + 20,000 min at 170°C . Four copolymer films corresponding to dilute and concentrated systems of both islands and holes have been studied.

Figure 12 shows the evolution of the dilute system of islands (DI) which corresponds to the smallest excess of copolymer in the top layer. During the annealing at 140°C , in addition to the islands created in the central part of the film, a ring of height L is formed at the perimeter of the sample ; as for larger samples, the number of islands is constant and the individual areas of both the islands and the ring do not vary with the annealing time. After the temperature jump,

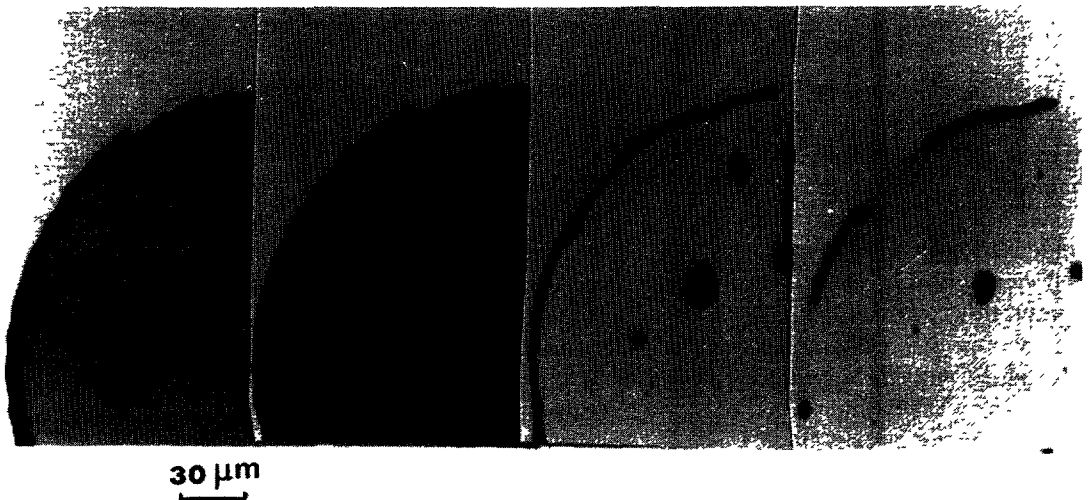


Fig. 12. — Time-evolution of the dilute system of islands (DI). From left to right : before the jump, $T = 140^\circ\text{C}$, $t = 18\,300$ min ; $T = 140^\circ\text{C}$, $t = 24\,460$ min ; after the jump, $T = 170^\circ\text{C}$, $t = 5\,760$ min ; $T = 170^\circ\text{C}$, $t = 16\,680$ min. The black zones correspond to the $3L$ top layer and the grey one to the $2L$ layer.

the evolution of the free surface is clearly visible : the individual areas of both the islands and the ring decrease with time and, after about 20,000 min at 170 °C, both the islands and the ring have disappeared. Thus, the existence and the duration of the stage of « no-growth » observed at 140 °C depends on the annealing temperature. On the other hand, at 170 °C, the kinetics does not exhibit any evaporation-condensation mechanism and any asymptotic behavior in $t^{1/3}$; but the evolution is such as to eliminate the 3 L top layer. The evolution of the dilute system of holes (DH) is basically the same. The major difference is that, after about 20,000 min of annealing at 170 °C, the 3 L top layer has not totally disappeared (Fig. 13).

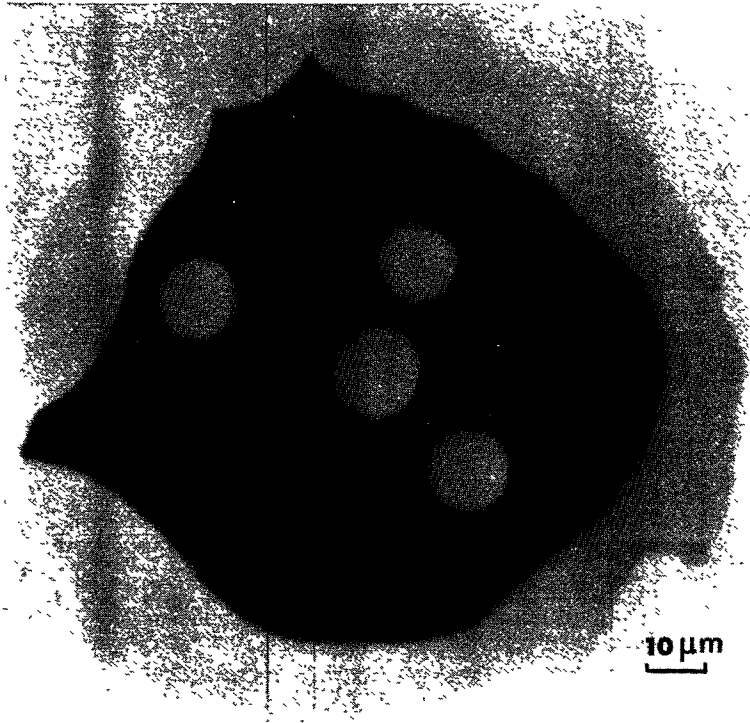


Fig. 13. — Dilute system of holes (DH) : morphology of the free surface of the thin film after annealing at 140 °C for 24 060 min plus annealing at 170 °C for 17 000 min. The black background corresponds to the 3 L top layer and the grey areas to the 2 L layer.

In figure 14, the evolution of the concentrated system of islands is shown. After the temperature jump, a continuous decrease of the area of the ring of height L is observed ; there are no coalescences, the rate of dissolution of the smallest islands is very high, but the size of the largest ones does not increase with time and is constant. This global behavior of the free surface does not correspond to the evaporation-condensation mechanism which leads to an asymptotic growth law in $t^{1/3}$. As observed in the previous cases, the total area of the 3 L top layer decreases with time and after 20,000 min, there are no more islands in the central part of the film, only limited zones of the ring are still present.

For the concentrated system of holes, the jump of temperature induces a significant increase of the rate of coalescences and the latter mechanism prevails over the dissolution one. Again, the evolution of the free surface cannot be identified as a Lifshitz-Slyosov process and the

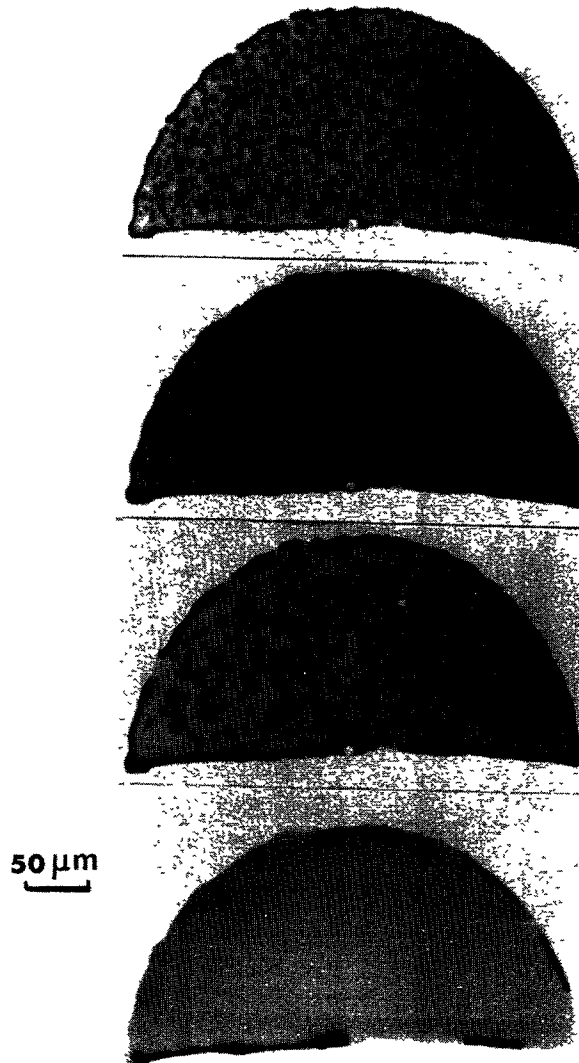


Fig. 14. — Time-evolution of the concentrated system of islands (CI). From top to bottom : before the jump, $T = 140\text{ }^{\circ}\text{C}$, $t = 18\ 300\text{ min}$; $T = 140\text{ }^{\circ}\text{C}$, $t = 24\ 460\text{ min}$; after the jump, $T = 170\text{ }^{\circ}\text{C}$, $t = 5\ 760\text{ min}$; $T = 170\text{ }^{\circ}\text{C}$, $t = 16\ 680\text{ min}$. The black color corresponds to the $3L$ top layer and the grey one to the $2L$ layer.

tendency for the holes to invade the whole area of the film leads to a decrease of the surface occupied by the top layer (Fig. 15).

The same behavior has been encountered for larger films and we can assert that at $170\text{ }^{\circ}\text{C}$, the typical size of islands or holes does not vary as $t^{1/3}$ during the late stage of the kinetics of growth. For all the different systems, it is observed that the top layer disappears progressively with time. We should notice that, at $140\text{ }^{\circ}\text{C}$, this tendency was only noticeable for the systems of holes (their surface coverage increases slightly).

The question is now to find an explanation of this phenomenon. The decrease of the area occupied by the top layer can be seen as a diminution of the film thickness. Since the amount of

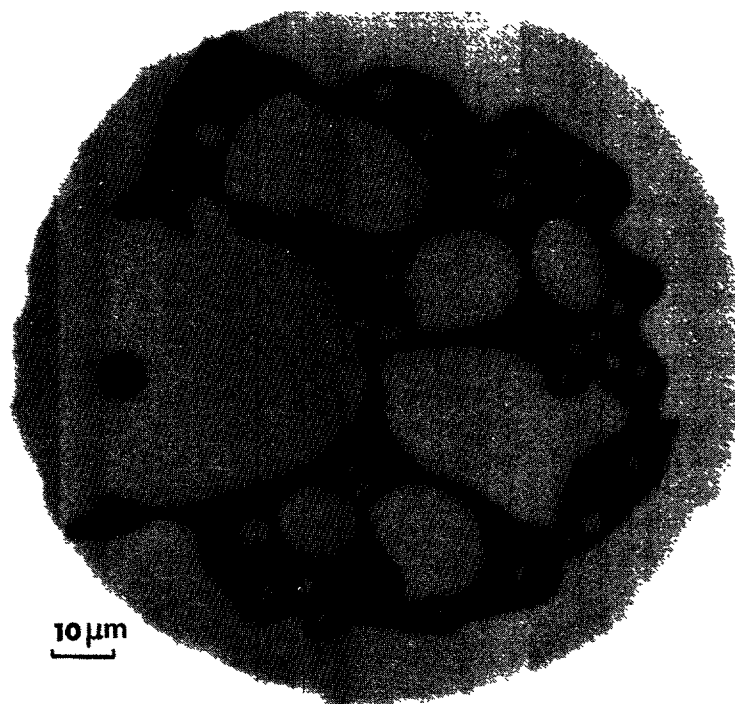


Fig. 15. — Concentrated system of holes (CH) : morphology of the free surface of the thin film after annealing at 140 °C for 24 060 min plus annealing at 170 °C for 17 000 min. The black background corresponds to the 3 *L* top layer and the grey areas to the 2 *L* layer.

copolymer deposited on the silicon substrate is constant, the thinning could be due to the spreading of the copolymer on the substrate at the perimeter of the film. No displacement of the perimeter of the film has been detected by optical microscopy even at a high magnification ($\times 100$). It does not prove, of course, that there is no spreading of the copolymer on the substrate; indeed, if only a small amount of copolymer flows onto the wafer, the corresponding shift of the perimeter of the film could be less than the resolving power of the microscope. A crude calculation of this shift can be made, for example, in the case of the dilute system of islands (DI). The surface coverage %*S* of islands decays of about 10 % after 4,320 min of annealing at 170 °C. By assuming that the corresponding quantity of copolymer « disappeared » from the central part of the film goes entirely to the perimeter of the film, a displacement of the perimeter of 4.5 μm is found if both the *L* and 2 *L* layers spread; if only the *L* layer flows, the displacement is twice : 9 μm. In any case, these values are large enough to be detectable by optical microscopy. Thus, we can conclude there is no spreading of the copolymer at the periphery of the film and consequently, the thickness of the film does not decrease.

An alternative could be that the copolymer molecules, which were initially in the top layer, move into the inner layers as the annealing time progresses. If these molecules are uniformly distributed in both *L* and 2 *L* layers, the number of molecules becomes larger inside each inner layer; thus, the area par molecule decreases and the molecule adopts a stretched conformation. As a consequence, there should be an increase of the lamellar period *L* and, if the variation of *L* is large enough, a change in the interference colors corresponding to thicknesses

L , $2L$ and $3L$ should be observable by interference microscopy [12]. A close examination of the free surface of the copolymer films before and after the temperature jump of $30\text{ }^{\circ}\text{C}$ reveals without ambiguity a variation in the interference colors. At $140\text{ }^{\circ}\text{C}$, the observed interference colors corresponding to thicknesses $2L$ and $3L$ are light-brown and indigo respectively. At $170\text{ }^{\circ}\text{C}$, after 7,200 min of annealing, the colors change into yellowish-brown and blue respectively ; from the Newton scale, it corresponds to an increase of L of about 5-10 %. It could be argued that the observed increase of the lamellar period could be due to the thermal expansion resulting from the temperature jump of $30\text{ }^{\circ}\text{C}$. Several features suggest strongly that it cannot be the case. First, in a previous paper [14], it has been shown that a thermal expansion of L of about 8 % was produced by a temperature jump as large as $165\text{ }^{\circ}\text{C}$ ($\geq 30\text{ }^{\circ}\text{C}$). Thus, assuming a constant thermal expansion coefficient, a temperature jump of $30\text{ }^{\circ}\text{C}$ should induce an increase of L of only 1.5 %. Second, another point is that, for all the experiments we did up to now at constant temperature, the interference colors do not vary with time when the surface coverage %S of islands or holes is quasi-constant. In contrast, here, after a temperature jump of $30\text{ }^{\circ}\text{C}$, a continuous change in the interference colors is seen at $170\text{ }^{\circ}\text{C}$ as the area occupied by the $3L$ top layer decreases with time. Finally, the increase of L can be crudely estimated from the variation of the surface coverage of islands or holes. Let us focus again on the dilute system of islands. Their surface coverage decays of about 20 % (remember it was constant at $140\text{ }^{\circ}\text{C}$) when the film is annealed for 7,200 min at $170\text{ }^{\circ}\text{C}$. Assuming that all the molecules, which have « disappeared » from the top layer, go equally into both the L and $2L$ layers, it is easy to show that the volume of each inner lamella will increase of about 8 % and thus, the lamellar period is expected to rise of 8 % as well. This value is in good agreement with the measured one.

Thus, our data indicates clearly that the ultimate behavior of the copolymer film is to remove the incomplete top layer from the free surface, i.e. to eliminate the islands and the holes by allowing the permeation of the copolymer molecules into the inner layers of the film. The concept of permeation has been first introduced by Helfrich [46] to explain the high viscosity of smectic liquid crystals ; indeed, the capillary flow of such materials could not be described by Poiseuille's law only. More recently, this mechanism has been invoked to account for the spreading of stratified liquid droplets [47] ; basically, two types of flow are predicted : shear between layers and permeation normal to the layers. It could be argued that the permeation of copolymer molecules should be ruled out since the strong incompatibility between the two blocks A and B should impede the crossing of an — ABBA — (or — BAAB —) lamella by an AB molecule. However, it has been shown recently that, even in strongly segregated diblock copolymer systems having microdomains of species A and B arranged in a regular way, a polymeric block of A can cross a B domain provided that a small part of the A block is highly stretched as it crosses the B region [48].

Looking at figures 12 and 14, it is clear that, after 25,000 min of annealing at $170\text{ }^{\circ}\text{C}$, the whole top layer has almost disappeared from the free surface of the film in the case of islands (for both concentrated and dilute systems) while it is not true for holes (Figs. 13 and 15). It is not very surprising since, as we mentioned it in the introduction, the formation of holes on the free surface requires a larger excess of material in the top layer than the formation of islands. However, the question is whether, for longer annealing times, the holes will or will not occupy the total area of the film ; i.e. how much the copolymer film is able to swell and thus what is the limit of stretching of the molecules inside the lamellae. Experiments are currently in progress to conclude on this important point.

Conclusion.

It has been shown that the evolution of the free surface of symmetric diblock copolymer films results from the competition between several parameters, namely : the interfacial energies (air/polymer and substrate/polymer), the line tension (islands and holes) and the elastic free energy of the chains. For short annealing times, during the lamellar ordering, earlier data [18] have shown that the interfacial energies are prevailing ; indeed, if the thickness of the as-cast film is not exactly equal to $2L$ or $3L$, islands or holes are formed on the free surface in order to minimize the interfacial energies by putting the PBMA block at both the air/polymer and silicon/polymer interfaces.

In this paper, it has been shown that, once the islands and holes are formed, i.e. once the lamellar stacking is built up, their kinetics of growth depends on their initial density. At $140\text{ }^{\circ}\text{C}$, for intermediate annealing times, there is no time-evolution of the free surface for dilute systems while, for semi-concentrated and concentrated ones, the free surface evolves in order to decrease the line tension : both a decay of the total number of islands (or holes) per unit area D and an increase of their mean size S_N are observed. The time-dependence of D and S_N can be described by power laws and results from the competition between 3 mechanisms : individual growth, coalescence and dissolution. At a molecular level, these 3 mechanisms can be interpreted in terms of the shear between lamellae [15, 49] ; however, it should be pointed out that the slight increase of the surface coverage of holes (whatever their initial density D) indicates that there is some permeation of the copolymer molecules from the top lamella into the inner ones. In contrast, this phenomenon has not been detected during the kinetics of growth of islands ; for islands, the permeation of molecules has been revealed at higher annealing temperatures ($T = 170\text{ }^{\circ}\text{C}$) only.

For longer annealing times at $170\text{ }^{\circ}\text{C}$, it is clear that the ultimate stage is governed mainly by the permeation mechanism ; as a consequence, the copolymer film is able to make the line tension almost vanish while the elastic free energy per chain increases. The final morphology of the free surface depends on the balance between the line tension and the elastic energy per chain.

However, the question arises to know if the permeation mechanism is thermally activated ; i.e. if, at $170\text{ }^{\circ}\text{C}$, the permeation mechanism is active at intermediate times of annealing and if the ultimate stage observed at $170\text{ }^{\circ}\text{C}$ is universal or not. Second, the kinetics of growth will be faster at $170\text{ }^{\circ}\text{C}$, the late stage of the growth laws should be accessible and it should allow us to check if the analysis in terms of a power law is right or not. Thus, kinetics experiments at $170\text{ }^{\circ}\text{C}$, from the formation of the islands (or holes) to their ultimate behavior, are planned in the near future. On the other hand, the influence of the film thickness (i.e. of the silicon substrate) on the kinetics of growth of islands and holes has not been taken up in the present study, which has been focused on thin films with thicknesses e_{ac} such as : $2L < e_{ac} < 3L$. Recent studies [35] on very thin films ($e_{ac} < L$) has pointed out the important role played by the silicon wafer on the formation of islands. The next experiments on the kinetics of growth of islands and holes will deal with thinner ($L < e_{ac} < 2L$) and thicker films.

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