



**HAL**  
open science

# Islands and holes on the free surface of thin diblock copolymer films. I. Characteristics of formation and growth

G. Coulon, B. Collin, D. Ausserre, D. Chatenay, T.P. Russell

► **To cite this version:**

G. Coulon, B. Collin, D. Ausserre, D. Chatenay, T.P. Russell. Islands and holes on the free surface of thin diblock copolymer films. I. Characteristics of formation and growth. *Journal de Physique*, 1990, 51 (24), pp.2801-2811. 10.1051/jphys:0199000510240280100 . jpa-00212572

**HAL Id: jpa-00212572**

**<https://hal.science/jpa-00212572>**

Submitted on 4 Feb 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification

Physics Abstracts

68.00 — 64.70 — 78.65

## Islands and holes on the free surface of thin diblock copolymer films. I. Characteristics of formation and growth

G. Coulon <sup>(1)</sup>, B. Collin <sup>(1)</sup>, D. Ausserre <sup>(1)</sup>, D. Chatenay <sup>(1)</sup> and T. P. Russell <sup>(2)</sup>

<sup>(1)</sup> Institut Curie, Section de Physique et Chimie, Université P. M. Curie and CNRS URA 1379, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France

<sup>(2)</sup> IBM Research Division, Almaden Research Center, 650 Harry Road, San Jose, CA 95120, U.S.A.

(Received 9 July 1989, accepted 6 September 1990)

**Résumé.** — Les copolymères diblocs symétriques polystyrène/polyméthylméthacrylate P(S-b-MMA), déposés sur un substrat de silicium, forment à l'équilibre thermodynamique, une structure multicouche parallèle au substrat. Si la couche supérieure est incomplète, des îlots ou des trous se forment dans celle-ci. La cinétique de formation et de croissance des îlots et des trous est étudiée ici, par microscopie interférométrique *in situ*. Seuls les systèmes denses ( $\approx 30\%$  d'îlots ou de trous en taux de couverture) sont envisagés. Aux temps courts, la formation des îlots est différente de celle des trous. Aux temps longs, la croissance des îlots et des trous est contrôlée par les mêmes mécanismes : croissance individuelle, coalescence et disparition.

**Abstract.** — When deposited on a silicon substrate, symmetric polystyrene/polymethylmethacrylate P(S-b-MMA) diblock copolymers form, at equilibrium, a multilayer structure parallel to the substrate. If the top layer is incomplete, islands or holes are formed in this layer. The kinetics of formation and growth of islands or holes is investigated, here, by *in situ* interference microscopy. The present study is focused on dense systems ( $\approx 30\%$  of islands (or holes) in area coverage). In the early stage, the way of formation of elevations and holes appears to be different. For longer times, the growth of islands and holes is controlled by the same mechanisms : individual growth, coalescence and dissolution.

### Introduction.

In the microphase-separated state, symmetric, diblock copolymers in the bulk exhibit a lamellar morphology [1-4]. Recently, numerous studies have been focused on the influence of surfaces on the lamellar ordering in thin copolymer films. It has been shown that, at equilibrium, the lamellar microdomains orient parallel to the free surface [5-12]. In the case of thin films of symmetric, diblock copolymers of poly(styrene) and poly(methyl methacrylate), denoted P(S-b-MMA) on silicon substrates, the total film thickness  $t$  was found to be quantized at equilibrium, i.e.  $t = \left(i + \frac{1}{2}\right) L$  where  $L$  is the lamellar period and  $i$  is an integer [7-9, 11, 12]. Time-dependent annealing studies on very thin films where the total

thickness of the film was  $2-3 L$  have shown that the lamellar ordering begins at the silicon substrate and then propagates to the free surface through the entire specimen thickness [8]. Recent optical microscopic studies have shown that the thickness of solution cast-films is uniform with a free surface which is flat and smooth [10]. When this thickness does not correspond to  $\left(i + \frac{1}{2}\right) L$ , elevations or depressions are formed on the free surface after annealing above the glass transition temperature. It was shown that, at equilibrium, their height (islands) or depth (holes) is equal to the lamellar period  $L$ . The existence of such islands (or holes), and the variation of their average size and their spatial distribution as a function of annealing time was discussed [10]. In that study, the solution cast-film thickness was chosen so that, after annealing, the resulting holes were located in the incomplete top layer lying between  $t = 3 L/2$  and  $t = 5 L/2$ . The choice of such very thin films was mainly motivated by previous T.E.M. observations on thick copolymer films [4] which demonstrated the existence of numerous defects in the lamellar stacking in the bulk. If these defects are sensitive to temperature, then they could affect noticeably the kinetics of holes (or islands) growth on the free surface. In very thin films (very few lamellae), the constraints of the external surfaces should preclude the presence of such defects in the lamellar ordering, i.e. defects should be attracted by the external surface. It was also noted previously, that the growth of islands could be different from that of holes. In this article, data obtained by *in situ* optical microscopic observations on the kinetics of islands growth is presented which affords a partial answer to this question. It is shown that, in the early stages, the mechanism for the formation of elevations and depressions appears to be different, and that it should cost more energy to create islands than holes on the free surface. However, for longer times, the growth of islands and holes is governed by the same mechanisms; i.e.: individual growth, coalescence and dissolution. The 2D Fourier Transforms obtained from the digitized real images exhibit a diffuse ring demonstrating that the topology is isotropic and that it can be described by a unique characteristic length.

### Experimental.

A symmetric, diblock copolymer of perdeuterated poly(styrene) and poly(methylmethacrylate), denoted P(d-S-b-MMA), purchased from Polymer Laboratories, was used in this study. The molecular weights of the blocks ( $M_{\text{PSD}} = 52\,900$ ,  $M_{\text{PMMA}} = 48\,000$ ) and the polydispersity ( $M_w/M_n = 1.07$ ) were determined from size-exclusion chromatography in reference to PS standards <sup>(1)</sup>. Copolymer films, c.a.  $700 \text{ \AA}$  and  $900 \text{ \AA}$  in thickness, were prepared by spin coating a  $2 \text{ g}/100 \text{ cc}$  toluene solution of the copolymer onto a silicon substrate at spinning speeds of  $3\,000$  and  $2\,000 \text{ rpm}$ , respectively. The film thicknesses were chosen to obtain, after annealing, either islands or holes, located in the incomplete top layer between  $t = 3 L/2$  and  $t = 5 L/2$ , with the same area coverage (c.a.  $30 \%$ ). The  $2.5 \text{ cm}$ -diameter silicon wafers were cleaned by oxydation of the surface impurities by UV irradiation under oxygen flow [13]. Before annealing, the copolymer films were placed under vacuum at room temperature to remove residual solvent. The copolymer films were then annealed at  $190 \text{ }^\circ\text{C}$  for the desired period in a Mettler hot stage fixed onto the stage of the optical microscope. A Reichert Polyvar-Met microscope was used under reflection conditions to obtain interference colors from the white light source. The source lamp iris was closed down to ensure a parallel beam of light. The use of interference microscopy to investigate the free surface topology of thin

<sup>(1)</sup> For optical microscopy, the deuteration of the PS block is, of course, not necessary. The P(d-S-b-MMA) copolymer has been used here only in order to allow us quantitative comparisons with previous studies [7, 8, 10].

copolymer films has been presented previously [10]. However, it should be noted that the sequence of the observed interference colors, given in a previous paper [10], for the P(d-S-b-MMA) copolymer was obtained from optical observations of samples which were annealed above the glass transition but then cooled to room temperature. Here, the observations are made *in situ*, i.e. at  $T = 190^\circ\text{C}$ . Consequently, due to the thermal expansion, the lamellar period  $L$  was found to increase from  $L = 390 \text{ \AA}$  to  $L = 430 \text{ \AA}$  ( $\Delta L/L \approx 8\%$ ). As a result, the sequence of the observed interference colors is shifted and at  $T = 190^\circ\text{C}$  the expected colors for the thicknesses of  $3L/2$  and  $5L/2$  are respectively light yellowish-brown and blue (instead of light brown and indigo blue for the room temperature cooled samples), respectively. All the in-situ observations were made with a ( $\times 50$ ) objective lens. Color slides of the morphology of the free surface were taken at different times (Kodak Ektachrome film, 50 ASA, for a tungsten lamp). Then the digitization of the color slides was performed by means of a microdensitometer. The size of the digitized images was  $512 \times 512$  pixels (1 pixel =  $25 \mu\text{m}$  (color slide) =  $0.22 \mu\text{m}$  (sample)). The digitized images were finally analyzed by using the image processing system SPHINX; all the operations were carried out by a Hewlett-Packard computer using a UNIX operating system. From the analysis of the image in the real space, the following parameters can be extracted: surface, perimeter, coordinates of the mass center of each island (or hole), the percentage of area occupied by the islands (or holes), their total number and the histogram of size distribution. From the image in the real space, it was possible to obtain the corresponding 2D-Fourier Transform in the reciprocal space and thus to obtain the characteristic length scale of the morphology in the real space.

### Results and discussion.

The formation of islands and holes occurs in a very different way. When the thickness  $t$  of the as-cast film is such as  $2L < t < \frac{5L}{2}$ , annealing the film at  $190^\circ\text{C}$  will create holes on the free



Fig. 1. — Optical micrograph of P(d-S-b-MMA) copolymer film, annealed at  $190^\circ\text{C}$  for 90 min, the initial film thickness is  $\approx 900 \text{ \AA}$ : round-shaped holes are spread over the free surface. The full, long dimension of the micrograph is  $320 \mu\text{m}$ .

surface [10]. *In situ* optical microscopic observations show that, after 10 min of annealing, the free surface begins to be rough. After a subsequent annealing of 80 min, well-defined small round-shaped holes are visible on the free surface. They appear as light yellowish brown patches on a blue background (Fig. 1). On the other hand, when the thickness of the as-cast film is such that :  $\frac{3L}{2} < t < 2L$ , islands of circular shape appear on the free surface only after a much longer annealing time. As in the previous case, a roughness is seen on the free surface after approximately 10 min of annealing. After an additional 80 min, elevations are present. They appear as very thin elongated bluish-green patches, more or less connected, on a very light yellow-brown background (Fig. 2). As time progresses, this network tends to split into

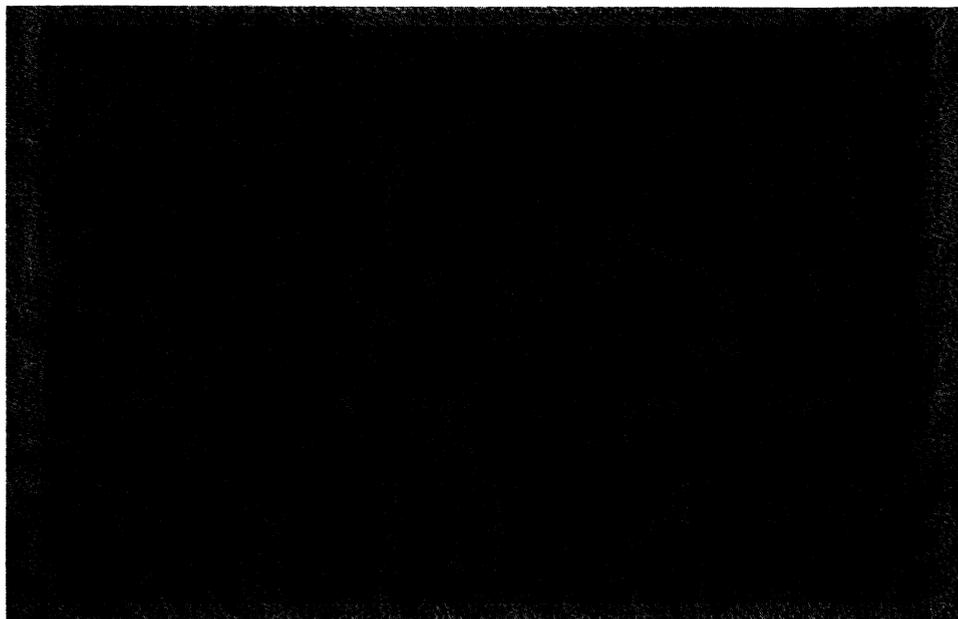


Fig. 2. — Optical micrograph of a P(d-S-b-MMA) copolymer film, annealed at 190 °C for 90 min, the initial film thickness is  $\approx 700 \text{ \AA}$  : thin elongated elevations are spread over the free surface. The full, long dimension of the micrograph is 320  $\mu\text{m}$ .

long, thin segments which themselves split again into shorter ones and so on. The splitting of the segments is accompanied by an increase in their widths. A significant number of round-shaped elevations is only visible after about 480 min annealing (Fig. 3).

The bluish-green color is not the expected color for islands of height  $L$  (from the Newton's scale, it corresponds to a larger thickness). However, the appearance of the bluish-green color instead of the expected blue in the early stage cannot be attributed to a variation in the height of the elevations. It could result from the very small lateral size of the elevations (in comparison with the resolution limit of the microscope ( $\approx 1 \mu\text{m}$ )) and effects such as light diffraction. Consequently, optical microscopy cannot discern, quantitatively, the height of the elevations in the early stage. Quantitative assessment must be addressed by other techniques as STM (Scanning Tunnelling Microscope) for example. It should be noted that a close examination of the contours of the elevations in the early stage shows that they are not well-defined, i.e. that they do not correspond to sharp steps. The bluish-green color changes continuously to blue with increasing time. After approximately 480-900 min of annealing, a



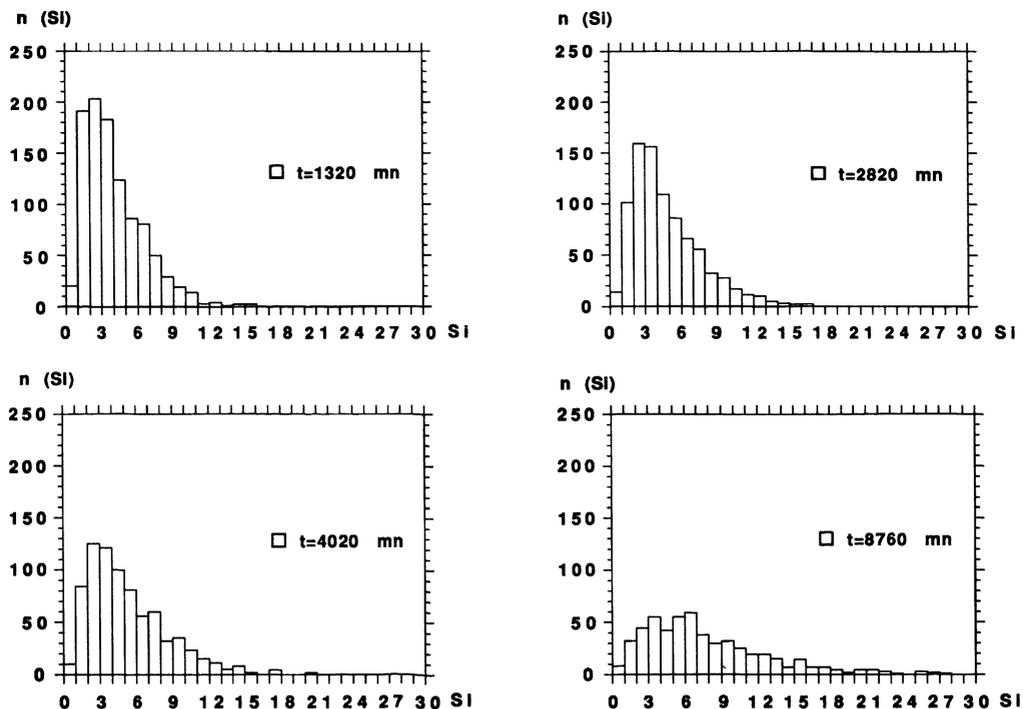


Fig. 4. — The size distribution function of islands for annealing times of 1 320 min, 2 820 min, 4 020 min and 8 760 min.  $S_i$  is the island area in  $\mu\text{m}^2$ .

Nevertheless, an important feature of the growth of islands (or holes) is that their centers of mass do not change with annealing time. For the dense systems under study (i.e. about 30 % of islands (or holes) in surface coverage), three mechanisms are observed: growth of individual islands (or holes), growth by coalescence and the disappearance of the smallest islands (or holes). In such dense systems, the individual growth was observed as a temporary mechanism interrupted from time to time by the coalescence mechanism. Coalescence always occurs between two nearest neighbor islands (or holes). However, diffusion of islands (or holes) towards an other one has never been observed. Rather, the two nearest neighbors fixed in space grow separately and coalesce when their perimeters come closer. After coalescence, the « new » island (or hole) has a dumbbell shape. As time progresses, it turns into a round shape in order to decrease its line free energy (Fig. 5). If the islands (or holes) do not grow, they tend to decrease and to disappear, the dissolution occurs without any lateral shifting as it can be seen in figure 5. Both coalescence and dissolution make the total number of islands (or holes) decrease drastically with time. This behavior is usually observed in the coarsening stage of the phase separation of binary mixtures [15-18] and the dissolution mechanism is known as the Oswald ripening [15, 18, 19].

This study indicates that the decrease of the total number of islands at long times is due mainly to the high dissolution rate. For example, if the total number of islands  $N_t$  is equal to 744 after 1 320 min annealing, there are only 420 islands left after 8 760 min; i.e. a relative decrease of  $\approx 43$  % (during the same time, the area coverage %  $S$  of the total

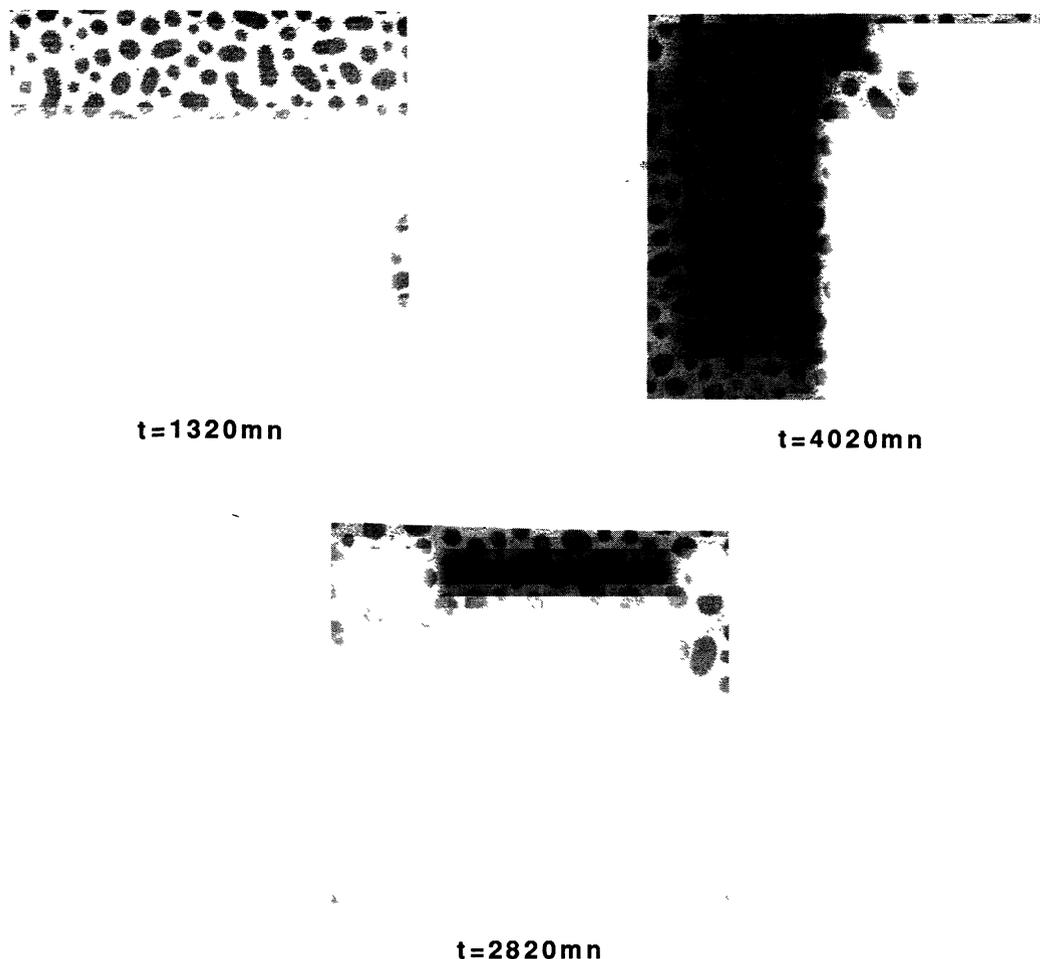


Fig. 5. — Digitized images of optical micrographs of a P(d-S-b-MMA) copolymer film annealed at 190 °C for different annealing times : 1 320 min, 2 820 min, 4 020 min. The initial film thickness is  $\approx 700 \text{ \AA}$ . The elevations appear as black patches on a white background. The size of the digitized images is  $(78 \times 78) \mu\text{m}^2$ .

number of islands was found to be constant) (Fig. 6). During this same time, the cumulated number of coalescences  $N_c$  was found to vary from 17 to 44, as shown in figure 7. One coalescence implies two islands which means that only 54 islands are involved in the coalescence mechanism from 1 320 min to 8 760 min of annealing. On the other hand, the cumulated number of dissolutions  $N_d$  varies from 57 at 1 320 min to 344 at 8 760 min ; i.e. 287 islands are dissolved during this time range (Fig. 7). This shows clearly that the growth of the islands is controlled mainly by the dissolution process. Both  $N_c$  and  $N_t$  increase with time ; however, the variation of  $N_c$  versus time exhibits a clear saturation, while  $N_t$  seems to vary linearly with time over the investigated time range. As a consequence, the prevalence of the dissolution mechanism is more and more pronounced for longer times.

The behavior of holes was found to be quite similar to that of islands in the same time range in that the same growth mechanisms were observed : individual growth, growth by coalescence and dissolution. However, in the case of holes, the decreasing of their total

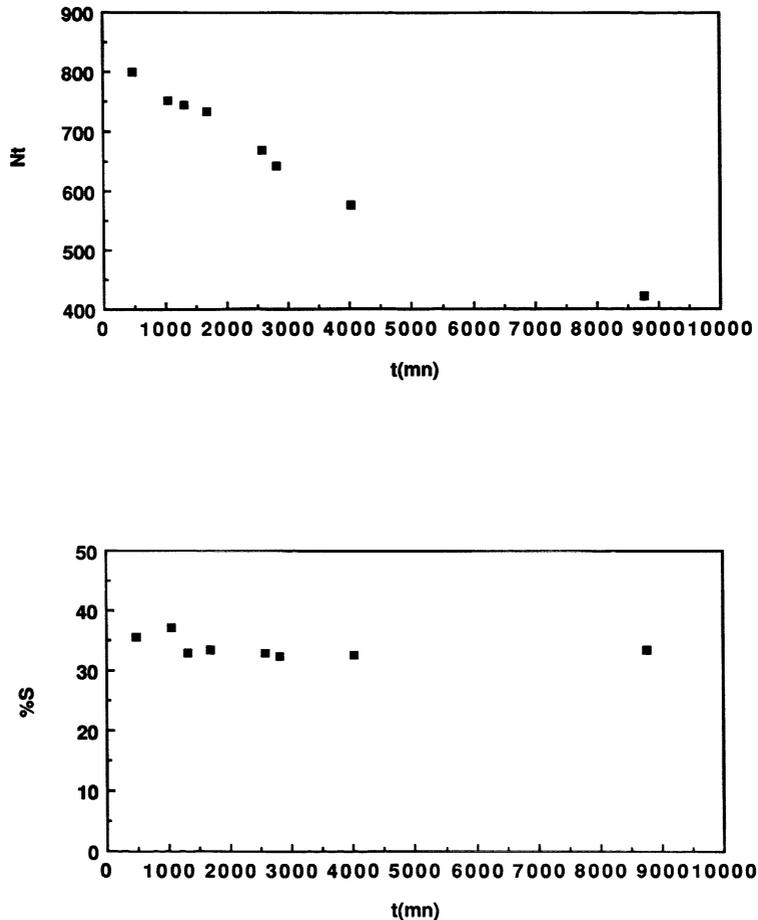


Fig. 6. — Evolution of the total number of islands  $N_t$  and of their total area coverage  $\%S$  with the annealing time (in minutes). These data are extracted from the  $(512 \times 512)$  pixels digitized images.

number is mainly due to the coalescence mechanism which prevails over the dissolution one (9 000 min). It should be noted the dissolution of holes starts only after  $\approx 4\,000$  min of annealing, i.e. much later than the dissolution of islands. Nevertheless, longer times kinetics need to be performed in both cases. Indeed, for times  $\leq 9\,000$  min, the data allow us to give only a general trend but it is not possible to deduce any quantitative laws such as the total number or the mean size of islands *versus* time. Furthermore, it should be interesting to see what is the relative evolution of the dissolution and the coalescence rates at longer times.

*In situ* observations by optical microscopy coupled with Digital image analysis make possible the study of the formation and growth of islands both in real and reciprocal space [20]. In real space, local mechanisms can be identified as it has been shown above, while in reciprocal space a more global approach (symmetry of the morphology) can be made *via* the 2D Fourier Transform.

The  $(512 \times 512)$  2 DFT was calculated from the digitized optical micrographs and, thus, correspond to the same area of the copolymer film. Only the 2 DFT's obtained in the case of

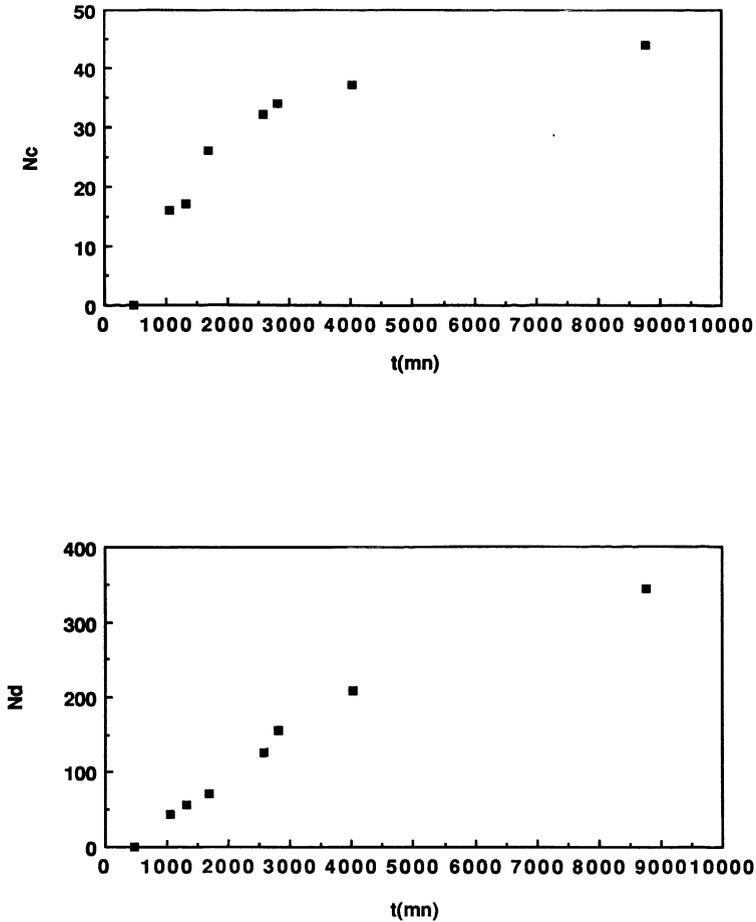
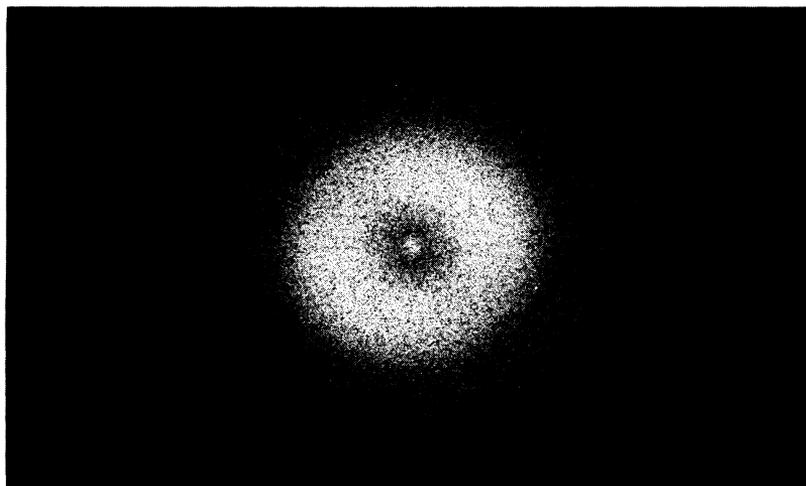
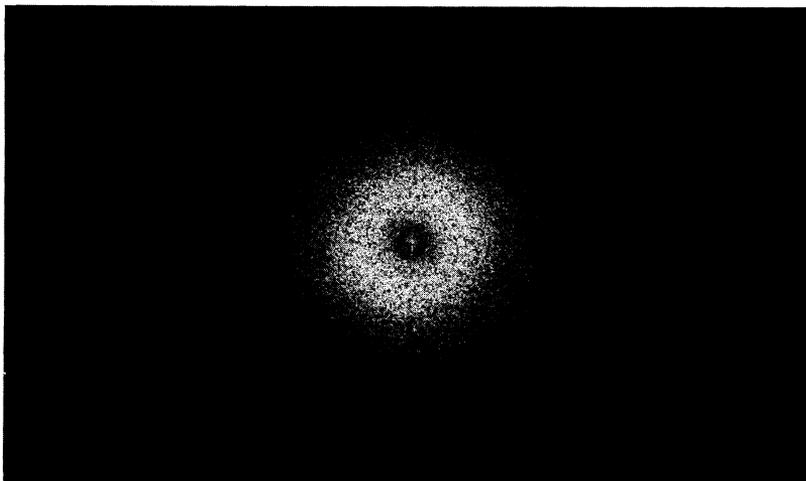


Fig. 7. — Evolution of the cumulated number of coalescences  $N_c$  and of dissolutions  $N_d$  of islands with the annealing time (in minutes). These data are extracted from the  $(512 \times 512)$  pixels digitized images.

islands will be presented here. Figure 8a in the 2 DFT obtained after 140 min of annealing (early stage with a, more or less connected, network of elevations). A diffuse, broad, isotropic ring is clearly visible. The isotropic ring is seen in the whole investigated time-range ; as an example, figure 8b shows the 2 DFT obtained after 1 320 min of annealing (in this case, most of the islands are round shaped). The existence of an isotropic ring shows that the topology can be described by a unique characteristic length  $\ell_c$  in the whole investigated time range. A radial cross section of the isotropic ring allows to obtain the intensity profile *versus* the spatial frequency  $\nu$  (in  $(\text{pixel})^{-1}$ ).  $\ell_c$  is defined as the inverse of the spatial frequency  $\nu_{\text{max}}$  which corresponds to the maximum of the intensity profile. The fast Fourier Transform algorithm we used was not corrected for parasitic noise, however, a crude analysis shows that the characteristic length  $\ell_c$  increases with time. For example, at times of 140, 480 and 1 320 min,  $\ell_c$  is equal to  $2.5 \mu\text{m}$ ,  $3.5 \mu\text{m}$  and  $4.25 \mu\text{m}$ , respectively. The correction of noise has to be done in the 2 DFT algorithm and longer kinetics have to be performed in order to get a quantitative law describing the time evolution of  $\ell_c$ . It has to be noted that, in the case of



a)



b)

Fig. 8. — 2 DFT patterns of the islands topology obtained after 140 min (a) and 1 320 min (b) of annealing. The full, long dimension of the pattern is  $4.55 \mu\text{m}^{-1}$ .

holes, the 2 DFT patterns also exhibit an isotropic ring demonstrating that the hole morphology is also characterized by a unique length  $\ell_c$ .

During the last stage of phase separation in binary mixtures, a unique length characterizes the decomposing structure so that the pattern of the structure at different times differs only in its scale, i.e. spatial self-similarity and dynamic scaling are expected to describe the evolution of the morphology at late times [21]. We do not know, at present, if the existence of a unique characteristic length describing the island (or hole) topology can be related to spatial self-similarity and dynamic scaling. To address this basic question, longer (about 2 decades in time) kinetic experiments are being performed in order to test if parameters such as the structure factor or  $n_s(t)$ , the number of islands of size  $s$  at time  $t$ , satisfies a scaling law [21, 22].

To summarize, at equilibrium, thin diblock copolymer films exhibit a multilayer structure parallel to the external surface. Islands or holes are formed on the free surface if the thickness of the as-cast film is not equal to  $\left(i + \frac{1}{2}\right) L$ . For dense systems (30 % in area coverage), the formation of islands appears to be very different from that of holes. In the early stage, thin, elongated elevations are created. This, more or less, connected network splits progressively into shorter and shorter segments and leads, finally, to round-shaped islands. Contrary to this, holes, once formed, assume circular shape. At longer times, the growth of islands and holes is similar in that the same growth mechanisms are observed ; namely, individual growth, coalescence and dissolution. But, the prevailing mechanism for islands growth is the dissolution one while for holes growth the coalescence mechanism is the preponderant one. It would be, of course, of great interest to study dilute systems (5-10 % in area coverage) ; first to see if, in the early stage, the behavior of islands is still different from that of holes. Furthermore, for longer times, dilute systems make possible the study of the individual growth of islands and holes over larger time scale since the coalescence mechanism is expected to be less active than in dense systems. For dense systems, the island (or hole) morphology is characterized by a unique characteristic length.

#### Acknowledgements.

The digitization of the images was performed at the Institut d'Optique (Orsay-France) and the image processing at the Laboratoire d'Optique Atmosphérique (L.O.A.) at the University of Lille (France). G. Coulon would like to thank L. Gonzalez, C. Deroo and J. C. Roger for their kind hospitality at the L.O.A. and for their helpful discussions.

#### References

- [1] SKOULIOS A., in Block and Graft Copolymers, Eds. J. J. Burke and V. Weiss (Syracuse University Press, Syracuse, New York) 1973.
- [2] HADZIOANNOU G. and SKOULIOS A., *Macromolecules* **15** (1982) 258.
- [3] INOUE T., SOEN T., HASHIMOTO T. and KAWAI H., *J. Polym. Sci. Part A-2*, **7** (1969) 1283.
- [4] HASHIMOTO T., TODO A., ITOI H. and KAWAI H., *Macromolecules* **10** (1977) 377.
- [5] HASEGAWA H. and HASHIMOTO T., *Macromolecules* **18** (1983) 589.
- [6] HENKEE C. S., THOMAS E. L. and FETTERS L. J., *J. Mater. Sci.* **23** (1988) 1685.
- [7] COULON G., RUSSELL T. P., DELINE V. R. and GREEN P. F., *Macromolecules* **22** (1989) 2581.
- [8] RUSSELL T. P., COULON G., DELINE V. R. and MILLER D. C., *Macromolecules* **22** (1989) 4600.
- [9] ANASTASIADIS S. H., RUSSELL T. P., SATIJA S. K. and MAJKRZAK C. F., *Phys. Rev. Lett.* **62** (1989) 1852.
- [10] COULON G., AUSSERRÉ D. and RUSSELL T. P., *J. Phys. France* **51** (1990) 777.
- [11] ANASTASIADIS S. H., RUSSELL T. P., SATIJA S. K. and MAJKRZAK C. F., *J. Chem. Phys.* **92** (1990) 5677.
- [12] RUSSELL T. P., ANASTASIADIS S. H., SATIJA S. K. and MAJKRZAK C. F., *Phys. Rev. Lett* (in press).
- [13] VIG J. R., *J. Vac. Technol. A* **3** (1985) 1027.
- [14] FRANÇON M., Progress in Microscopy (Pergamon Press, Oxford) 1961.
- [15] LIFSHITZ I. M. and SLYOZOV V. V., *J. Phys. Chem. Solids* **19** (1961) 35.
- [16] ROGERS T. M. and DESAI R. C., *Phys. Rev. B* **39** (1989) 11956.
- [17] MARQUSEE J. A., *J. Chem. Phys.* **81** (1984) 976.
- [18] MARQUSEE J. A. and ROSS J., *J. Chem. Phys.* **80** (1984) 536.
- [19] VOORHEES P. W., *J. Stat. Phys.* **38** (1985) 231.
- [20] NISHI T., HAYASHI T. and TANAKA H., *Makromol. Chem. Macromol. Symp.* **16** (1988) 91.
- [21] GUNTON J. D., SAN MIGUEL M. and SAHN P. M., in Phase Transitions and Critical Phenomena, Ed. C. Domb (Academic, New York, 1983) vol. 8.
- [22] BINDER K., *Physica* **140A** (1986) 35.