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Nanometer-Scale Surface Patterns with Long-Range Order Created by Crystallization of Diblock Copolymers

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We report experimental observations on the ordered surface patterns resulting from the crystallization of annealed thin films of microphase-separated low-molecular-weight hydrogenated poly(butadiene-*b*-ethyleneoxide) diblock copolymers. For crystal growth rates higher than about 1 nm/sec the resulting orientation of the crystalline lamellae was perpendicular to the substrate. Alignment of these lamellae on large length scales was found when crystallization occurred at boundaries created by a dewetting process.

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Creating order by arranging molecules in a regular fashion is a highly relevant process in many scientific areas. Material properties or the function of biological systems is strongly affected by, or even depends on, such molecular order. Crystallization is the most prominent molecular self-organization process in nature. Polymer crystallization, however, is usually kinetically hindered, due to the connectivity of the segments, resulting in the lack of long-range order [1,2]. In addition, noncrystallizable moieties may create entropic and steric constraints [3–6]. Many physical, chemical, and biological systems show some degree of order, resulting in macroscopic patterns. However, except for crystallization of small molecules, regularity is often restricted to small dimensions and long-range order is not the rule [7,8].

Block copolymers provide a possibility to create various morphologies with regular features on the length scale of the molecular size [9,10]. Rod-coil polymers have already been recognized as potential materials for the formation of superstructures [11,12]. Next to an interface block copolymers can be aligned. Mainly due to selective surface interactions [13] preferring one component of the block copolymer, the ensuing lamellar structures are oriented parallel to the substrate, giving rise to uniform and featureless surface properties. To measure physical properties of molecules in confined spaces of molecular dimensions, to determine deviations due to surfaces and finite size or quantum effects, and for the technological application of nanostructures in modern devices one attempts to produce surfaces patterned on a molecular scale with long-range order. Parallel lines with nanometer spacings perfectly aligned over distances larger than micrometers are looked for. Molecular patterns at surfaces can be obtained with diblock copolymers at "neutralized" interfaces [14–16], triblock copolymers [17], ultrathin films of diblock [18] or hybrid liquid crystalline block copolymers [19], or electric fields [20]. However, in none of these cases long-range order of the perpendicular lamellae could be obtained. Shear alignment [3], as used for bulk samples, cannot be applied to thin films. However, if the substrates are prepatterned on the correct length scale, polymers may be forced to align according to such patterns [21]. Unfortunately, the preparation of such prepatterned substrates is itself a highly nontrivial process. Consequently, intrinsic processes like the one presented in this Letter, resulting automatically in ordered nanoscopic polymer patterns, are preferable.

Crystallization, one of the most basic processes of self-organization, has not yet been used to create regularly patterned polymer surfaces. Here we present a simple technique based on crystallization of diblock copolymers. Several polymers can crystallize but due to slow kinetics they usually exhibit only local order. On larger scales, the spherulitic superstructures are quite disordered. Kinetic effects are also responsible if equilibrium properties are not obtained. For example, for diblock copolymers with one crystallizable block an equilibrium number of chain folds in the crystalline layer, balanced by the stretching of the other block, is expected but not always observed [22]. In most cases, even if thermodynamics would predict a *nonfolded* crystalline state, the kinetics of the crystallization process results in frequently folded polymers.

Polymer crystallization is a nucleation and growth process. In contrast to, e.g., spinodal decomposition of mixtures, which sets out simultaneously everywhere, a starting point is selected by nucleation and a preferred direction is determined by the growth of the crystals. Different morphologies of block copolymers in the molten, microphase-separated state may also influence the growth direction [3–6]. Boundaries like three-phase contact lines, as provided by wetting and dewetting processes (i.e., spreading or retracting the polymeric liquid on the substrate), may affect both the probability to nucleate and the growth direction [23]. Combining these three phenomena in one process, the crystallization of microphase-separated block copolymers starting from the contact line formed by a dewetting process, should present a highly versatile tool for pattern formation on different length scales.

For our studies, we used a small diblock copolymer, hydrogenated poly(butadiene-b-ethyleneoxide), abbreviated by PB$_h$-b-PEO, obtained by hydrogenation of the polybutadiene block (about 50% 1-2 and 50% 1-4 units, statistically distributed). $M_w = 3700 + 2900$ g/mol, polydispersity <1.1. The radius of gyration of the PB$_h$ block is 2.5 nm; the length of the fully extended crystallized PEO block is 18.4 nm. The polymer has been synthesized anionically in the research laboratories of Th. Goldschmidt AG/Essen, Germany, and its quality has been checked by gel permeation chromatography and NMR. Thin films (approximately 100 nm), obtained by spin coating of dilute toluene or methyl-cyclohexane solutions, were used. The morphology and its evolution at different temperatures were observed in real time by light microscopy, with a vertical resolution of a few nm. More detailed information, after crystallization, was obtained by atomic force microscopy. Thermal treatment was performed directly under the microscope in an inert atmosphere (nitrogen flow).

Optical microscopy on molten thin films of PB$_h$-b-PEO, up to more than 150 °C, revealed a layered structure with discrete steps of approximately 25 nm oriented parallel to the substrate. The observed island-hole patterns are typical for thin diblock copolymer films whose thicknesses are not an integer number of the thickness L of a lamellae [24]. Lowering the temperature and approaching the melting temperature (T_m) resulted in an increase of L [9], caused by an increase of the incompatibility of the two blocks, indicated by the disappearance of islands and the appearance of holes during slow cooling. Thus, upon cooling below T_m we were dealing with crystallization of PEO from a phase-separated lamellar structure. Typical results are shown in Fig. 1. There phase contrast reflects the different viscoelastic properties between the hard crystalline PEO and the soft amorphous PB$_h$ regions, indicated by "lines" with light and dark shades of grey, respectively. After crystallization, the initially smooth surface was quite "rough" [see Fig. 1(A)]. A characteristic distance of about 22 ± 1 nm, caused by the sequence of "hard" and "soft" regions, can be seen in Figs. 1(B) and 1(D). This implies that the lamellae were oriented vertically. The observed patterning is fully reversible. Upon melting, the vertical orientation of the lamellae disappeared. As indicated in Figs. 1(C) and 1(D), the presence of a three-phase contact line preferentially aligned the lamellae.

The scheme in Fig. 2 attempts to explain why the lamellae had to change their orientation from parallel to perpendicular to the substrate. The crystallizable blocks were sandwiched between amorphous layers. Transport between layers was strongly hindered and thus highly unlikely, in particular, on the limited time scale of the crystallization process, while transport within layers was more easily possible. Thus, for such a system of effective confinement, resulting in a conservation of the number of molecules per layer, the key question is: "Does the thickness d_{PEO} of the PEO part of the lamellae *increase* or *decrease* upon crystallization?" Energetic or kinetic arguments (chain stretching, number of folds of the crystalline blocks, cocrystallization) may demand a decrease. A significant decrease of d_{PEO} would prohibit crystallization with crystalline stems perpendicular to the PB$_h$/PEO interface as the corresponding lateral expansion cannot be accommodated for laterally quasi-infinitely extended lamellae. In the case of conserved layered geometry, the crystalline stems may then be aligned parallel to the PB$_h$/PEO interface. However, this is not an ideal situation, as the crystallinity is forced to be significantly lower compared to a vertical arrangement of the stems [3] due to a highly increased number of additional chain folds. For thin films with a *free* surface

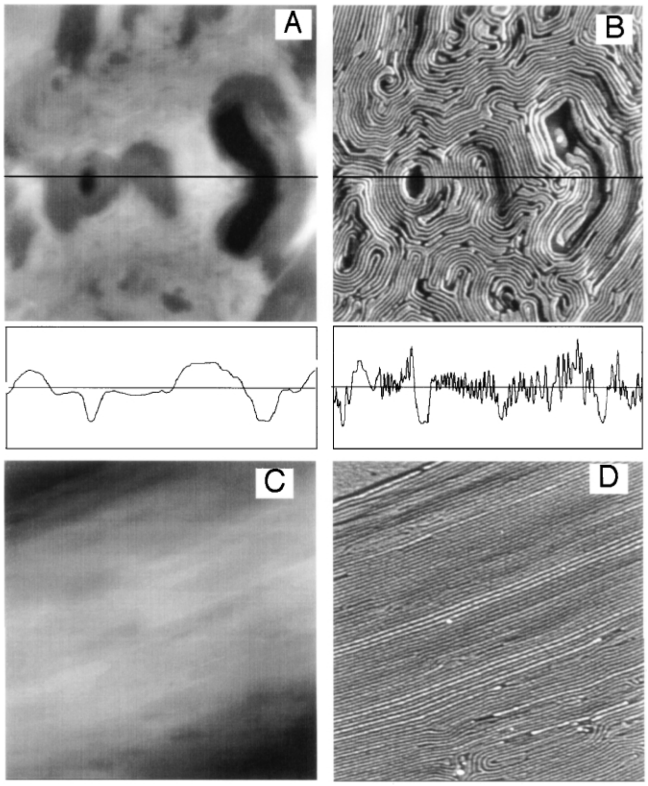

FIG. 1. Typical tapping mode atomic force microscopy images from a thin diblock copolymer film crystallized at 35 °C. (A) and (B) were taken from an area in the middle of the sample while (C) and (D) were taken close to a three-phase contact line (visible in the upper left corner) created by a dewetting process which occurred in the molten state. Topography (A),(C) and phase contrast (B),(D) are shown. The size of the images is $2 \times 2\ \mu\mathrm{m}^2$. The maximum height in (A) and (C) is 100 and 150 nm, respectively. Cross sections from (A) and (B) (length: 2 μm; height: 100 nm and 40 deg, respectively, indicated by the full lines, are also shown.

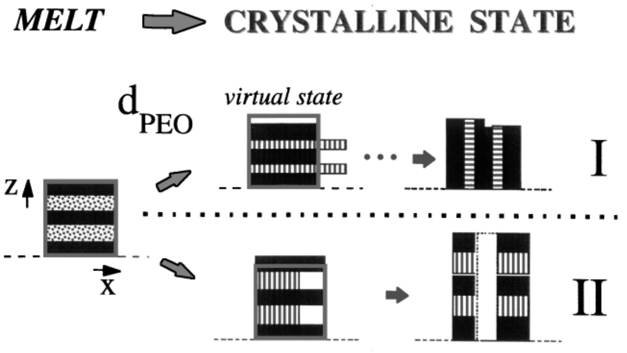

FIG. 2. Schematic representation of the two possible changes of the thickness (d_{PEO}) of the PEO layers upon crystallization. The substrate is indicated by the broken line along the x direction. Path I indicates that a reduction of d_{PEO} (beyond what corresponds to the change in specific density from the molten to the crystalline state) would result in a lateral expansion of the PEO layers. However, as the lateral extension of our samples is quasi-infinite (centimeters as compared to nanometers for the film thickness), this is impossible resulting in rather incomplete crystallization as found in bulk samples of a similar system [3]. In thin films with a free surface, however, there exists an alternative. The lamellae may switch into a vertical orientation. In the latter case, the height (in the z direction) of the lamellae is not controlled. Path II indicates that an increase of d_{PEO} would result in a lateral shrinkage of the PEO layers. As there are always amorphous PB_h blocks connected to the PEO blocks this forces stretching of the PB_h blocks and, as a further consequence, the formation of "craters" or "cracks" which may not have the same diameter for all lamellar layers.

a different ordering, vertically oriented lamella with stems parallel to the substrate, would allow for a much higher crystallinity (as such it would avoid most of the chain folds; see [3]) and thus would represent a state of lower free energy. Consequently, in thin films, for a kinetically induced chain-folded state which caused a decrease of d_{PEO}, there is an energetically driven tendency to orient the lamellae perpendicular to the substrate.

At what places does crystallization most likely start? The effect of confinement of the PEO blocks between PB_h layers is significantly less if this lamellar stack has an edge [25,26], such as at boundaries formed by contact lines, which also can be formed by discrete nonwettable patterns on the substrate. At such places chain folding and reorientation are less hindered. Assuming that crystallization starts at such boundaries, then the first vertically oriented lamella will just reflect the shape of this boundary. Adding further lamellae in the course of crystallization will result in regular patterns determined by the shape of the boundary. The crystal growth velocity can be easily controlled by varying the crystallization temperature. Slow crystallization allows one to build crystals with only few "defects." This may be expressed by a characteristic length w_{PEO} [23]. Only at some distance w_{PEO} from the contact line its orienting influence should start to disappear.

We wanted to verify if our basic assumption, a decrease of d_{PEO} caused by kinetically induced chain folding, is correct and responsible for the observed behavior. Thus, we crystallized samples at different temperatures, increasingly closer to T_m and thus at increasingly slower growth rates. Thermodynamic equilibrium for the number of chain folds may be attained at low growth rates. In addition, the small length of the polymer we used helped to avoid "kinetic traps." As is well known from other experiments on polymer crystallization [1,2], on approaching T_m, the thickness of the crystalline lamellae, i.e., d_{PEO}, increases due to a decrease in the number of chain folds. For our system, this implies a transition from once folded chains to fully extended nonfolded molecules. The experimental results, shown in Fig. 3, indicate that such a transition is indeed possible. Approaching T_m led to an increase in L, and eventually, at 48 °C and a growth rate of about 0.2 nm/sec, to a parallel orientation of the lamellae, without any characteristic lateral spacing. Thus, at 48 °C d_{PEO} is sufficiently big so that the system chooses path II (see Fig. 2). Figure 3 points out that kinetic effects (resulting in metastable chain-folded states) provide interesting possibilities for pattern formation. By varying the rate of crystallization we have proven that the vertical orientation of the lamellae is kinetically controlled but *not* thermodynamically favored.

Although our interpretation accounts for the effect of temperature and can explain the final states, a detailed

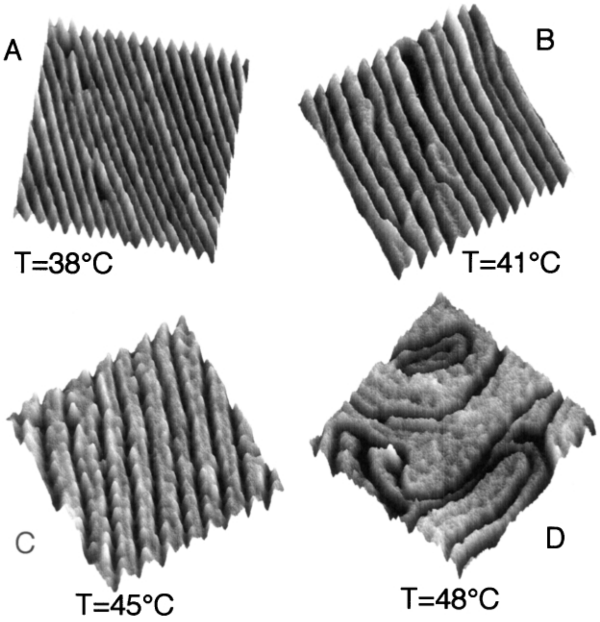

FIG. 3. Typical tapping mode atomic force microscopy images from thin diblock copolymer films crystallized at different temperatures. Only the phase contrast is shown. The size of the images is 400 × 400 nm^2. Note that the periodic spacing increases with temperature and is lost at 48 °C. Moreover, at 48 °C the depression in the phase image is correlated with depressions in the topography (not shown). These depressions relate to the cracks expected for path II in Fig. 2.

description of the evolution of the corresponding nonequilibrium processes is not yet available. It is not clear if the crystallization process involves a one-step or a multistep transition from the melt to the final crystalline state with perpendicular lamellae. The latter is more likely because of the following arguments: The order of the molten state frustrates the optimal crystalline state of the copolymer. Still, partial crystallization may take place leading to a metastable often folded intermediate state. A spontaneous reorganization into the energetically favorable less folded state is unlikely because of the energetic barriers which act due to the existing confinement. Therefore, only a rather strong perturbation of the prevailing order, as given by three-phase contact lines and defects, can spawn a growth process into the favored state. The energy barriers created by the morphology of the melt avoid crystal growth in random directions, which would result in low order spherulitelike patterns as in homopolymer systems, and makes long-range order possible. Note that the idea of metastable intermediate states even in homopolymer crystallization has recently been put forward [27].

In summary, we have shown that in film films crystallization of diblock copolymers from a microphase separated state, combined with a dewetting process, can produce long-range order as a consequence of directed growth. Thereby, the lamellae are oriented vertically, resulting in patterned surfaces with molecular periodicity, well aligned on macroscopic distances. The phenomenon is strongly influenced by chain folding of the crystallizable blocks confined between two layers of amorphous blocks. This comparatively simple process provides regular nanophases of soft-hard, hydrophobic-hydrophilic units for model experiments on the nanometer scale and for potential applications.

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[1] G. Strobl, *The Physics of Polymers* (Springer-Verlag, Berlin, 1996).

[2] D. C. Bassett, *Principles of Polymer Morphology* (Cambridge University Press, Cambridge, England, 1981).

[3] I. W. Hamley *et al.*, Macromolecules **29**, 8835 (1996).

[4] D. J. Quiram, R. A. Register, and G. R. Marchand, Macromolecules **30**, 4551 (1997).

[5] M. D. Whitmore and J. Noolandi, Macromolecules **21**, 1482 (1988).

[6] S.-M. Mai *et al.*, Macromolecules **30**, 8392 (1997).

[7] M. Seul and D. Andelman, Science **267**, 476 (1995).

[8] M. Muthukumar, C. K. Ober, and E. L. Thomas, Science **277**, 1225 (1997).

[9] M. A. Hillmyer *et al.*, Science **271**, 976 (1996).

[10] J. Ruokolainen *et al.*, Science **280**, 557 (1998).

[11] S. I. Stupp *et al.*, Science **276**, 384 (1997).

[12] J. T. Chen, E. L. Thomas, C. K. Ober, and G.-P. Mao, Science **273**, 343 (1996).

[13] P. Mansky, Y. Liu, E. Huang, T. P. Russell, and C. Hawker, Science **275**, 1458 (1997).

[14] P. Mansky *et al.*, Macromolecules **30**, 6810 (1997).

[15] E. Huang, L. Rockford, T. P. Russell, and C. J. Hawker, Nature (London) **395**, 757 (1998).

[16] E. Huang *et al.*, Macromolecules **31**, 7641 (1998).

[17] W. Stocker, J. Beckmann, R. Stadler, and J. P. Rabe, Macromolecules **29**, 7502 (1996).

[18] T. L. Morkved and H. M. Jaeger, Europhys. Lett. **40**, 643 (1997).

[19] G. C. L. Wong, J. Commandeur, H. Fischer, and W. H. de Jeu, Phys. Rev. Lett. **77**, 5221 (1996).

[20] T. L. Morkved *et al.*, Science **273**, 931 (1996).

[21] L. Rockford *et al.*, Phys. Rev. Lett. **82**, 2602 (1999).

[22] E. K. Lin and A. P. Gast, Macromolecules **29**, 4432 (1996).

[23] G. Reiter and J.-U. Sommer, Phys. Rev. Lett. **80**, 3771 (1998).

[24] G. Coulon, B. Collin, D. Ausserre, D. Chatenay, and T. P. Russell, J. Phys. (Paris) **51**, 2801 (1990).

[25] E. Raphaël and P. G. de Gennes, Physica (Amsterdam) **177A**, 294 (1991); Makromol. Chem. Macromol. Symp. **62**, 1 1992.

[26] M. S. Turner, A. Johner, and J.-F. Joanny, J. Phys. I (France) **5**, 917 (1995).

[27] P. D. Olmsted *et al.*, Phys. Rev. Lett. **81**, 373 (1998).