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Nucleation and growth in order-to-order transitions of a block copolymer

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Abstract. – A poly(isoprene-*b*-ethyleneoxide) diblock undergoes multiple ordered state transitions: from a crystalline lamellar (L_c), to a hexagonal (Hex) mesophase, to a bicontinuous cubic phase (Gyroid) before disordering (Dis). We have studied the kinetics of the Hex-to-Gyroid, Hex-to- L_c and L_c -to-Gyroid transitions using synchrotron SAXS and rheology. The Hex-to-Gyroid transformation proceeds via a nucleation and growth mechanism with a small mismatch between the two phases, as anticipated by recent theoretical predictions (M.W. Matsen, *Phys. Rev. Lett.*, **80** (1998) 4470). We provide the first quantitative measure of the activation barrier involved in an order-to-order transition and show the importance of nucleation and growth in these transformations.

Introduction. – Block copolymer morphology (Lam: lamellar, Hex: hexagonally packed cylinders, bcc: spheres in a body-centered cubic lattice and bicontinuous cubic phase with the $Ia\bar{3}d$ symmetry (Gyroid)) [1,2] and the associated order-to-disorder transitions have been investigated in detail. The latter is described as a nucleation and growth process (NG) [3,4] with similarities to the melting of semicrystalline polymers, *i.e.* a first-order transition. However, despite earlier work in surfactants [5,6] and lipids [7,8], the kinetics of the phase transformation between the different microphases, with consequences in processing and applications in nanotechnology, have started to be explored only recently. In exploring the polymorphism of some order-to-order transitions there are many issues that deserve attention: stability *vs.* metastability and more specifically, induction times, supercooling, phase coexistence, nucleation sites, existence and nature of intermediate states, time-scales, activation barriers and the role of fluctuations.

On the theoretical side, Qi and Wang [9] employed a time-dependent Landau-Ginzburg approach and studied the Hex-to-Dis and Hex-to-bcc transformations. Laradji *et al.* [10] employed a theory of anisotropic fluctuations and discussed the Lam-to-Hex transition. Goveas and Milner [11] studied the latter transformation by focusing on a subset of wave vectors of the two phases. Lastly, Matsen [12] applied a self-consistent field theory to the Hex-to-Gyroid transformation. In all of the above studies epitaxy was either found [9,10,12] or assumed [11]. On the experimental side, there have been reports for near epitaxy in the transformations

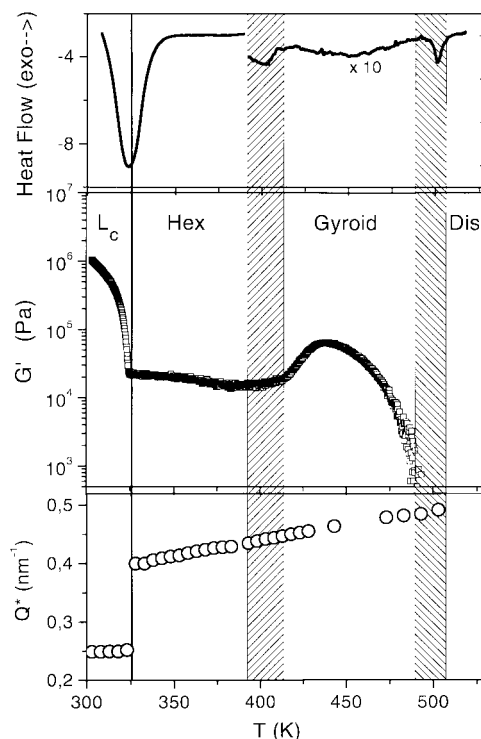


Fig. 1 – Composite plot showing: the heat flow curve obtained by calorimetry (heating rate 1 K/min) (top), isochronal measurement of the storage modulus taken with $\omega = 1$ rad/s, strain amplitude of 0.5% on heating (heating rate = 1 K/min) (middle) and the T -dependence of the Q^* obtained by SAXS (bottom). The vertical line gives the (apparent) melting temperature and dashed regions delineate the Hex-to-Gyroid and Gyroid-to-Dis transitions. Notice the strong endothermic peak associated with the Lc-to-Hex transition and the smaller peaks for the Hex-to-Gyroid and Gyroid-to-Dis transitions.

between Hex-to-bcc [13,14] and Hex-to-Gyroid [15] and some recent real-time experiments on the Hex-to-bcc [16] and HPL (hexagonally perforated layers)-to-Gyroid [17] transitions. Recently, we reported [18] on the phase state of poly(isoprene-*b*-ethyleneoxide) diblock copolymers with compositions in the range $0.25 < f_{PI} < 0.92$. The interaction parameter was determined within the mean-field theory as $\chi = 0.125 + 65/T$, *i.e.*, much stronger than in the poly(styrene-*b*-isoprene) system. The strong $\chi(T)$ resulted in a rich polymorphism within a small T -range [19]. We have studied the dynamics of the order-to-order transformations by performing T -jump experiments between the mesophases (L_c, Hex, Gyroid) using synchrotron SAXS and rheology. Our results for the Hex-to-Gyroid transformation are in excellent agreement with recent theoretical predictions [12] and provide the first quantitative measure of the activation barrier involved. These results emphasize the importance of nucleation and growth in the phase transformation kinetics.

Experimental. – The PI-PEO 5-4 diblock copolymer was synthesized via anionic polymerization, as described elsewhere in detail [18]. The number-averaged molecular weights of PI and PEO were 5400 and 4400, respectively, and the polydispersity (M_W/M_n) was 1.08. Based on the densities for PI and PEO (0.895 and 1.12 g/cm³, respectively) the PI volume fraction was $f_{PI} = 0.61$. Real-time-resolved synchrotron SAXS measurements were performed at the X27C beamline of the National Synchrotron Light Source at Brookhaven National Laboratory. The wavelength of X-rays was 0.1307 nm and a position-sensitive detector was used at

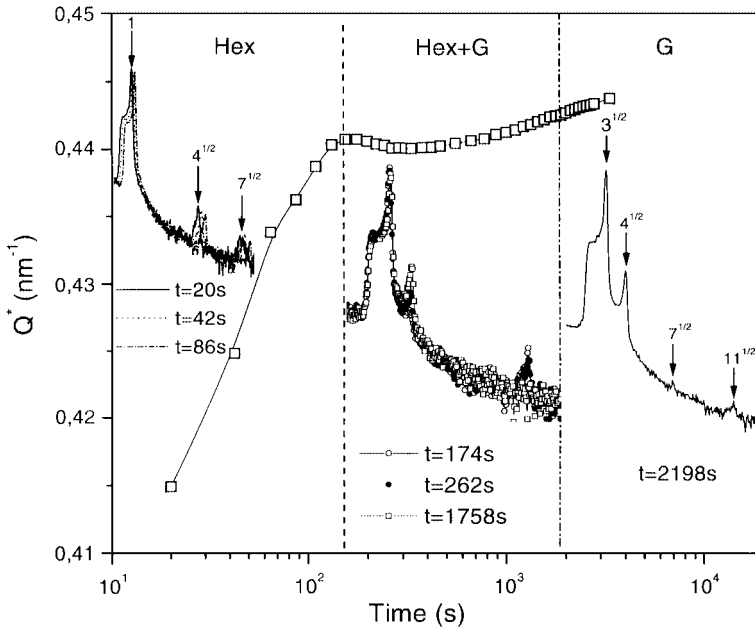


Fig. 2 – Time-evolution of the peak at Q^* following a T -jump from 353 K (Hex) to 413 K (Gyroid). Some representative spectra are shown corresponding to the Hex structure (for times shorter than 150 s), coexisting Hex and Gyroid phases for $174 < t < 1800$ s and final Gyroid phase. The arrows indicate the positions of the higher-order reflections in the Hex and Gyroid phases.

a distance of 1.26 m from the sample. In the kinetic experiments the sample was set in an oven at the initial temperature and subsequently brought to another T -unit at the preset final T .

Results. – Figure 1 shows the results from three experiments; calorimetry, rheology and SAXS, all obtained on heating, with a low heating rate (1 K/min in DSC and rheology and 0.1 K/min in SAXS) for the PI-PEO 5-4 copolymer. In DSC (top), there was a strong endothermic peak at about 325 K associated with the melting of the L_c phase (with a latent heat ΔH_f of 56 J/g resulting in a PEO crystallinity of 75%). Two smaller in magnitude endothermic peaks at about 400 and 500 K with latent heats of 0.3 and 4 J/g, respectively, could also be detected. The latter value corresponding to the order-to-disorder transition can be completely accounted for from [20] $\Delta H_f = RT_{ODT}f(1-f)(\chi N)_{ODT}/M_n$, where R is the gas constant, N is the total degree of polymerization and M_n is the total number-averaged molecular weight. Implicit in the DSC result is the notion of a 1st-order transition not only for the order-to-disorder but also for the order-to-order transitions. In rheology (middle) the storage modulus G' exhibit distinct changes of elasticity at about the same temperatures: The phase with the highest modulus (L_c) melts to the elastic Hex mesophase which then transforms to the bicontinuous phase (Gyroid). At about 500 K the Gyroid melts to the disordered phase. In the same figure (bottom) the T -dependence of the most dangerous wave vector is shown and reveals a large mismatch between the L_c and the Hex mesophases (strong 1st-order transition) and only a weak T -dependence within the other mesophases.

We have explored the kinetics of the order-to-order transitions by means of SAXS and rheology using, as a probe, the distinctly different scattering patterns and elasticity of the mesophases. First we treat the Hex-to-Gyroid transition. Different T -jump experiments from a starting T of 353 K (Hex) to final temperatures in the range 413–433 K, corresponding to the Gyroid phase, have been performed with SAXS and representative spectra are shown

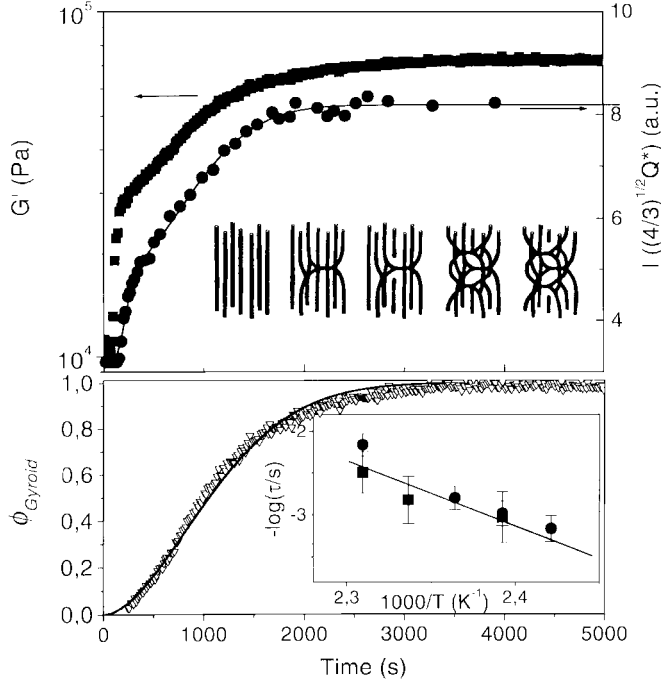


Fig. 3 – Top: Isothermal kinetic experiments of the transformation from the Hex ($T = 353$ K) to the Gyroid phase ($T = 418$ K) obtained by monitoring the storage modulus (squares), and of the intensity of the $(4/3)^{1/2}Q^*$ reflection (circles). The conditions in the former experiment were: $\omega = 1$ rad/s, strain amplitude = 0.5%. The line in the latter experiment is a fit to eq. (3). The inset gives a schematic illustration of the theoretically predicted evolution in the Hex-to-Gyroid transformation (from ref. [12]). Bottom: The evolution of the volume fraction of the Gyroid phase using a simple mechanical model of composite materials (parallel model) is shown in the bottom and the line is a fit to the Avrami equation. In the inset the characteristic times from SAXS (circles) and rheology (squares) are plotted in the usual Arrhenius representation.

in fig. 2, as well as the $Q^*(T)$ for a transition from 353 K to 413 K. For the first 150 s the sample remained in the Hex phase with a strong $Q^*(T)$ within the first 90 s, originating largely by thermal expansion effects (*i.e.*, fig. 1, bottom). After 150 s the spectra nearly locked in position and a new reflection corresponding to the (220) reflection of the Gyroid phase appeared. The formation of the new phase was followed by subsequent growth at the expense of the Hex phase and after 2×10^3 s a stable Gyroid phase was formed, as indicated by the (220) and (321) reflections (the latter differentiates the Gyroid from the fcc structure). The results shown in fig. 2 revealed a short incubation time (~ 60 s) and a long-time phase coexistence, in favor of a nucleation and growth process (see below). To get an estimate of the time-scale and activation barrier involved in the transformation we have used as a probe the growth of the intensity at the $(4/3)^{1/2}Q^*$ reflection corresponding to the (220) reflection of the Gyroid phase and model it as

$$I\left(\sqrt{\frac{4}{3}}Q^*, t\right) = I\left(\sqrt{\frac{4}{3}}Q^*, 0\right) + \Delta I(1 - e^{-kt^n}), \quad (1)$$

where k and n are the rate constant and the Avrami exponent, respectively. The characteristic times (actually half-times) were obtained as $\tau = (\ln 2/k)^{1/n}$ as shown in the inset to fig. 3. In the same plot we show the result of the same T -jump now performed with rheology. The evolution of $G'(t)$ after the first 200 s—which could not be decoupled from the

T -stabilization effects— shows an S-shape which in view of the SAXS results (fig. 2) reflected the Hex-to-Gyroid phase transformation. To obtain the characteristic times in rheology we have used simple mechanical models of composite materials to extract the volume fraction of the newly formed phase $\phi_{\text{Gyroid}}(t)$ from the evolution of $G'(t)$ and $G''(t)$. In the limiting case of homogeneous distribution of strain (parallel model) the modulus of the two-phase system can be expressed as a linear combination of the moduli of the constituent phases as

$$G^* = \varphi_{\text{Hex}} G_{\text{Hex}}^* + \varphi_{\text{Gyroid}} G_{\text{Gyroid}}^*, \quad (2)$$

where ϕ_{Hex} and $\phi_{\text{Gyroid}} (= 1 - \phi_{\text{Hex}})$ are the volume fractions of the Hex and Gyroid phases, respectively. The volume fraction of the newly formed phase $\phi_{\text{Gyroid}}(t)$ is then fitted to the Avrami equation

$$\varphi_{\text{Gyroid}}(t) = 1 - e^{-kt^n}. \quad (3)$$

The Avrami exponent from both experiments was 2 ± 0.2 implying an anisotropic growth of either rodlike objects from homogeneous nuclei or disklike objects from heterogeneous nuclei, the presence of interfaces being in favor of a heterogeneous process. The corresponding kinetic times from rheology are also plotted in the inset of fig. 3 and show a quantitative agreement with SAXS. The activation energy is about 50 kcal/mol which corresponds largely to a collective process. It is worth mentioning that the homopolymer segmental and chain dynamics at these high temperatures (*i.e.*, $T_g + 200$ K, both homopolymers have a glass transition temperature, T_g , of 208 K) have an apparent activation energy of only 7 kcal/mol. Despite the value of the activation energy being an order of magnitude higher than the energy associated with the chain relaxation, it is not excessively high and permits the transformation.

In reviewing the experimental results for the Hex-to-Gyroid transition, we found a short incubation time with fluctuations within the hexagonal structure, nucleation and phase coexistence with nearly epitaxial match of periodicity, highly anisotropic growth and long time scales associated with highly collective processes. The above experimental results can be compared with recent SCFT [12] treating the Hex-to-Gyroid transformation. The barrier for the Gyroid-to-Hex transition was found to vanish near the Hex/Sphere spinodal line while in the forward direction (*i.e.*, Hex-to-Gyroid) the system experiences two instabilities at the Hex-to-Lam and Hex-to-Gyroid spinodals. Notably, the spinodals were well separated from the Hex/Gyroid boundary and the separation was found to increase with increasing segregation, which implied a nucleation and growth mechanism. Furthermore, the small kinetic barrier suggested an epitaxial transformation, *i.e.*, nearly complete match in orientation and domain size [8]. A possible scenario for the Hex-to-Gyroid transition involves the formation of a nucleus of a single fivefold junction from three neighbor cylinders which finally produce the required threefold junctions. The above scenario results in a highly anisotropic growth with the Gyroid phase growing predominantly along the cylinder axis and is consistent with our experimental results both for the anisotropy and for the highly collective process (nucleation and growth) involved. Furthermore, the transformation is nearly epitaxial with only a 1% mismatch in length scale which is well within the theoretical prediction and is responsible for the small energy barrier involved. We have also examined the reverse transformation, *i.e.*, Gyroid-to-Hex and found a near epitaxial nucleation and growth mechanism with very long (more than 2×10^3 s) coexistence between the Gyroid and Hex phases partly due to mobility reasons. The theoretical scenario for this transformation [12] involves the nucleation of a fivefold junction and the rapture of the original threefold junctions resulting in a slow unzip of the Gyroid phase to cylinders.

Next we have studied the transformation between the L_c and Hex phases. First, the Hex-to- L_c transition was studied by SAXS and rheology. Some typical SAXS spectra for the transition from 353 to 313 K are shown in fig. 4 together with the domain spacings. The spectra

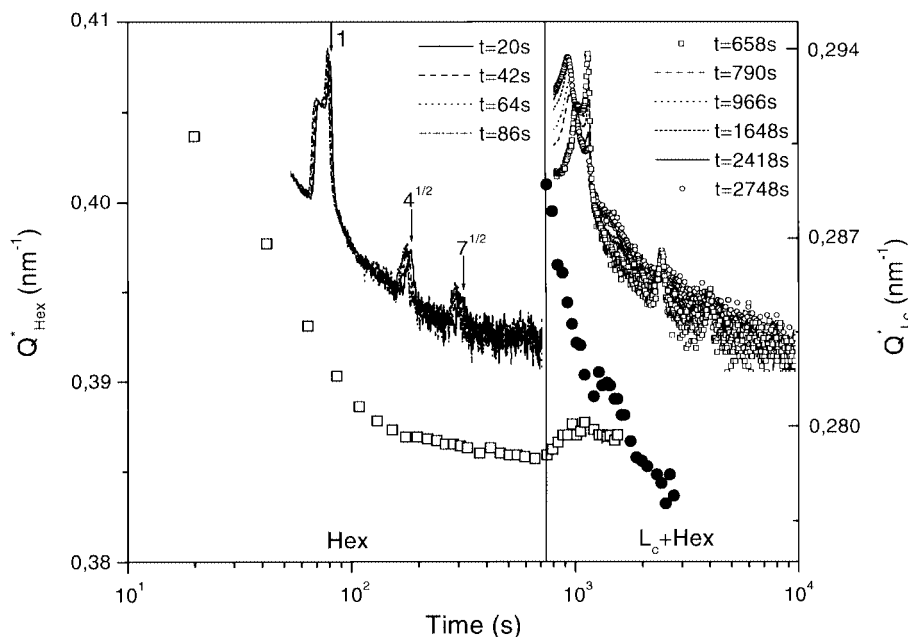


Fig. 4 – SAXS spectra taken for a T -jump from 353 (Hex) to 313 K (L_c) and corresponding peak positions for the Hex and L_c phases. The Hex phase is supercooled for about 700 s and for longer times there is a coexistence of two phases with very disparate length scales.

reveal a supercooled Hex phase for about 700 s followed by the nucleation and growth of L_c at the expense of the Hex phase. Since the crystallizable block is the minority component, the nucleation sites can be located anywhere within the PEO-PI interface. There are two distinct and competing length scales associated with the folded PEO chains in the L_c phase and the all amorphous Hex mesophase. Following T -equilibration within the sample (~ 90 s) the domain spacing corresponding to the quenched Hex phase remains nearly constant, whereas the growing L_c phase shows an increasing size reflecting stretching of the PEO chains over long times. Using the long period, crystallinity, crystalline lamellar thickness and the thickness of a fully extended PEO chain we obtained a single crystalline lamellar per PEO domain with 2 chain folds. Overall, the results of fig. 4 provide a clear evidence of nucleation and subsequent growth of PEO crystals.

The L_c -to-Hex transition was studied next by SAXS for a T -jump from 313 to 353 K. In contrast to the reverse transition shown in fig. 4, the L_c phase was found to melt on a much faster time-scale to the Hex phase with a short-time coexistence (20 s) of the two phases, indicative of the 1st-order nature of the transition. Up on melting the system has a memory of its equilibrium phase —crystallization disrupted the equilibrium Hex mesophase— and it reverts spontaneously due to the large driving force (strong 1st-order transition) by fast chain diffusion to the curved (Hex) mesophase.

Subsequently we have performed larger T -jumps from 313 to 418 K, *i.e.* from the L_c to the Gyroid phase trying to bypass the Hex mesophase. We found that this is not actually possible. First the L_c melts to the Hex phase and subsequently the Gyroid nucleates on the Hex as described above with respect to the L_c -to-Hex and Hex-to-Gyroid transitions, respectively. The reverse transition from 418 to 313 K, *i.e.*, Gyroid-to- L_c was found to contain a double nucleation and growth mechanism; first the Hex nucleates on the Gyroid phase and then the L_c nucleates on the Hex phase, *i.e.*, Gyroid-to-Hex and Hex-to- L_c in a single T -jump. The time-scales involved were very long and we will describe this finding in more detail in the future.

Conclusion. – We have studied the Hex-to-Gyroid, Hex-to- L_c and L_c -to-Gyroid transitions in a PI-PEO diblock copolymer, with $f_{PI} = 0.61$, by performing T -jumps between the mesophases involved with synchrotron SAXS and rheology. We found that i) the Hex-to-Gyroid transition involved the nucleation and highly anisotropic growth of the Gyroid phase along the cylinder axis and this was a highly cooperative process (~ 50 kcal/mol). The process shows a near epitaxy which explains the small activation barrier. The reverse transition is also described as a nucleation and growth but it involves longer time-scales. These results are in excellent agreement with recent SCFT calculations. For the ii) Hex-to- L_c we found that we can undercool the Hex phase for long times before the nucleation of the PEO starts leading to a long-time coexistence between two phases with very different domain spacings. The forward transition occurs on a much faster time-scale and there is a short-time coexistence of the two phases. Lastly, we have studied the iii) L_c -to-Gyroid transition trying to bypass the Hex mesophase and found that the final Gyroid phase nucleates on the Hex phase which in turn provides the required intermediate length scale for the transformation. The reverse transformation shows a novel double nucleation and growth mechanism which will be discussed in more detail in the future. Overall the above findings suggest nucleation and growth as an important mechanism involved in the transformation dynamics between ordered mesophases in block copolymers.

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