

MOLECULAR AND SUPRAMOLECULAR ORDERING IN CONFINED ENVIRONMENTS

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Abstract Crystal and phase morphologies and structures determined by self-organization of crystalline-amorphous diblock copolymers, crystallization of the crystallizable blocks, and vitrification of the amorphous blocks are reviewed through a systematic study on a series of poly(ethylene oxide)-*b*-polystyrene (PEO-*b*-PS) diblock copolymers. On the base of competitions among these three processes, molecular and supramolecular ordering in confined environments can be investigated. In a concentration-fluctuation-induced disordered (D_{CF}) diblock copolymer, the competition between crystallization of the PEO blocks and vitrification of the PS blocks is monitored by time-resolved simultaneous small angle X-ray scattering (SAXS) and wide angle X-ray diffraction (WAXD) techniques. In the case of $T_c < T_g^{PS-rich}$, the crystallization of the PEO blocks is observed to be confined within the bicontinuous D_{CF} phase due to the rapid vitrification of the PS-rich phase. Overall crystallization rate, crystal melting behavior, and crystallinity results further confirm the competition between crystallization and vitrification at different temperatures. In an ordered lamellar PEO-*b*-PS diblock copolymer, the crystallization of the PEO blocks is completely confined within the ordered lamellae due to rapid vitrification of the PS layers as observed by time-resolved SAXS and WAXD experiments. From the combined two-dimensional SAXS and WAXD measurements, the crystal orientation within the confined lamellar geometry is found parallel to the lamellar surface normal when it is isothermally crystallized at 35°C. In an ordered cylindrical PEO-*b*-PS sample, the crystallization of the PEO blocks is also observed to be confined within the ordered cylinders because of rapid vitrification of the PS matrix. The crystal orientation within the confined cylinders is found perpendicular to the cylinder axis as it is crystallized at 35°C.

Keywords Poly(ethylene oxide)-*b*-polystyrene diblock copolymer, Molecular ordering, Supramolecular ordering, Confined environment

INTRODUCTION

Block copolymers possess self-assembled supramolecular structures formed under various conditions^[1-3]. In most cases, microphase separation is driven by the immiscibility between dissimilar block copolymer components, which are covalently linked. Theoretically, two limiting segregation regimes have been recognized, i.e., the strong segregation limit (SSL)^[4, 5] and the weak segregation limit (WSL)^[6]. In the SSL regime, a variety of ordered morphologies, such as lamellae, cylinders (hexagonal) and spheres (body-centered cubic), have been recognized as a consequence of minimizing free energy of the system by balancing interfacial energy, chain stretching, and maintaining constant density^[4, 5]. In the WSL regime, new ordered phases, including double gyroid and double diamond, have also been observed in block copolymers^[7]. The order-to-order phase transitions, the order-to-disorder transition (ODT), and the structures of disordered states are among the most

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attractive subjects. Besides amorphous-amorphous diblock copolymers, other diblock copolymers, such as liquid crystalline-amorphous diblock copolymers^[8] and crystalline-amorphous diblock copolymers^[9, 10], have received substantial attention. Molecular and supramolecular self-assemblies can form at different length scales^[11]. For example, microphase separation of the diblock copolymer usually occurs on a scale of tens of nm, low ordered liquid-crystalline phase formed by the liquid crystalline layers is usually on a scale of a few nm, and crystallization of the crystalline blocks is in an atomic packing scheme on a scale of a few tenths of nm.

In bulk crystalline-amorphous block copolymer systems, there are three factors that determine the final phase and crystalline morphology of these diblock copolymers, i.e., the self-organization of the diblock copolymer (the order-disorder transition temperature, T_{ODT}), the crystallization of the crystallizable blocks (the crystallization temperature, T_c), and the vitrification of the amorphous blocks (the glass transition temperature, T_g^a)^[12]. Therefore, competitions among these three processes can be understood by comparing these three temperature parameters. Generally speaking, when microphase separation precedes crystallization, the crystallization of the crystallizable blocks can be either confined or unconfined by the pre-existing phase morphologies. In disordered and weakly segregated low molecular weight crystalline-amorphous diblock copolymers, when the $T_g^a \ll T_{ODT}$ and T_c , and the viscosity of the system is relatively low, unconfined crystallization takes place, since crystallization involves much stronger molecular interaction compared to that in microphase separation. The crystallization thus overwrites the existing phase morphology to form lamellar crystalline morphology, and memory of the initial phase morphology is lost. When $T_{ODT} < T_c$ in the case of $T_c > T_{ODT} \gg T_g^a$, unconfined crystallization occurs in a disordered phase^[12–20]. While $T_{ODT} > T_c > T_g^a$, unconfined crystallization takes place in an ordered phase^[15–26]. Unconfined crystallization may also occur when the crystallizable blocks are a major component, especially in some terblock copolymers. The initial ordered phase morphology is overridden by the crystalline lamellar structure, evidenced by the formation of crystal spherulites^[27–32].

On the other hand, if $T_g^a > T_c$, crystallization becomes confined, and the existing phase morphology exerts strong restrictions on crystallization of the crystallizable blocks. As a consequence, the existing phase morphology is preserved after crystallization. Confined crystallization has been observed in both disordered and ordered phases, depending upon the T_{ODT} . When $T_g^a > T_c$ and T_{ODT} , the crystallization is confined in a concentration-fluctuation-induced disordered (D_{CF}) phase^[12]. If $T_{ODT} > T_g^a > T_c$, the crystallization is confined within the existing ordered phase due to the rapid vitrification of the amorphous phases^[33–43]. Furthermore, although in some cases T_c is higher than T_g^a , at least partially confined crystallization may occur in strongly segregated crystalline-amorphous diblock copolymers^[44–46], in which $T_{ODT} \gg T_c$ and T_g^a . This may be due to a strong microphase separation between the two immiscible blocks, and only local segmental arrangements occur when a relatively rapid crystallization takes place.

Recently, investigation of confined crystallization using crystalline-amorphous diblock copolymers has received substantial attention. It is interesting to understand crystal orientation with respect to the confined geometry. For confined crystallization within a lamellar geometry, there are two extremes of chain orientations in polymer crystals associated with microphase separated nano-lamellae, i.e., the chain direction (usually the c -axis of the crystal) is oriented either parallel^[14, 27, 47–49] or perpendicular^[37, 38, 41, 42, 50] to the lamellar surface normal ($\hat{n}$). In some other cases, tilted chain orientation in the crystals with respect to $\hat{n}$ is also formulated^[13, 51, 52]. For confined crystallization within a cylindrical geometry, crystal orientation with the c -axis perpendicular or tilted to the cylinder axis is observed in polyethylene-containing block copolymers^[44, 46].

In this review, confined PEO crystallization in a disordered poly(ethylene oxide)- b -polystyrene (PEO- b -PS) diblock copolymer and crystal orientations in ordered lamellar and cylindrical PEO- b -PS diblock copolymers have been summarized. The molecular characterization data of the PEO- b -PS samples are listed in Table 1. These samples provide a unique opportunity to investigate molecular and supramolecular ordering in well-defined confined environments with different dimensionalities. In the disordered sample, it is found that the final phase morphology is determined by the competition between crystallization of the PEO block and vitrification of the PS-rich phases. In the ordered lamellar PEO- b -PS diblock copolymer, the PEO crystal orientation (c -axis) between two PS layers is found parallel to $\hat{n}$ when isothermally crystallized at 35°C. In the ordered cylindrical

PEO-*b*-PS diblock copolymer, the *c*-axis of PEO crystals is found perpendicular to the cylinder axis at $T_c = 35^\circ\text{C}$.

Table 1. Molecular characterization of PEO-*b*-PS diblock copolymer samples

Sample	M_n^{PS} (g/mol) ^a	M_w/M_n (PS) ^a	M_n^{PEO} (g/mol) ^b	M_w/M_n (PEO- <i>b</i> -PS) ^c	f_{PEO} ^d (%)	T_g^{PS} (°C)
EOS-D	5200	1.05	11000	1.07	66	44 ^e
EOS-L	9200	1.02	8700	1.04	47	62 ^f
EOS-C	16000	1.02	9000	1.09	33	72 ^f

^a Determined by SEC using polystyrene standards for calibration
^b Determined by ¹H-NMR
^c Determined by SEC using universal calibration
^d Volume fraction of the PEO block in amorphous melt (The densities of amorphous PS, amorphous PEO, and crystalline PEO are 1.052 g/cm³, 1.124 g/cm³ and 1.239 g/cm³, respectively.)
^e The $T_g^{\text{PS-rich}}$ is determined by dilatometer mode TMA upon cooling from the isotropic melt.
^f Determined by DSC with 5 K/min cooling rate

CONFINED CRYSTALLIZATION IN A CONCENTRATION-FLUCTUATION-INDUCED DISORDERED (D_{CF}) PEO-*b*-PS SAMPLE

Phase Behavior of the Diblock Copolymer

Figure 1 shows a set of 1D SAXS results recorded during heating at 1 K/min in the melt. A scattering peak can be seen at $q = 0.367 \text{ nm}^{-1}$ at 50°C (long period $L = 2\pi/q = 17.1 \text{ nm}$). With increasing temperature, this peak gradually shifts to higher q values, and its intensity decreases and the half-width at half-maximum (HWHM) increases. No higher order scattering peak can be found in this figure. Based on this scattering profile, a disordered state can be qualitatively identified in the temperature range studied. The formation of this scattering peak (correlation hole scattering) originates from the local density fluctuation of the two components in the diblock copolymer. If we plot the relationship between the reciprocal maximum intensity (I_m^{-1}) and reciprocal temperature (T^{-1}), an initially linear decrease at higher temperatures can be seen followed by a non-linear decay at lower temperatures^[53, 54] as shown in Fig. 2. No sudden discontinuous change of the I_m^{-1} at a low temperature can be found for $T \geq 50^\circ\text{C}$. In this figure, the square of the HWHM (σ_q) data is also included, and a similar

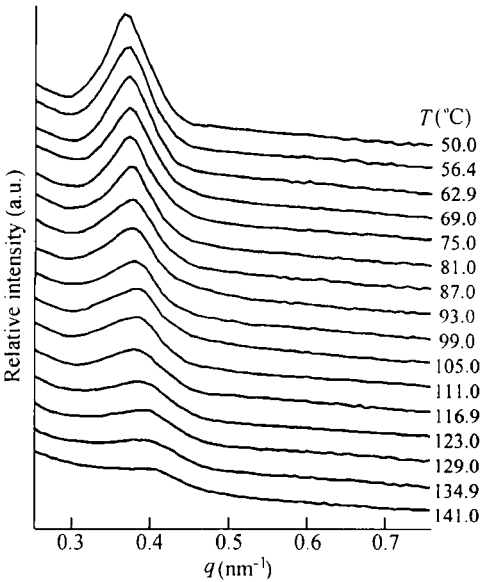


Fig. 1 A set of 1D SAXS results of EOS-D at different temperatures in the melt

relationship with respect to T^{-1} can be found. Both observations indicate that the ODT of the sample is not seen above 50 °C. As shown in this figure, the linear relationship between the I_m^{-1} and T^{-1} at higher temperatures ($> 125\text{ }^\circ\text{C}$) reveals that the disordered state can be described by the mean-field theory^[6], while the non-linear relationship at lower temperatures represents the disordered state which can be described by the concentration fluctuation theory^[4, 5]. Therefore, in the T_c range, the sample is in a D_{CF} state.

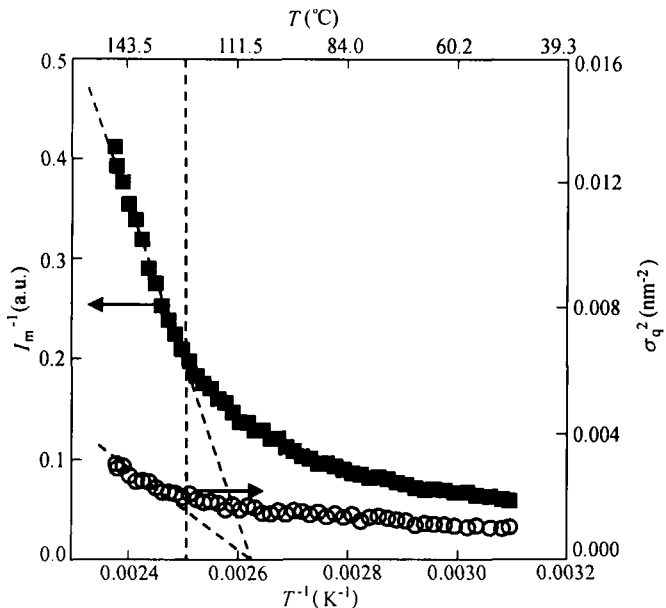


Fig. 2 Relationships between the reciprocal X-ray scattering intensity (I_m^{-1}) and square of half-width at half-maximum (σ_q) with respect to reciprocal temperature (T^{-1})

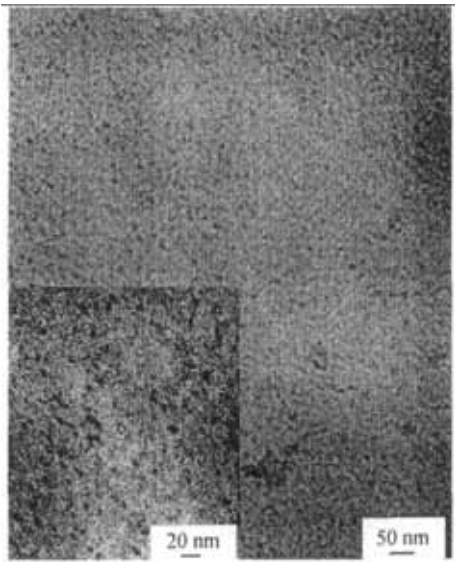


Fig. 3 TEM observation of the concentration-fluctuation-induced disordered phase morphology (D_{CF}) of an ultramicrotomed EOS-D thin film after staining using RuO_4

Figure 3 shows the real space TEM observation of the D_{CF} phase. There is no obvious ordered structure in the micrograph. However, concentration fluctuations can be clearly seen in this micrograph. Since PEO-rich phases are more easily stained using RuO_4 , they appear darker than PS-rich phase (see the TEM micrograph in

Fig. 16, PEO cylinders appear darker than the PS matrix). This result is consistent with those obtained by other research groups^[53]. Thus, the D_{CF} phase is observed to possess a bicontinuous structure with both PEO-rich and PS-rich phases. It is important to note that both the PEO-rich and PS-rich microdomains do not possess sharp interfaces, but sinusoidal-wave-type profile interfaces^[55, 56].

Confined Crystallization when T_c lies below $T_g^{PS-rich}$

When the sample is quenched to well below the $T_g^{PS-rich}$, the vitrification process takes place rapidly. Note that a quick quenching leads to a shift of the $T_g^{PS-rich}$ towards higher temperatures. Therefore, it is expected that the crystallization of PEO blocks take place in the confined environment provided by the PS-rich phase. Figure 4 shows a set of real-time resolved SAXS results during isothermal crystallization at 27°C (17 K below the $T_g^{PS-rich}$, see Table 1). Figure 5 is a set of corresponding WAXD data recorded simultaneously. At the beginning of crystallization ($t_c = 0.17$ min), SAXS results show a weak scattering peak at $L = 17.1$ nm. This peak has the identical intensity and HWHM as those observed at high temperatures in the D_{CF} state (Fig. 1). Before crystallization of the PEO-blocks, therefore, the system is still in this D_{CF} state. It can be further supported by the observation that no Bragg reflections in the WAXD experiments can be found during this short period of time. After $t_c = 0.5$ min, crystallization starts to take place, evidenced by substantial increases of the SAXS scattering (Fig. 4) and Bragg reflection intensities (Fig. 5). More importantly, although the SAXS intensity significantly increases, the L of the scattering peak remains constant during the entire crystallization process; no second-order scattering peak can be found after complete crystallization. These results indicate that the crystallization of the PEO blocks is confined within the constrained glassy phase, which is a continuous phase.

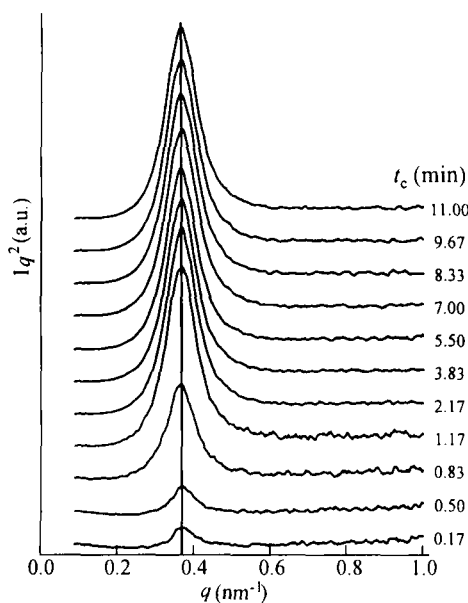


Fig. 4 Sets of time-resolved SAXS results of EOS-D isothermally crystallized at 27°C

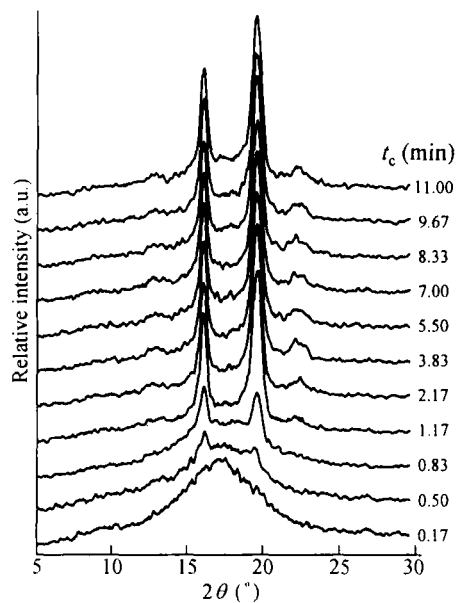


Fig. 5 Sets of time-resolved WAXD results of EOS-D isothermally crystallized at 27°C

If the sample is heated starting at 27.0°C, the SAXS results show that the L does not change until $T = 38^\circ\text{C}$ is reached (Fig. 6). The L then thickens progressively up to 19.0 nm at 52.3°C beyond which the crystal melting starts (Fig. 7). This temperature of 38°C where the thickening starts is 6 K lower than the $T_g^{PS-rich}$ due to the driving force of crystal annealing which reduces the T_g . As long as the PEO-*b*-PS is crystallized below 30°C, the onset of lamellar thickening is always found to be at 38°C. These experimental results provide additional evidence that the PEO crystals can be annealed to break the geometrically constrained phase morphology only when the temperature is in the vicinity of, or higher than, the $T_g^{PS-rich}$, depending on the metastability of the frustrated PEO-block crystals.

The direct consequence of this study is the lower limit of the glassy phase size. In polymer physics, an interesting question is how small a phase can be and still be called a phase. In other words, where is the lower limit of the phase size at which the macroscopic phase properties are still retained? Based on our experimental results, the size of the PS-rich phase can be estimated to be close to 7–8 nm through a simple calculation, which converts the volume fraction of the copolymer components to the linear dimension assuming a disordered two-phase model as a first approximation. We expect that a glassy state can exist in polymers at least down to this size range. The estimation of the size of the PEO component is thus roughly 9–10 nm. Note that in a linear PEO with the same molecular weight, its L after being crystallized at 27°C is estimated to be 15.0 nm^[60], which is much greater than the PEO crystal size in the diblock copolymer. This clearly demonstrates the constrained PEO-block crystallization caused by the PS-rich glassy phase.

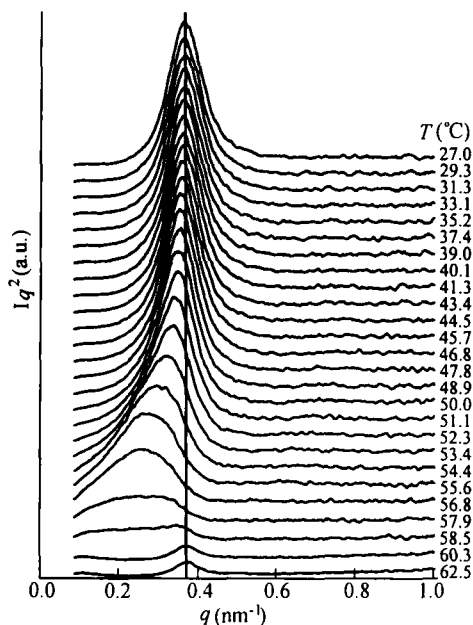


Fig. 6 Sets of time-resolved SAXS heating results of EOS-D after crystallization at 27°C at a heating rate of 1 K/min

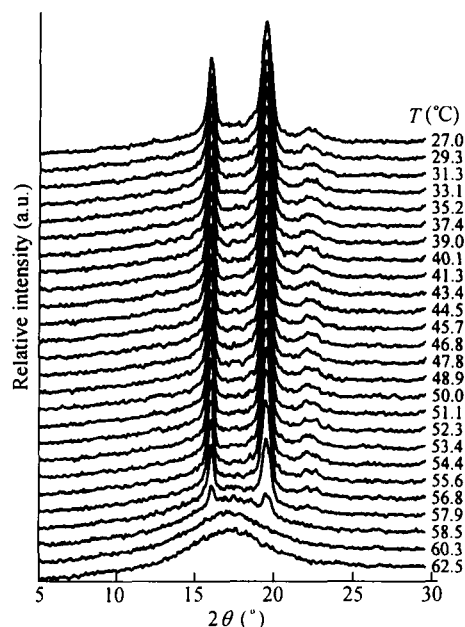


Fig. 7 Sets of time-resolved WAXD heating results of EOS-D after crystallization at 27°C at a heating rate of 1 K/min

Crystal Melting Behavior and Overall Crystallization Kinetics

DSC heating diagrams in Fig. 8 show a single melting endotherm for the EOS-D sample after complete crystallization at different T_c s. This endothermic process is clearly attributed to the crystal melting of the PEO blocks. The T_m appears at a constant temperature of 57.5°C when the T_c is below 38°C. Between $T_c = 38^\circ\text{C}$ and 46°C, the T_m gradually increases with increasing T_c . After $T_c = 46^\circ\text{C}$, the increase of the T_m speeds up, and finally, it reaches 60°C at $T_c = 48.1^\circ\text{C}$.

Figure 9 provides the T_m and crystallinity dependence on isothermal T_c s. Three T_c regions can be identified based on the T_m changes as described in the previous paragraph (dashed vertical lines in the insert). It is interesting that three regions in the crystallinity changes of the PEO-blocks can also be observed: a slight increase from 62% at $T_c = 30^\circ\text{C}$ to 65% at $T_c = 38^\circ\text{C}$ in region I; a gradual increase to 82% as T_c reaches 46°C (region II); and a plateau of the crystallinity (82%) in region III with further increasing T_c . When we consider the three regions observed in T_m and crystallinity changes with T_c , it becomes evident that region I roughly corresponds to the system below the $T_g^{\text{PS-rich}}$, region II is within the $T_g^{\text{PS-rich}}$, and region III is above the $T_g^{\text{PS-rich}}$. Therefore, these changes in T_m and crystallinity in the three regions may reflect the PEO-block crystallization in different environments (confined *versus* non-confined). Furthermore, a 20% difference in the crystallinity of the PEO-

block crystallized below and above the T_g^{PS-nch} may provide additional evidence for the constrained environment effect on crystallization.

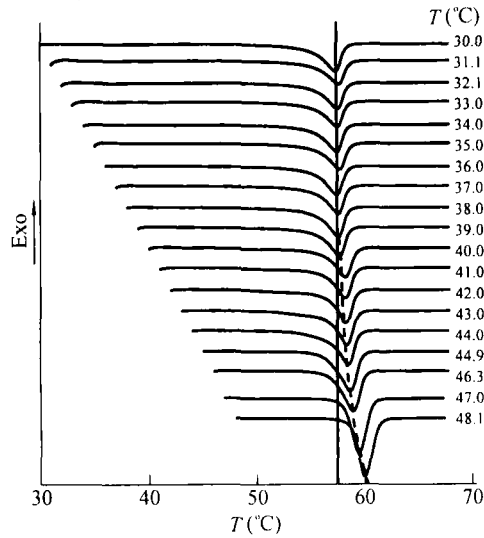


Fig. 8 DSC heating diagrams of EOS-D after crystallization at different T_c s
The heating rate was 5 K/min.

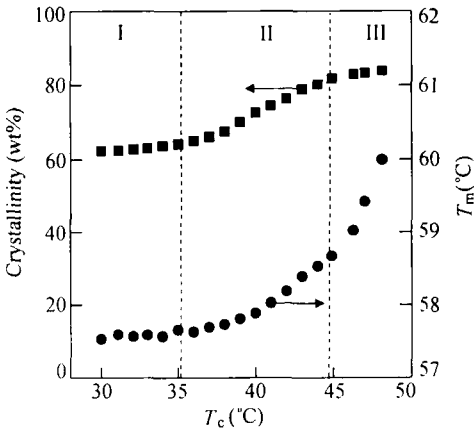


Fig. 9 Melting temperature and crystallinity changes with T_c observed by DSC

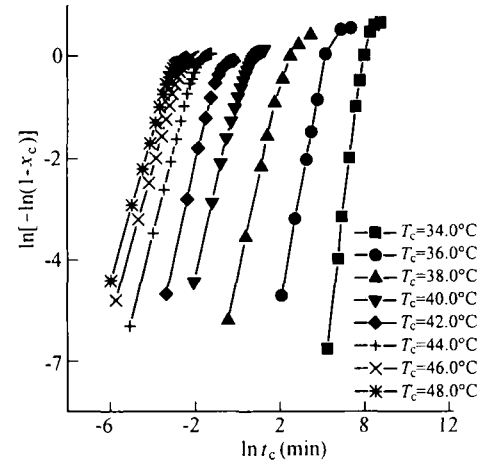


Fig. 10 The Avrami plots of EOS-D crystallized at different T_c s

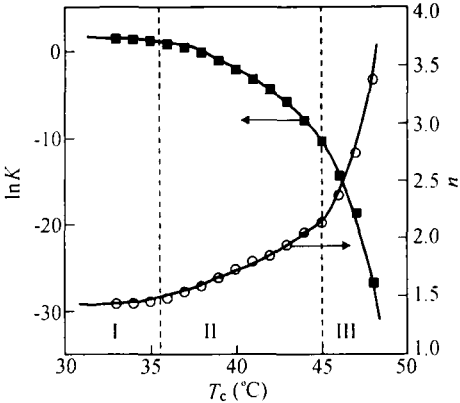


Fig. 11 Changes of the Avrami rate, $\ln K$ and the Avrami exponent n with respect to different T_c s

The overall crystallization kinetics is studied by DSC, and plotted using $\ln[-\ln(1-x_c)]$ versus $\ln t_c$ (x_c is weight crystallinity and t_c is crystallization time) as shown in Fig. 10. The initial crystallization obeys the Avrami equation, as evidenced by the linear relationship between $\ln[-\ln(1-x_c)]$ and $\ln t_c$ in the early stage of crystallization. From the slope and intersect, the Avrami parameters, $\ln K$ and n , can be obtained, as plotted in Fig. 11. There are also three temperature regions that can be observed. When $T_c < 35^\circ\text{C}$ (region I), there are only small changes in $\ln K$ and n . In region II ($35^\circ\text{C} < T_c < 44^\circ\text{C}$), $\ln K$ gradually decreases and n gradually increases with increasing T_c . At $T_c > 45^\circ\text{C}$ (region III), $\ln K$ further decreases and the n value increases with steeper slopes. The $\ln K$ includes the geometric factor and linear growth rate terms, and can be roughly viewed as representative of the crystallization rate. From the changes in $\ln K$, one can see that compared with confined

crystallization (in region I) the rate of unconfined crystallization (in region III) is much slower than that of confined crystallization. It is understandable that in unconfined crystallization the crystallization of PEO blocks involves reorganizations of the one-end-tethered PS block, which drastically decreases the overall crystallization rate.

CONFINED CRYSTALLIZATION IN LAMELLAR AND CYLINDRICAL PEO-*B*-PS SAMPLES

Crystallization Restricted in a Two-Dimensional Space

Figure 12 shows the TEM micrograph of a thin section of EOS-L sample stained by RuO₄ at room temperature. Layer structures can be clearly observed in this micrograph. Since PEO layers are more susceptible to RuO₄, they appear darker than the PS layers. SAXS results in the melt at 55°C and after crystallization at 35°C also reveals the well-ordered lamellar phase morphology as shown in Fig. 13. The SAXS Bragg scattering peaks possess ratios of $q/q^* = 1:2:3:4$ (q^* is the scattering vector of the first-order peak) in both the melt and crystalline state. The first-order scattering peak corresponds to a length scale of 18.7 nm ($2\pi/q^*$). Therefore, from TEM and SAXS results the thicknesses of the PEO and PS layers can be calculated to be 8.8 nm and 9.9 nm, respectively. The scattering intensity in the molten state is lower than that after crystallization of the PEO blocks, because electron densities increase in the order of amorphous PS, amorphous PEO, and crystalline PEO (341 e/nm³, 369 e/nm³, and 407 e/nm³). As one may notice, the first-order scattering peak keeps exactly its position after crystallization. Therefore, the crystallization of the PEO blocks is completely confined within the ordered supramolecular lamellar structure because of rapid vitrification of the PS layers.



Fig. 12 TEM observation of the lamellar morphology of an ultramicrotomed EOS-L thin film sectioned along the thickness direction after staining by RuO₄

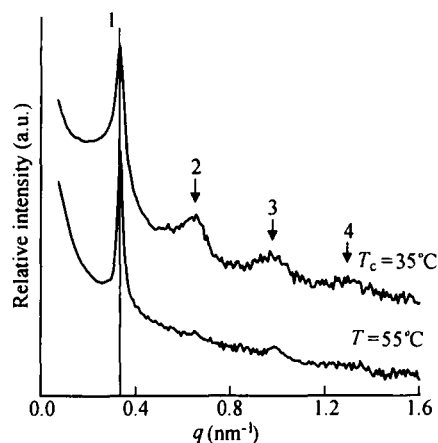


Fig. 13 1D SAXS results of EOS-L in the melt at 55°C and after isothermal crystallization at 35°C

Crystal orientation within the confined lamellar geometry is studied using combined 2D SAXS and WAXD. The lamellar morphology is shear-aligned using reciprocal planar shearing apparatus at 0.5 Hz shear frequency and 150% shear amplitude at 110°C for 20 min. The shear force acts in the x direction, and the shear gradient is along the z direction as shown in Fig. 14. The 2D SAXS and WAXD patterns through both x and y directions for the shear-aligned sample are observed to be the same. Therefore, only the 2D SAXS and WAXD patterns through the y direction are presented here to avoid redundancy. The 2D SAXS and WAXD patterns through the y and z directions for the shear-aligned EOS-L sample after isothermal crystallization at 35°C are shown in Fig. 14. From 2D SAXS result along y (Fig. 14a), there are clear three order diffractions can be observed on the meridian with $q/q^* = 1:2:3$. There is no obvious diffraction in the SAXS pattern along z (Fig. 14b). Both results indicate that the diblock copolymer lamellae are perfectly aligned horizontally by large amplitude oscillating shear, with

the z parallel to the lamellar surface normal ($\hat{n}$). In the WAXD pattern along y (Fig. 14c), one can observe that the (120) reflections are exclusively located on the equator, and the overlapped ($\bar{1}32$), (032), ($\bar{2}12$), and (112) reflections are located 23° away from the equator. This 2D WAXD pattern can be explained as in Fig. 15. The c -axis of the PEO crystal is parallel to $\hat{n}$. Whenever any pair of (120) planes is parallel to the X-ray beam, the (120) reflections will appear on the equator. Since ($\bar{1}32$), (032), ($\bar{2}12$), and (112) planes are tilted 23° from the c -axis of the PEO crystal, the overlapped reflections are thus located 23° away from the equator. The WAXD pattern along z (Fig. 14d) shows isotropic ring reflections, indicating the random distribution of crystallographic a and b axes around the z direction. The overlapped ($\bar{1}32$), (032), ($\bar{2}12$), and (112) reflections are still observable at this time, due to slight misalignment of the diblock copolymer lamellar morphology and/or the crystal orientation within the confined lamellae.

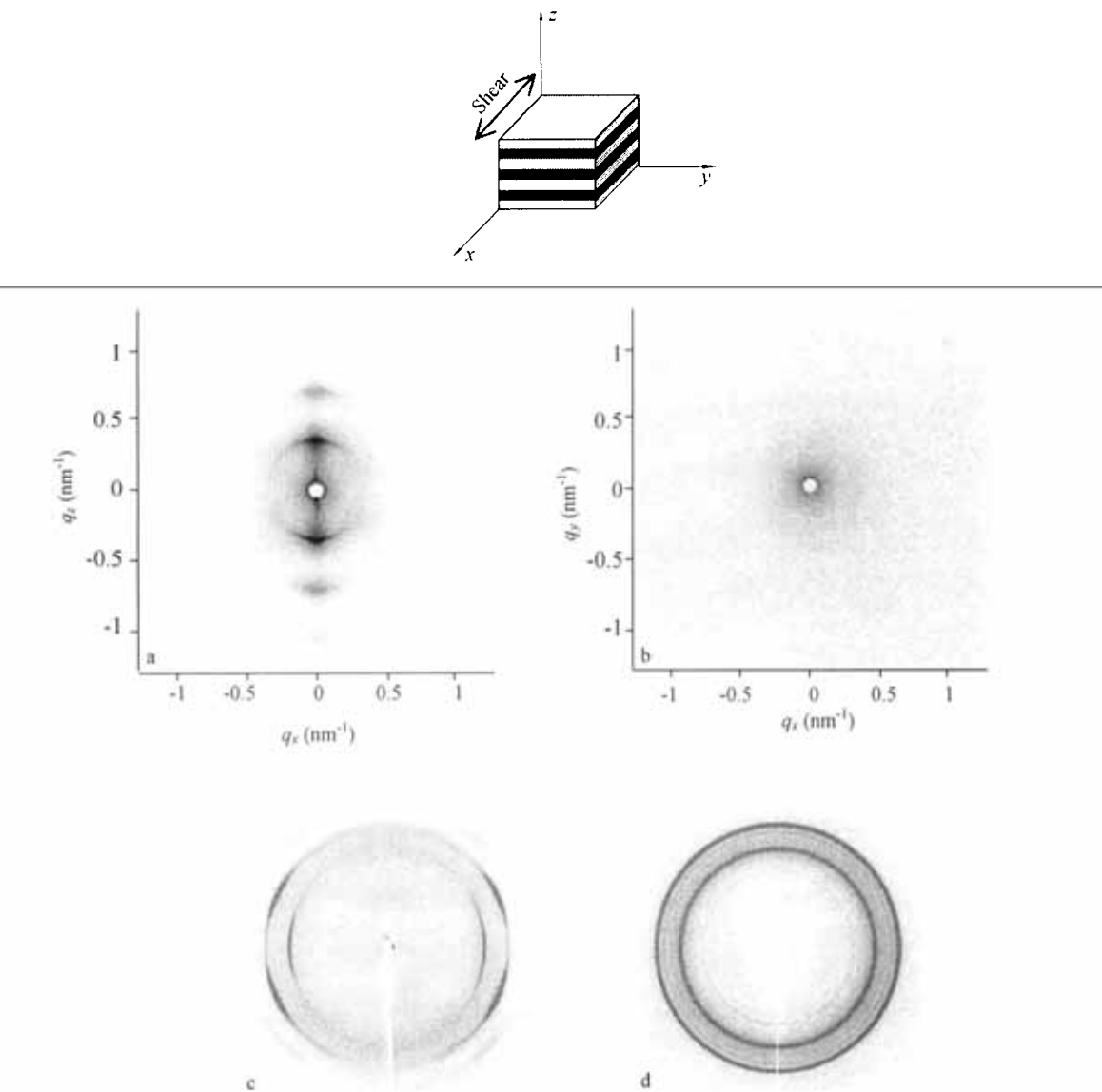


Fig. 14 2D SAXS along y (a), 2D SAXS along z (b), 2D WAXD along y (c), 2D WAXD along z (d) results for the shear-aligned EOS-L after isothermal crystallization at 35°C

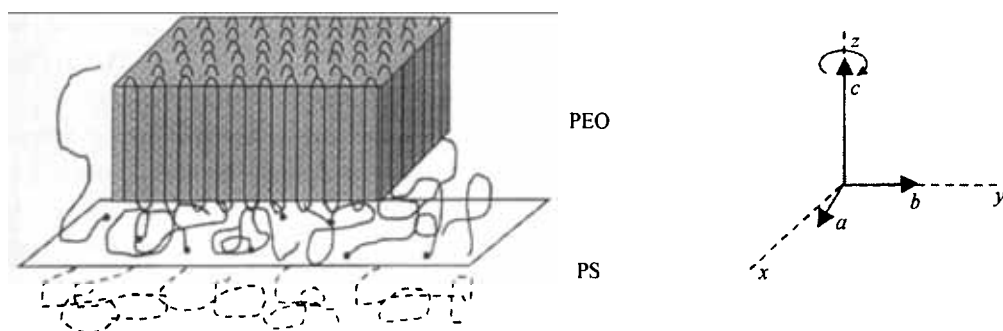


Fig. 15 Schematic representation of parallel chain orientation with respect to lamellar surface normal. The x , y , and z directions define the microphase separated lamellar geometry, and the a , b , and c directions define the PEO crystal unit cell in the real space. Here, the x and y plane defines the equator direction.

Crystallization Restricted in a One-Dimensional Space

Figure 16 shows TEM micrographs of thin sections of EOS-C sample stained by RuO_4 both as a side-view and as a through-view. It is evident that hexagonal cylinder morphology exists. Again, the darker domains in the TEM micrograph belong to PEO blocks. The SAXS patterns in the melt at 60°C and after isothermal crystallization at 35°C are shown in Fig. 17. The SAXS Bragg scattering peaks possess ratios of $q/q^* = 1:3^{1/2}:4^{1/2}:7^{1/2}:9^{1/2}$ in both melt and crystalline state. The first-order scattering peak corresponds to a length scale of 22.2 nm ($2\pi/q^*$). Therefore, the diameter of the PEO cylinders can be calculated to be 15.5 nm from the volume fraction of PEO blocks. The scattering intensity in the molten state is lower than that after crystallization of the PEO blocks, because electron densities increase in the order of amorphous PS, amorphous PEO, and crystalline PEO. Note that the first-order scattering peak keeps exactly the same position after crystallization. It thus indicates that the crystallization of the PEO blocks is completely confined within the ordered supramolecular cylinders because of rapid vitrification of the PS matrix.

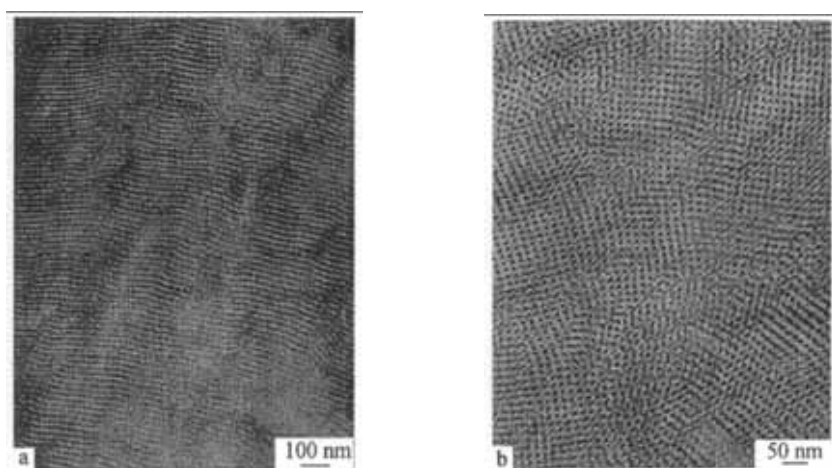


Fig. 16 TEM observation of the hexagonal cylinder morphology of ultramicrotomed EOS-C thin section after staining by RuO_4 , side-view (a) and through-view (b)

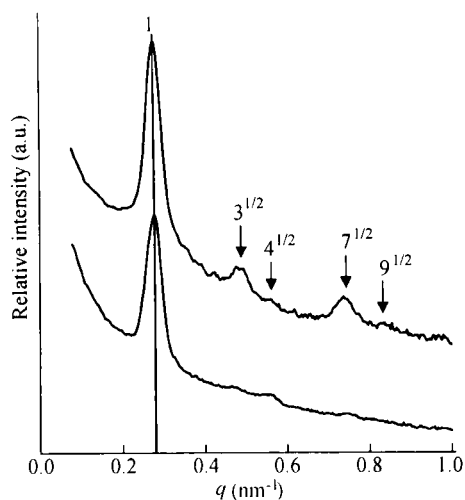


Fig. 17 1D SAXS results of EOS-C in the melt at 60°C and after isothermal crystallization at 35°C

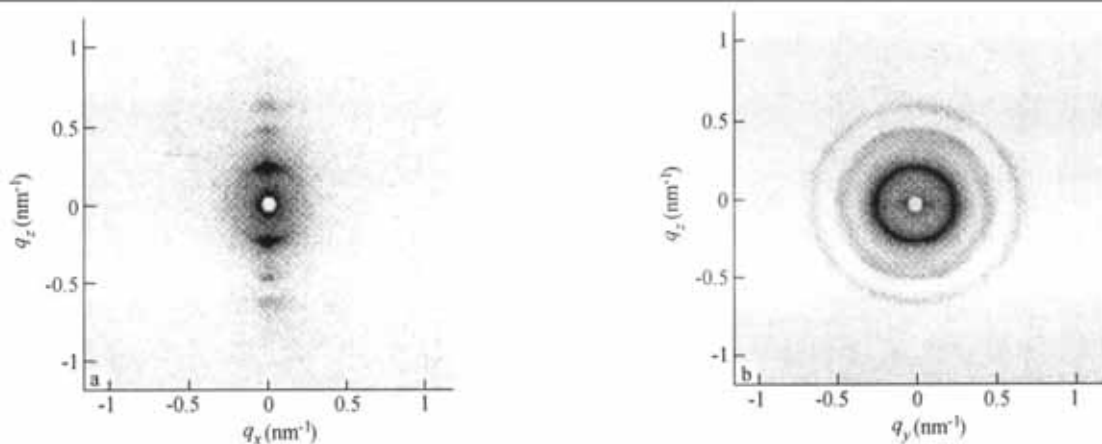
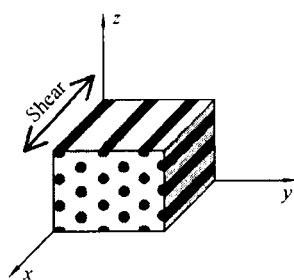


Fig. 18 2D SAXS pattern along y (a) and 2D SAXS pattern along x (b) of EOS-C after isothermal crystallization at 35°C

The cylinders are also shear-aligned using reciprocate planar shearing apparatus at 0.5 Hz shear frequency and 150% shear amplitude at 110°C for 20 min. The shear direction is along x , and the shear gradient is along z .

Figures 18a and 18b show the 2D SAXS patterns along both y and x after EOS-C isothermally crystallized at 35 °C, respectively. One can clearly observe that both SAXS results have well-oriented cylinder patterns with the $q/q^* = 1:3^{1/2}:4^{1/2}:7^{1/2}:9^{1/2}$. It is evidenced by the SAXS results that the cylinders are shear-aligned into a macroscopic “single crystal”, which gives a unique oriented SAXS reflection with the z parallel to the cylinder axis. The 2D WAXD pattern along y for EOS-C isothermally crystallized at 35 °C is shown in Fig. 19a. The (120) reflections can be found on both meridian and equator, and the overlapped reflections are on the quadrant. This WAXD pattern is explained using the model shown in Fig. 19b. The c -axis of PEO crystals is oriented perpendicular to the cylinder axis. Therefore, the WAXD pattern is more or less like the PEO single crystal pattern, in which two sets of (120) reflections are found 90° apart from each other. The overlapped ($\bar{1}32$), (032), ($\bar{2}12$), and (112) reflections are also observed, due to slight misalignment of the diblock copolymer lamellar morphology and/or the crystal orientation within the confined cylinders.

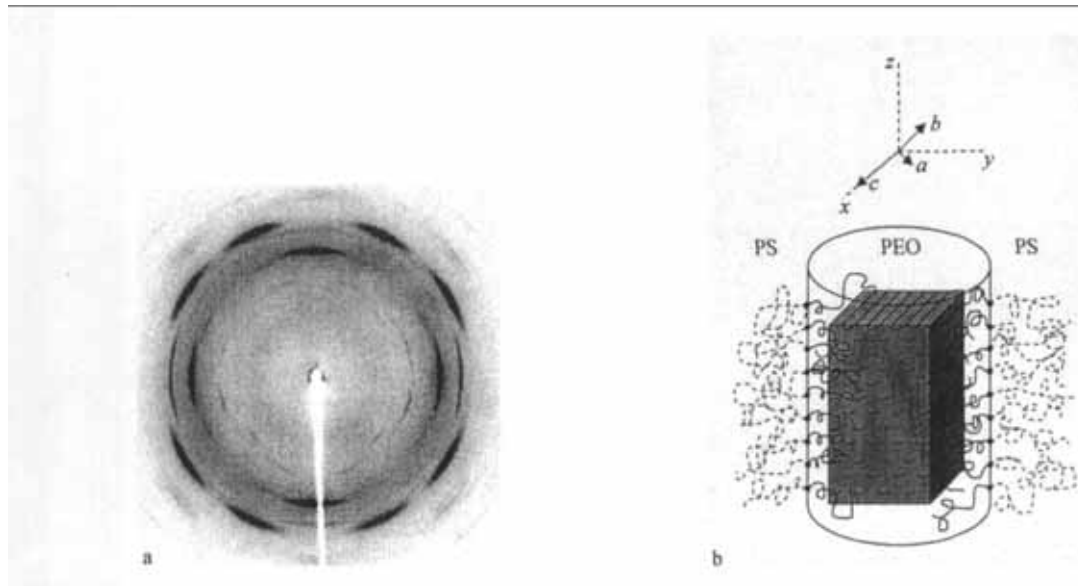


Fig. 19 2D WAXD pattern along y (a) of EOS-C after isothermal crystallization at 35 °C and the schematic representation of perpendicular chain orientation with respect to the cylinder axis (b)

SUMMARY

The phase behaviors of diblock copolymers have been one of the most active research topics in polymer physics in the past twenty years. This review covers a small part of the research efforts in the area which deals with crystallizable diblock copolymers. By careful molecular designs and controls, it is possible to study phase relationships among crystallization, vitrification, and self-organization by using three temperature parameters: T_c , T_g and T_{ODT} . It is important to recognize that the metastable crystals of the crystallizable blocks formed in the confined nano-length scale environments are frustrated. Although the crystals may possess a different length scale compared with the phase morphology, which is a supramolecular structure, the crystal structure, orientation, and morphology can be affected by these environments. On the other hand, it is interesting to identify *via* these studies the lower limit of phase size at which the bulk phase characteristics can still be retained. This is certainly a significant topic in condensed matter physics.

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