Self-Assembly of ATRP-Synthesized PCH-*b*-PtBA-*b*-PCH Triblock Copolymers Observed by Time-Resolved SAXS

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The phase behavior of PCH-*b*-PtBA-*b*-PCH triblock copolymers has been studied. Measurements in the wide-angle region probed the existence of microphase segregation through variation of block mobility and thermal expansion coefficients. SAXS experiments pointed out that most copolymers present ordered nanostructures, mostly hexagonally packed cylinders, the morphology being confirmed by AFM. An unusual disorder-to-order transition is observed in one copolymer synthesized from a macroinitiator with intermediate length and the highest outer-block molecular weight, whereas none of the copolymers shows an order-to-disorder transition upon heating over the temperature range analyzed.

Introduction

Block copolymers have been recognized as advanced nanomaterials because they can self-assemble into various patterns with periodicity in the condensed state as well as in solution (spheres, cylinders, lamellae, or bicontinuous double diamonds, depending on the volume fraction of the block components, the difference in their solubility parameters, sample preparation, and thermal history^[1]) and can be used as templates towards advanced practical applications.^[2–4]

The recent development of controlled free radical polymerization techniques,^[5–7] and more distinctively atom

transfer radical polymerization (ATRP),^[8] has allowed the synthesis of block copolymers with controlled molecular weights and low polydispersity indexes. In addition, a better control of the structure may require information on the process and kinetics of the phase transitions of the block copolymers, such as the order-to-disorder transition (ODT) and the order-to-order transition (OOT),^[9–11] which enables the morphology to be controlled by changing the temperature without varying the block copolymer composition.

Few block copolymers^[12–17] undergo a transition from a phase-mixed to other phase-separated states upon heating, referred to as the lower disorder-to-order transition (LDOT). This occurs when the thermal expansion, the so-called free volume effect, dominates the reduction in the enthalpic repulsive energy.

Small-angle X-ray scattering (SAXS) is a powerful tool to study phase separation processes in block copolymers and

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to determine microdomain sizes. The combination of SAXS results with those obtained by atomic force microscopy (AFM) allows a more reliable establishment of the block morphology.

The synthesis of well-defined triblock copolymers by the ATRP of *tert*-butyl acrylate (*t*BA) as an inner block with cyclohexyl methacrylate (CH) as outer segments, i.e., poly(cyclohexyl methacrylate)-*block*-poly(*tert*-butyl acrylate)-*block*-poly(cyclohexyl methacrylate) (PCH-*b*-PtBA-*b*-PCH) copolymers, has been reported^[18] in a previous work. DSC measurements showed almost complete phase segregation between the blocks since the location of the single glass transition detected, which was associated with cooperative motions of the outer blocks (T_g^{PCH}), was very similar to that observed in the corresponding PCH homopolymer. This article describes the morphology assignment found within these triblock copolymers by means of results obtained by SAXS experiments, using a mono or bidimensional detector, together with those attained by AFM. The existence of phase separation in block copolymers has been probed by wide-angle time-resolved temperature-variable X-ray scattering (WAXS) measurements for the first time, to the best of our knowledge. All of these PCH-*b*-PtBA-*b*-PCH ATRP-synthesized copolymers have been analyzed considering the global composition, the PtBA macroinitiator length, and the molecular weight of the PCH outer segments.

Experimental Part

Difunctional α,ω -dibromopoly(*tert*-butyl acrylate) macroinitiators of different chain lengths were synthesized in bulk by ATRP from *t*BA. Once these macroinitiators were prepared, PCH_{*x*}-*b*-PtBA_{*y*}-*b*-PCH_{*x*} triblock copolymers were then synthesized in a sequential manner by ATRP with different chain lengths of the inner *t*BA segments and the outer PCH segments in 50 vol.-% toluene solutions with an exchange halide macroinitiator/catalyst system ([CH]/[Br-PtBA-Br]/[CuCl]/[PMDETA] = 800:1:1:1).^[18] Table 1 summarizes the morphological characteristics found in the different PCH-*b*-PtBA-*b*-PCH copolymers synthesized for the present study. The subscripts that follow the label ascribed to each block are related to their corresponding degree of polymerization.

Specimen Preparation

On the one hand, copolymer films were prepared by casting from 8 vol.-% toluene solution for X-ray measurements. On the other hand, thin-films of each copolymer were obtained from toluene solutions (5 mg·mL⁻¹) by spin-coating onto supported mica for AFM measurements. To further promote the formation of equilibrium morphologies within both types of films, they were annealed under vacuum at 130 °C for 72 h. The films were then slowly cooled to room temperature.

Table 1. Cyclohexyl methacrylate weight fraction in the copolymer, w^{CH} , types of nanostructure developed at 10 °C after a previous heating/cooling cycle, and a characteristic domain spacing determined from SAXS experiments.

Copolymer	w^{CH}	Morphology	$d^{\text{a)}}$
			nm
PCH ₈₁ - <i>b</i> -PtBA ₁₀₇ - <i>b</i> -PCH ₈₁	0.664	HEX	41.5
PCH ₁₁₃ - <i>b</i> -PtBA ₁₀₇ - <i>b</i> -PCH ₁₁₃	0.735	HEX	49.5
PCH ₂₂₁ - <i>b</i> -PtBA ₁₀₇ - <i>b</i> -PCH ₂₂₁	0.844	—	—
PCH ₂₇₆ - <i>b</i> -PtBA ₁₀₇ - <i>b</i> -PCH ₂₇₆	0.872	—	—
PCH ₃₃ - <i>b</i> -PtBA ₁₄₇ - <i>b</i> -PCH ₃₃	0.368	BCC	60.0
PCH ₈₄ - <i>b</i> -PtBA ₁₄₇ - <i>b</i> -PCH ₈₄	0.599	HEX	31.2
PCH ₁₂₃ - <i>b</i> -PtBA ₁₄₇ - <i>b</i> -PCH ₁₂₃	0.687	HEX	35.1
PCH ₂₁₆ - <i>b</i> -PtBA ₁₄₇ - <i>b</i> -PCH ₂₁₆	0.794	HEX	40.9
PCH ₂₁₉ - <i>b</i> -PtBA ₁₄₇ - <i>b</i> -PCH ₂₁₉	0.796	HEX	42.3
PCH ₂₆₀ - <i>b</i> -PtBA ₁₄₇ - <i>b</i> -PCH ₂₆₀	0.822	HEX	38.6
PCH ₁₇₄ - <i>b</i> -PtBA ₂₁₃ - <i>b</i> -PCH ₁₇₄	0.683	HEX	37.5
PCH ₂₄₈ - <i>b</i> -PtBA ₂₁₃ - <i>b</i> -PCH ₂₄₈	0.754	HEX	39.4
PCH ₂₆₀ - <i>b</i> -PtBA ₂₁₃ - <i>b</i> -PCH ₂₆₀	0.763	HEX	36.6
PCH ₃₁₅ - <i>b</i> -PtBA ₂₁₃ - <i>b</i> -PCH ₃₁₅	0.796	HEX	37.3
PCH ₃₄₂ - <i>b</i> -PtBA ₂₁₃ - <i>b</i> -PCH ₃₄₂	0.809	HEX	35.7

^{a)}The domain spacing for sphere and hexagonally packed patterns were determined as $(2\pi/q^*)(3/2)^{1/2}$ and $(2\pi/q^*)(4/3)^{1/2}$, respectively.

SAXS

The morphologies developed in the annealed PCH_{*x*}-*b*-PtBA_{*y*}-*b*-PCH_{*x*} copolymers with different compositions, macroinitiator lengths, and outer PCH molecular weights were analyzed by time-resolved SAXS measurements using synchrotron radiation in the A2 Soft Condensed Matter beamline of Hasylab at DESY (Hamburg, Germany), working at a wavelength of 0.150 nm. Simultaneous WAXS patterns were recorded to explore the feasibility of determining the existence of phase separation. Two different setups were utilized. In the first one, two linear position-sensitive detectors were used simultaneously, one of them at about 280 cm from the sample (which was inside the temperature controller of the beamline), covering the SAXS region, and the other at around 25 cm from the sample ranging, approximately, in the 2θ WAXS region from 10 to 25°. The WAXS detector was calibrated with the distinct diffractions of a triclinic semicrystalline poly(ethylene terephthalate) (PET) sample, and the SAXS detector was calibrated with the different orders of the long spacing of a rat-tail cornea ($L = 65$ nm). A scanning rate of 10 °C·min⁻¹ was used for the different applied temperature scans, and frames were acquired every 30 s. The rate used is relatively high because of the limited synchrotron beam time. All experiments comprised the heating of the initial annealed sample from 10 to 190 °C followed by its cooling and a subsequent heating run. Profiles were normalized for the intensity of the primary beam and the scattering of an empty sample was subtracted.

In the second setup, a MAR CCD detector, at a distance of 260 cm from the sample, was utilized to confirm the one-dimensional (1D) recorded SAXS results since the combination of synchrotron radiation with two-dimensional (2D) detection makes it possible to observe more clearly the weak scattering peaks, which would otherwise be difficult to correctly assign. Therefore, 2D SAXS images were integrated 360° azimuthally to verify the position of the weak high-order diffractions. A rat-tail cornea specimen was again used for calibration. A heating rate of 10 °C · min⁻¹ was employed, and images were acquired every 30 s from 10 to 190 °C. The 2D X-ray patterns were processed with the FIT2D program of Dr. Hammersley (ESRF), and converted into 1D arrays after normalization of the intensity of the primary beam and subtraction of the scattering of an empty sample.

Atomic Force Microscopy (AFM)

The surface morphology of the thin films was observed using tapping mode AFM (Multimode Nanoscope IVa, Digital Instrument/Veeco) under ambient conditions. In tapping mode, the stylus oscillates and touches the sample only at the end of its downward movement. The nominal resonance frequency for the tapping mode was between 265–309 kHz with a phosphorous (n) doped Si cantilever which had a spring constant that ranged from 20 to 80 N · m⁻¹. The set point in the AFM control program was adjusted to change the contact force between the tip and surface in order to detect the existence of morphologies.

Results and Discussion

The thermal analysis determined by DSC of the PCH_{*x*}-*b*-PtBA_{*y*}-*b*-PCH_{*x*} triblock copolymers revealed that, although the glass transition corresponding to the PtBA macro-initiator was not observed, the microphase separation was almost complete in these ABA triblock copolymers because the glass transition temperature that related to the PCH blocks was very similar to that observed in the corresponding PCH homopolymer. In addition, this thermal characterization pointed out the amorphous nature of these copolymers. Therefore, the WAXS profiles that they exhibit consist of a single amorphous halo with the absence of other diffraction peaks, as seen in Figure 1(a) for the PCH₂₇₆-*b*-PtBA₁₀₇-*b*-PCH₂₇₆ copolymer. In spite of the relative simplicity of the patterns in the wide-angle region, the detailed assessment of the variation with temperature of the amorphous halo peak, whose position in the maximum (d^{halo}) is directly ascribed to the most probable intermolecular distance between macromolecular chains,^[19] provides important quantitative information on the existence of microphase separation in these ABA copolymers. As depicted in Figure 1(b) for PCH₂₇₆-*b*-PtBA₁₀₇-*b*-PCH₂₇₆, at the lowest temperatures, from 10 °C to around 40 °C, the location of the amorphous halo

Figure 1. (a) Time-resolved WAXS profiles for PCH₂₇₆-*b*-PtBA₁₀₇-*b*-PCH₂₇₆ triblock copolymer during the first heating process and (b) dependence of d^{halo} on temperature.

maximum varies very subtly because of the small motion capability of the whole block copolymer since both inner and outer segments are below their corresponding glass transition temperatures and, consequently, they are in their respective glassy states. Once the inner block gains mobility at temperatures higher than about 40 °C, the T_g^{PtBA} , the position of the most probable intermolecular distance between macromolecules is moved to lower $1/d$ values and, consequently, higher d^{halo} spacings. Therefore, its temperature coefficient gradually increases up to around 110 °C, i.e., the T_g^{PCH} , and more abruptly from that to the final empirical temperature measured (190 °C), which is attributable to the capability of cooperative and generalized motions within macromolecules of this block copolymer because of its elastomeric state at these

Figure 2. Time-resolved SAXS profiles of PCH_{113} - b - $PtBA_{107}$ - b - PCH_{113} and PCH_{276} - b - $PtBA_{107}$ - b - PCH_{276} triblock copolymers as a function of scattering vector: (a) first heating, (b) cooling, and (c) second heating.

high temperatures. Accordingly, the glass transition temperatures of each individual block, i.e., the inner and outer $PtBA$ and PCH segments, respectively, can be determined from the intersections of these different slopes (fits to straight lines are represented in Figure 1(b)), which are associated with the change of thermal expansion coefficients and, thus, to the variation of the copolymer mobility. The agreement with the T_g values obtained by DSC^[18] for the $PtBA$ macroinitiator and outer blocks is extremely good and confirms the microphase separation of these ABA triblock copolymers.

The microdomains that exist in a block copolymer, when phase separation occurs,^[9] can be randomly distributed or, in other cases, may form a regular arrangement that gives rise to a periodic structure that usually generates profiles in the small-angle X ray region. Therefore, the SAXS profile analysis allows, if the electron density contrast is high enough, identification of the morphology developed. Figure 2 shows, for two of the PCH_x - b - $PtBA_y$ - b - PCH_x triblock copolymers with the shortest inner $PtBA$ block length, the variation with temperature of the scattered radiation intensity versus the magnitude of the scattering

vector, q , this being defined as:

$$q = \frac{4\pi \sin \theta}{\lambda} \quad (1)$$

where 2θ is the scattering angle and λ is the wavelength. The profiles ascribed to PCH_{113} - b - $PtBA_{107}$ - b - PCH_{113} are represented in the upper part of Figure 2. A monotonic drop of the intensity that reaches the SAXS detector is observed but no scattering peak appears during the first heating run, probably because of the disorder that exists between the inner and outer blocks and because of the small electron density contrast between both of them. However, with subsequent cooling, nascent peaks begin to become visible, and become more evident as the temperature diminishes. Therefore, a disorder-to-order transition upon cooling seems to take place in this block copolymer although the block arrangement developed is quite imperfect. This not well-defined morphology is slightly improved further during the second heating, which shows that the spatial concentration fluctuation of the block copolymer segments seems to deviate from the

sinusoidal-wave-type fluctuation characteristic of the weak segregation limit, and to generate a certain long-range spatial order extremely defective. The primary maximum peak position, q^* , allows estimation of the Bragg spacing, d , through Bragg's law:

$$q^* = \frac{2\pi}{d} \quad (2)$$

where d is the periodicity or spacing. The PCH₁₁₃-*b*-PtBA₁₀₇-*b*-PCH₁₁₃ copolymer exhibits a Bragg spacing of 42.9 nm at ambient temperature after the first heating and its subsequent cooling at 10 °C · min⁻¹. The spacing is lowered for the PCH₈₁-*b*-PtBA₁₀₇-*b*-PCH₈₁ copolymer with the lowest molecular weight in the outer PCH blocks. In the temperature range analyzed the order-to-disorder transition on heating is not observed for these two copolymers. An enlargement of the temperature interval evaluated has not been considered appropriate since these block copolymers might degrade, which would change their chemical structures and lead to misleading results.

However, no scattering peaks are observed in the time-resolved profiles for the copolymers with the same low-molecular-weight macroinitiator but with higher molecular weight outer blocks. The PCH₂₇₆-*b*-PtBA₁₀₇-*b*-PCH₂₇₆ copolymer is represented in the lower pictures of Figure 2 for the three temperature-variable processes analyzed: first heating, cooling, and second heating. This characteristic seems to point out, i) that the microdomains are disorderly allocated and are not able to gain any order with thermal treatment, in spite of the existence of phase separation as estimated by DSC and WAXS, and ii) that fluctuations of electronic density between segregated phases become even smaller than for PCH₈₁-*b*-PtBA₁₀₇-*b*-PCH₈₁ and PCH₁₁₃-*b*-PtBA₁₀₇-*b*-PCH₁₁₃, probably because of the greater difference between the molecular weights of both the inner and outer blocks. The PCH₂₂₁-*b*-PtBA₁₀₇-*b*-PCH₂₂₁ triblock copolymer shows identical profiles.

All of the PCH_{*x*}-*b*-PtBA₁₄₇-*b*-PCH_{*x*} copolymers, synthesized from the PtBA₁₄₇ macroinitiator with intermediate molecular weight, exhibit well-defined first-order peaks at 10 °C. Figure 3(a) shows the 2D SAXS image at 10 °C after a first heating and cooling process for the PCH₃₃-*b*-PtBA₁₄₇-*b*-PCH₃₃ copolymer, i.e., the triblock with the lowest CH block composition. This copolymer was synthesized by ATRP on purpose, using a concentration relationship of [CH]/[macroinitiator] = 200/1, to obtain a lower molecular weight in the outer blocks and to examine the effect of this variable on the morphology. Concentric and uniform intensity rings ascribed to the first-order diffraction and several higher-orders are clearly observed in this figure, which indicates that the PCH₃₃-*b*-PtBA₁₄₇-*b*-PCH₃₃ film exhibits a random microdomain orientation. Moreover, the 360° azimuthal integration using the FIT2D

Figure 3. (a) SAXS-2D profile at 10 °C for the CH₃₃-*b*-PtBA₁₄₇-*b*-PCH₃₃ triblock copolymer. (b) 360° azimuthally integrated 1D SAXS profile at 10 °C and its corresponding decomposition into the different higher orders.

program, as mentioned in the Experimental Part, leads to the profile represented in Figure 3(b) that is identical to those obtained by using the linear detector and represented as a function of temperature in Figure 4. The high-order maxima at the peak position of $1:\sqrt{2}:\sqrt{3}:\sqrt{4} \dots$ relative to that of the first-order primary peak^[2,3] supports the assumption of a morphology based on PCH spherical microdomains within the PtBA matrix with a long-range spatial order for this copolymer, as seen in the upper 2D profiles in Figure 3, and after its decomposition into different Gaussian functions as shown in the lower plots of Figure 3. The arrows labeled i ($i=1-2$) indicate the form factor scattering from the isolated spheres. Additional information might be obtained from its AFM image represented in Figure 5(a). The initial ordering of the annealed spin-coated film is defective and the PCH spherical microdomains seem to adopt a liquid-like arrangement within the matrix.^[20] However, this distorted morphology becomes more perfect after thermal treatment and seems to turn into a PCH body cubic centered (bcc) lattice.

The temperature-variable SAXS profiles depicted in Figure 4 show the above-mentioned ordering enhancement

Figure 4. SAXS results for PCH₃₃-*b*-PtBA₁₄₇-*b*-PCH₃₃ triblock copolymer: (a) first heating, (b) cooling, and (c) second heating. Upper plots: SAXS profiles as a function of scattering vector. Middle plots: Dependence of scattering vector on temperature for the first order peak. Bottom plots: Dependence of invariant on temperature.

through the first heating and the subsequent cooling. Accordingly, the intensity of the primary peak increases, its width decreases, and the high order reflections become more visible as the ordering proceeds, mainly during the first heating process, as represented in the middle plots of Figure 4. The q^* position of the primary peak maximum is shifted to lower values, i.e., to larger Bragg's spacing, which suggests a stretched chain conformation at higher temperatures during the first heating because of the evolution to a more ordered spherical arrangement. The variation of q^* values is less considerable for cooling and the second heating, this being related to conformation changes that might take place when mobility varies down or up to the glass transition of the rigid blocks. These changes in mobility can be observed from a variation of

the relative invariant^[21] estimated from the whole SAXS profile and exclusively from the q^* first-order peak, as shown in the lower pictures of Figure 4 for the different thermal processes. The correlation is in agreement for both of them although the area is, as expected, sensibly less in the case when only the first order peak is considered. The invariant is defined as:

$$\text{Invariant} = \int_0^{\infty} q^2 I(q) dq$$

where q is the scattering vector and $I(q)$ is the measured scattering intensity. The invariant gives an idea about the macroscopic electron density fluctuations. During the first heating, at a low temperature up to around 40 °C, the

Figure 5. AFM height-image in tapping mode for the CH_3 -*b*-PtBA₁₄₇-*b*-PCH₃₃ triblock copolymer (a) and for the PCH₁₂₃-*b*-PtBA₁₄₇-*b*-PCH₁₂₃ triblock copolymer (b).

invariant is kept practically unchanged while a considerable increase is observed above this temperature up to about 110 °C. The electron density fluctuation becomes higher as the overall mobility is raised beyond the glass transition temperatures of both the inner and outer blocks. At temperatures higher than 110 °C, significant microdomain reorganization and, consequently, ordering improvement of the initial morphology within the PCH₃₃-*b*-PtBA₁₄₇-*b*-PCH₃₃ copolymer takes place. This morphological enhancement is correlated to the important invariant increase observed at high temperatures. As discussed for the PCH_{*x*}-*b*-PtBA₁₀₇-*b*-PCH_{*x*} copolymers with the lowest molecular weight PtBA macroinitiator, an order-to-disorder transition is not observed for the PCH₃₃-*b*-PtBA₁₄₇-*b*-PCH₃₃ copolymer over the temperature range analyzed. Therefore, the most important invariant changes found during the cooling and the second heating processes are those related to the glass transition of the

Figure 6. (a) SAXS-2D profile at 10 °C for the PCH₁₂₃-*b*-PtBA₁₄₇-*b*-PCH₁₂₃ triblock copolymer. (b) 360° azimuthally integrated 1D SAXS profile at 10 °C and its corresponding decomposition into the different higher orders.

more rigid PCH blocks because of the great variation of mobility for the whole block copolymer.

The effect of an increase of PCH block molecular weight in the copolymers synthesized using the macroinitiator with an intermediate length is seen in Figure 6 for the PCH₁₂₃-*b*-PtBA₁₄₇-*b*-PCH₁₂₃ triblock copolymer. This 2D SAXS image is rather different to that exhibited by the PCH₃₃-*b*-PtBA₁₄₇-*b*-PCH₃₃ copolymer and presents multiple-order scattering maxima at peak positions of $1:\sqrt{3}:\sqrt{4}:\sqrt{9}$ relative to that of the first-order q^* peak, as displayed directly from the 2D pattern and its decomposition into distinct high-order reflections after 360° integration. These high-order reflections point out the development of microdomains with hexagonally packed PtBA cylinders, HEX^{PtBA} , with long-range spatial arrangements. The AFM picture represented in the bottom of Figure 5 evidences this morphology, although it is also apparently defective in the initial spin-coated annealed cast film. Therefore, the scattering peak ascribed to the first order sharpens and intensifies during the first heating process in the temperature-variable experiments, as the temperature is raised mainly above the T_g^{CH} (see the upper plot in Figure 7 for the whole profile and the middle plot for

Figure 7. SAXS results for $\text{PCH}_{123}\text{-}b\text{-PtBA}_{147}\text{-}b\text{-PCH}_{123}$ triblock copolymer: (a) first heating, (b) cooling, and (c) second heating. Upper plots: SAXS profiles as a function of scattering vector. Middle plots: Dependence of scattering vector on temperature for the first order peak. Bottom plots: Dependence of invariant on temperature.

the primary peak). As mentioned previously, thermal treatments lead to an improvement of the original morphology. Invariant changes provide evidence, on the one hand, of such as enhancement and, on the other hand, of the mobility variations that exist below and above the corresponding glass transitions related to each block. An order-to-disorder transition is again not observed for this triblock copolymer in the temperature interval analyzed. Consequently, the effect of temperature on cooling and on a second heating is then less pronounced, and is ascribed to changes of mobility as depicted in the bottom plots in Figure 7.

The behavior of the rest of the $\text{PCH}_X\text{-}b\text{-PtBA}_{147}\text{-}b\text{-PCH}_X$ copolymers, except for the $\text{PCH}_{260}\text{-}b\text{-PtBA}_{147}\text{-}b\text{-PCH}_{260}$

copolymer, which has the highest PCH molecular weight, is similar to that just described for $\text{PCH}_{123}\text{-}b\text{-PtBA}_{147}\text{-}b\text{-PCH}_{123}$, i.e., a hexagonally packed PtBA cylindrical morphology, HEX^{PtBA} , with long-range spatial order that becomes more perfect after the application of the thermal treatments, is observed. However, although the $\text{PCH}_{260}\text{-}b\text{-PtBA}_{147}\text{-}b\text{-PCH}_{260}$ final morphology is analogous to that mentioned, the intermediate development is quite different. Figure 8 (left upper picture) shows the initial non-existence of an ordered arrangement of the different blocks in $\text{PCH}_{260}\text{-}b\text{-PtBA}_{147}\text{-}b\text{-PCH}_{260}$. Therefore, no SAXS peak is detected from 10 °C to ≈ 165 °C and a monotonic diminishment of the intensity with q is observed in the scattering profiles. However, different scatterings emerge

Figure 8. SAXS results for PCH₂₆₀-*b*-PtBA₁₄₇-*b*-PCH₂₆₀ triblock copolymer: (a) first heating, (b) cooling, and (c) second heating. Upper plots: SAXS profiles as a function of scattering vector. Middle plots: Dependence of scattering vector on temperature for the first order peak. Bottom plots: Dependence of invariant on temperature.

above 165 °C, i.e., a disorder-to-order transition upon heating takes place, as seen from the appearance of a primary peak in the left middle picture of Figure 8. It is important to notice how sensitive the invariant is to detect the new arrangement that is occurring within this PCH₂₆₀-*b*-PtBA₁₄₇-*b*-PCH₂₆₀ copolymer (left bottom picture), either the global invariant or that one only related to the first-order peak. This transition upon heating is not that usual in block copolymers.^[12–17] Generally, block copolymers undergo a disordered-to-order transition with decreasing temperature,^[9] which can also be termed an upper critical ordering transition (UCOT). This transition results from an increase in the interaction energy between the segments with decreasing temperature, as quantified by

the Flory-Huggins segmental interaction parameter. However, years after, the discovery of a diblock copolymer that undergoes ordering upon heating revealed that the phase behavior of block copolymers was far richer than previously thought.^[12]

No order-to-disorder transitions are found at higher temperatures, as observed for the rest of the block copolymers analyzed here. Coincident with the subsequent cooling and further heating processes, an improvement of the morphology developed upon the initial heating is observed. Therefore, the location of the q^* first-order peak with increasing temperature during the second heating run is slightly shifted to lower values, i.e., to larger Bragg's spacing, which suggests a stretched chain conformation

Figure 9. SAXS profiles of $\text{PCH}_{174}\text{-}b\text{-PtBA}_{213}\text{-}b\text{-PCH}_{174}$ triblock copolymer: (a) first heating, (b) cooling, and (c) second heating.

associated with a more ordered state. In relation to the corresponding invariant pictures, the effect of the mobility of, mainly, the rigid blocks on the invariant values is noticeable.

The type of arrangement obtained is again estimated from the relative location of the multiple-order scattering maxima with respect to the first-order q^* peak. The ratio

calculated for the $\text{PCH}_{260}\text{-}b\text{-PtBA}_{147}\text{-}b\text{-PCH}_{260}$ copolymer is $1:\sqrt{3}:\sqrt{4}:\sqrt{9}$, which indicates the development of microdomains with hexagonally packed PtBA cylinders, HEX^{PtBA} , with long-range spatial order, similar to the other $\text{PCH}_X\text{-}b\text{-PtBA}_{147}\text{-}b\text{-PCH}_X$ copolymers synthesized with this intermediate molecular weight macroinitiator, except for $\text{PCH}_{33}\text{-}b\text{-PtBA}_{147}\text{-}b\text{-PCH}_{33}$ which presents PCH spheres as previously discussed.

Regarding the triblock copolymers obtained from the highest molecular weight PtBA_{213} macroinitiator, all of them exhibit a HEX morphology and behave analogously to the ABA copolymers already described with a similar arrangement, and an ordering enhancement with increasing temperature is observed, as depicted in Figure 9 for the $\text{PCH}_{174}\text{-}b\text{-PtBA}_{213}\text{-}b\text{-PCH}_{174}$ triblock copolymer.

Figure 10. (a) SAXS profiles as a function of scattering vector at 10 °C after a previous heating/cooling cycle for all $\text{PCH}\text{-}b\text{-PtBA}\text{-}b\text{-PCH}$ triblock copolymers. (b) Tentative phase diagram proposed for the $\text{PCH}\text{-}b\text{-PtBA}\text{-}b\text{-PCH}$ triblock copolymers (represented as solid circles).

Conclusion

The ATRP-synthesized $\text{PCH}_X\text{-}b\text{-PtBA}_Y\text{-}b\text{-PCH}_X$ triblock copolymers show microdomain segregation as determined by WAXS and these domains are arranged to present an ordering at long range. Depending on inner block length and outer segment molecular weights, the initial ordering exhibited by the annealed films is, sometimes, rather defective. This feature might be ascribed to higher values of polydispersity associated with the synthetic method used compared to those obtained by anionic poly-

merization. On the other hand, a significant ordering improvement is observed by effect of thermal treatment. Accordingly, from all of the results as a function of PCH molecular weight at a given PtBA macroinitiator summarized in the upper pictures of Figure 10, a tentative empirical phase diagram is proposed for these PCH_{*x*}-*b*-PtBA_{*y*}-*b*-PCH_{*x*} copolymers, as seen in the bottom plot of Figure 10 at the composition interval analyzed. In contrast to AB diblock copolymers, the mean-field theory predictions point out an asymmetric phase diagram for ABA triblock copolymers as a result of the higher entropic penalty in deforming the central B segments to accommodate the two outer A blocks.^[22,23] Although non-theoretical predictions have been performed in this investigation, the experimental phase diagram is clearly asymmetric, being dominated by the lamellar phase, with smaller regions of hexagonally packed cylindrical and spherical phases, as expected.^[23] As can be seen, most of the block copolymers synthesized are found in a region with hexagonal PtBA cylinder arrangements, even the PCH₂₆₀-*b*-PtBA₁₄₇-*b*-PCH₂₆₀ copolymer that exhibited the unusual disorder-to-order transition upon its first heating. On the other hand, the block copolymers with the highest compositions, PCH₂₂₁-*b*-PtBA₁₀₇-*b*-PCH₂₂₁ and PCH₂₇₆-*b*-PtBA₁₀₇-*b*-PCH₂₇₆, present phase separation without ordering, while PCH spheres are attained for the PCH₃₃-*b*-PtBA₁₄₇-*b*-PCH₃₃ copolymer. This small region ordered in spheres is in agreement with that stated, after introduction of fluctuation corrections, for the asymmetric phase diagrams in other triblock copolymers.^[24]

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