Thermal and Morphological Behaviour of Well-Defined Amphiphilic Triblock Copolymers Based on Cyclohexyl and Di(ethylene glycol) Methyl Ether Methacrylates

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The microphase separation and morphology of PDEG-*b*-PCH-*b*-PDEG and PCH-*b*-PDEG-*b*-PCH amphiphilic triblock copolymers have been studied by DSC, SAXS and AFM. A clear first-order scattering peak was observed for most of the triblock copolymers, independent of the macroinitiator used. This diffraction has been ascribed to the development of a lamellar structure, which was confirmed by AFM. On the other hand, the existence of an ODT upon heating was observed for most of the triblock copolymers. The ODT location was dependent on the outer segment molecular weights, shifting at higher temperatures as the polymerisation degree increased. WAXS profiles were checked to determine the glass transition and ODT temperatures.

Introduction

Block copolymers are an interesting class of materials that have been extensively studied.^[1–7] One of their important features is based on their capability to self-assemble into various ordered arrays of 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. On the other hand, better control of the resulting structure may require information on the process and kinetics of the phase transitions for the block copolymers, such as the order-to-disorder transition (ODT) and the order-to-order transition (OOT),^[8–17] which enables the morphology to be controlled by changing the temperature without varying the block copolymer composition.

All of these nanostructured morphologies can be obtained in bulk, on surfaces and in thin films. The current interest in the regular nanometer scale patterns of block copolymers stems from the many opportunities that their assemblies present for the preparation of novel, tailor-made and advanced nanomaterials for drug

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delivery, catalysis and nanoreactor technology, molecular templates and nanolithographic masks, among other applications.^[18–20]

One of the most useful scattering techniques for determining the order in block copolymers is small-angle X-ray scattering (SAXS) which gives information on morphological aspects and enables the characterisation of the existing structural periodicity. On the other hand, the current development of two-dimensional (2D) detectors based on “charged-coupled devices” (CCD)^[21] allows in situ observations of phase transitions to be performed using SAXS measurements, which provides much greater information than that obtained with a one-dimensional detector, mainly in the case of preferential orientation development. Moreover, the combination of synchrotron radiation and 2D detectors makes it possible to observe weak scattering, which would otherwise be difficult to detect, because of the much higher signal-to-noise ratio. The interpretation of SAXS data is strongly ‘model dependent’ and a good understanding of the morphology is a pre-requisite for a thorough analysis. Supplementary information can be given by microscopy techniques like transmission electron microscopy (TEM) or atomic force microscopy (AFM). Although TEM has been extensively used to study block copolymers, much of the work is inconclusive, due to the inherent difficulties in sample preparation, the low contrast between microdomains and/or the possible misinterpretation of artefacts. Recently, AFM studies have provided a powerful tool to learn more about the morphology/topology of a great variety of materials.

In a previous work, synthesis by transition metal mediated living radical polymerisation and aggregation studies of the resulting amphiphilic triblock copolymers of

cyclohexyl methacrylate (CH) and di(ethylene glycol) methyl ether (DEG) methacrylate using ¹H NMR, dynamic and static light scattering were described.^[22] Their ability to form micelles and solubilise organic solvent inside them supported the feasibility of using them as interface agents in mixtures of solvents. This article describes the characteristics of these well-controlled polymers found in the condensed state (PDEG-*b*-PCH-*b*-PDEG and PCH-*b*-PDEG-*b*-PCH), in terms of their morphological aspects based on glass transition temperature analysis and real time variable temperature small angle X-ray scattering experiments using synchrotron radiation. In addition, the dependence of the morphology developed on the molecular weight of the outer blocks is addressed. The use of atomic force microscopy allowed the morphology of these amphiphilic triblock copolymers to be corroborated.

Experimental Part

The amphiphilic block copolymers were prepared via one pot synthesis consisting of the sequential addition of the second monomer directly into the reaction medium, after nearly complete consumption of the first monomer. In particular, the polymerisations of the inner blocks, PDEG or PCH, were carried out with 1,4-bis(bromoisobutyryloxy)benzene as a difunctional initiator and CuBr/*N*-propyl-2-pyridylmethanimine as a catalyst in toluene solution (50 vol.-%) at 70 °C, with [monomer]:[initiator]:[CuBr]:[ligand] = 100:1:1:2. The reaction reached a monomer conversion of approximately 75% for DEG ($\bar{M}_n = 14\,400\text{ g}\cdot\text{mol}^{-1}$, $\bar{M}_w/\bar{M}_n = 1.15$) or 80% for CH ($\bar{M}_n = 12\,600\text{ g}\cdot\text{mol}^{-1}$, $\bar{M}_w/\bar{M}_n = 1.07$) prior to addition of the second monomer (DEG or CH) in toluene solution (50 vol.-%), with [monomer]:[macroinitiator] = 200:1.^[22] The copolymer characteristics are collected in Table 1. The subscripts that follow the label ascribed to each block are related to their corresponding degree of polymerisation.

Table 1. Glass transition temperatures of PDEG-*b*-PCH-*b*-PDEG and PCH-*b*-PDEG-*b*-PCH amphiphilic triblock copolymers synthesised by ATRP.

Copolymer	$\bar{M}_n^{\text{SEC}}$	$\bar{M}_w/\bar{M}_n$	Composition	T_{g1}	T_{g2}
			mol-% PCH	°C	°C
PDEG ₂₈ - <i>b</i> -PCH ₇₅ - <i>b</i> -PDEG ₂₈	23 100	1.09	0.59 ₃	−30.0	74.5
PDEG ₆₂ - <i>b</i> -PCH ₇₅ - <i>b</i> -PDEG ₆₂	35 900	1.20	0.39 ₉	−28.8	79.1
PDEG ₇₃ - <i>b</i> -PCH ₇₅ - <i>b</i> -PDEG ₇₃	39 900	1.26	0.39 ₀	−24.7	81.2
PDEG ₈₀ - <i>b</i> -PCH ₇₅ - <i>b</i> -PDEG ₈₀	42 800	1.29	0.38 ₈	−24.8	82.0
PDEG ₈₁ - <i>b</i> -PCH ₇₅ - <i>b</i> -PDEG ₈₁	43 000	1.32	0.35 ₉	−26.0	80.3
PCH ₁₇ - <i>b</i> -PDEG ₇₇ - <i>b</i> -PCH ₁₇	20 100	1.17	0.30 ₁	−19.2	—
PCH ₄₀ - <i>b</i> -PDEG ₇₇ - <i>b</i> -PCH ₄₀	28 000	1.19	0.45 ₉	−25.9	63.6
PCH ₅₁ - <i>b</i> -PDEG ₇₇ - <i>b</i> -PCH ₅₁	31 600	1.28	0.51 ₄	−21.5	67.4
PCH ₅₈ - <i>b</i> -PDEG ₇₇ - <i>b</i> -PCH ₅₈	34 100	1.26	0.52 ₃	−30.6	66.3
PCH ₆₁ - <i>b</i> -PDEG ₇₇ - <i>b</i> -PCH ₆₁	35 000	1.24	0.53 ₂	−25.0	71.1
PCH ₆₂ - <i>b</i> -PDEG ₇₇ - <i>b</i> -PCH ₆₂	35 200	1.27	0.53 ₄	−30.6	66.3

Specimen Preparation

Copolymer films were obtained by casting from an 8% (w/v) toluene solution for X-ray measurements. For AFM, copolymer films were prepared by spin-coating, supported by mica or silicon, from toluene solutions ($5 \text{ mg} \cdot \text{mL}^{-1}$). To further promote the formation of equilibrium morphologies within both types of films, they were annealed under a vacuum at 130°C over 72 h and then films were slowly cooled down to room temperature.

Glass Transition Temperatures

DSC measurements were performed using a Perkin Elmer DSC/TA7DX, PC series with an Intra-cooler for low temperatures. The temperature scale was calibrated from the melting point of high-purity chemicals (lauric and stearic acids and indium). Samples weighing $\approx 20 \text{ mg}$ were scanned at $10^\circ\text{C} \cdot \text{min}^{-1}$ under dry nitrogen ($20 \text{ cm}^3 \cdot \text{min}^{-1}$). The first heating scan was performed after decreasing the temperature from room temperature to -70°C , then the sample was heated up to 140°C . Subsequent to this heating process, the sample was cooled down at the same rate and, after that, another heating run was conducted at the same heating rate.

The actual value for the glass transition temperature, T_g , was estimated as the temperature at the midpoint of a line drawn between the temperature of intersection of the initial tangent with the tangent drawn through the point of inflection of the trace and the temperature of intersection of the tangent drawn through the point of inflection with the final tangent. The quoted value is the average of several measurements on each sample.

X-Ray Measurements

The morphologies developed by the copolymers with different compositions and macroinitiator types were analysed by time-resolved SAXS measurements using synchrotron radiation at 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 from the results. Two different set-ups were utilised. In the first one, two linear position sensitive detectors were used simultaneously, one of them at about 260 cm from the sample (which was inside the temperature controller of the beamline), covering the small angle scattering (SAXS) region, and the other at around 20 cm from the sample ranging, approximately, in the 2θ WAXS region from 10 to 28° . The WAXS detector was calibrated using the diffractions of a crystalline poly(ethylene terephthalate) sample, and the SAXS detector was calibrated with the different orders of the long spacing of rat-tail cornea ($L=65 \text{ nm}$). A scanning rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ was used, acquiring frames every 30 s . All experiments comprised the heating of the initial sample from 25°C up to 190°C , followed by a cooling and a second heating run. Profiles were normalised for the intensity of the primary beam and the scattering of an empty sample was subtracted.

In the second set-up, a MAR CCD detector at a distance of 260 cm from the sample was utilised to confirm the one-dimensional recorded SAXS results. Then, 2D SAXS images were processed and integrated 360° azimuthally with the FIT2D

program of Dr. Hammersley (ESRF), normalised to the intensity of the primary beam, subtracting the scattering of an empty sample. A specimen of rat-tail cornea was used again for calibration. A heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ was employed, acquiring images every 30 s from 25°C to 190°C .

Atomic Force Microscopy

The surface morphology of the thin films was observed using a tapping mode AFM (Multimode Nanoscope IVa, Digital Instrument/Veeco) under ambient conditions. In tapping mode, the stylus oscillates, touching the sample only at the end of its downward movement. The oscillation frequency for the tapping mode was set to approximately 320 kHz with a Si cantilever which had a spring constant of about $42 \text{ N} \cdot \text{m}^{-1}$. 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

It is well established that the determination of glass transition temperatures provides information about the existence of phase segregation in block copolymers. The thermal characterisation of these two series of amphiphilic triblock copolymers, in which each copolymer presents the same inner block length with different molecular weights in the outer blocks, was performed by DSC.

The T_g s of the PDEG-*b*-PCH-*b*-PDEG and PCH-*b*-PDEG-*b*-PCH amphiphilic triblock copolymers are collected in the Table 1. The copolymers are labelled with the degree of polymerisation of each block, as previously mentioned. The homopolymer T_g s, PCH ($\overline{M}_n = 32\,600$ and $\overline{M}_w/\overline{M}_n = 1.28$) and PDEG ($\overline{M}_n = 11\,300$ and $\overline{M}_w/\overline{M}_n = 1.09$) were calculated for comparative purposes, their values being 92.0 and -31.9°C , respectively.

The thermograms of the PDEG-*b*-PCH-*b*-PDEG triblock copolymer series, as well as their corresponding homopolymers, are represented in the Figure 1. Two glass transition temperatures were observed for most of the copolymers, whose existence indicates that phase separation takes place. However, the location of these resulting T_g s did not exactly match up with those exhibited by the corresponding homopolymers. The T_g of the PDEG segments in the copolymers moved slightly toward higher values, while the T_g of the PCH blocks was, to some extent, shifted to lower temperatures. One of the reasons for this feature could be ascribed to the fact that phase separation between the inner and outer blocks is not actually complete. However, the values of these T_g s were rather constant for the different compositions analysed. Therefore, the explanation for glass transition temperature displacement might be associated with the existence,

Figure 1. DSC curves of PDEG-*b*-PCH-*b*-PDEG triblock copolymers and the corresponding homopolymers.

Figure 2. DSC curves of PCH-*b*-PDEG-*b*-PCH triblock copolymers and the corresponding homopolymers.

within the chain, of certain small amounts of statistical copolymer, since they were synthesised in a single step.

Similar results to those described above were observed for the PCH-*b*-PDEG-*b*-PCH triblock copolymers, as seen in Figure 2. A shift was again found for either the T_g of the PDEG inner block and for that corresponding to the PCH outer segments. However, only one broad glass transition corresponding to the block of PDEG was detected in the PCH₁₇-*b*-PDEG₇₇-*b*-PCH₁₇ copolymer with the smallest molecular weight in the outer blocks. The value of this T_g was higher than that expected based on the T_g found for the PDEG homopolymer. This shift to higher temperatures is probably due to the largest relative amount of the statistical copolymer located between the pure inner and outer blocks within this copolymer as a consequence of its low conversion.

Once the existence of the phase separation of distinct blocks was identified, a subsequent morphological study in the condensed phase was carried out by SAXS using synchrotron radiation. The existing microdomains can be randomly distributed or, in other cases, may form a regular arrangement, giving rise to periodic structures that usually generate profiles in the small angle X-ray region. Therefore, SAXS profile analysis allows, if the electron density contrast between blocks is high enough, identification of the morphology developed. Let us start the discussion with the analysis of the morphology in the PDEG-*b*-PCH-*b*-PDEG

triblock copolymers. The upper plots in Figure 3 show, for the PDEG₈₁-*b*-PCH₇₅-*b*-PDEG₈₁ copolymer, the heating-cooling-heating cycle variation with temperature of the scattered radiation intensity vs. 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. Solely the first order peak is clearly observed during the different heating-cooling-heating cycles for most of the block copolymers synthesised and analysed in the current research. However, it seems that a very diffuse second order peak could exist at a location of $2q^*$, q^* being the maximum value of the scattering vector in the PDEG₈₁-*b*-PCH₇₅-*b*-PDEG₈₁ copolymer. Curve decomposition into two diffractions was tentatively performed, as can be seen in the lower part of Figure 3. Moreover, a two-dimensional SAXS image was also obtained at 25 °C for this PDEG₈₁-*b*-PCH₇₅-*b*-PDEG₈₁ copolymer due to the higher sensitivity of the CCD detector, as depicted in Figure 4. A concentric and uniform intensity ring related to the first order peak was clearly observed, indicating that film preparation by solvent casting involved a random microdomain orientation. In addition, another very weak diffraction at a longer spacing could be seen. The 360° azimuthal integration

Figure 3. SAXS profiles of PDEG₈₁-*b*-PCH₇₅-*b*-PDEG₈₁ triblock copolymer as a function of scattering vector: upper plot (a) first heating, (b) cooling and (c) second heating; (d): decomposition of room temperature profile into two components.

using the FIT2D program, as mentioned in the Experimental Part, led to an identical profile to the one obtained at 25 °C using the linear detector, confirming the existence of a weak and broad second order diffraction.

Figure 4. SAXS 2D profiles of PDEG₈₁-*b*-PCH₇₅-*b*-PDEG₈₁ triblock copolymer at 25 °C.

Either the appearance of weak and broad second order peaks in the PDEG₈₁-*b*-PCH₇₅-*b*-PDEG₈₁ copolymer or the lack of higher order reflections in the rest of copolymers with PCH as the inner block might be, on the one hand, ascribed to the non-existence of an efficiently ordered nanostructure at long range in these copolymers or, on the other hand, might point to a small electron density difference between the inner and outer blocks.^[23] However, there are two more aspects to be taken into account which seem to have an important effect in these particular triblock copolymers. The first one is related to the presence of a small amount of statistical copolymer between the PCH and PDEG blocks due to the one pot single step synthetic protocol used for their preparation. Its existence might lead to a significant diffuseness of the phase boundaries due to partial mixing of the incompatible chains at the interfaces, probably hindering a stronger phase separation between them in those critical regions. This larger interfacial thickness could be responsible for a lack of high order reflections.^[24,25] Therefore, the weak and broad second order diffraction is

exclusively observed for PDEG₈₁-*b*-PCH₇₅-*b*-PDEG₈₁, since its statistical copolymer content is comparatively lower because of the higher molecular weight in the outer blocks. A parameter characterising the domain-boundary thickness could be estimated for systems with a sigmoidally varying electron density profile in the transition region, if the scattered intensity distribution at the large angle tail is known.^[26] However, data at those relatively higher angles was not available for these triblock copolymers.

Another feature that can reduce the ordering capability on a large scale in these copolymers, together with the previously mentioned diffuseness of the phase boundaries, is their polydispersity (see Table 1). Although the values reached are low, they are higher than those that can be obtained through living anionic polymerisation. Therefore, differences in the macrochain length make the development of ordered arrangements difficult, and a longer annealing at a temperature higher than the glass transition temperature of the rigid block is often necessary to promote ordering, even this sometimes being impossible.^[25]

In spite of the fact that the nanostructured arrangements developed are not perfectly organised on a large

Figure 5. Top curves: Variation of I^{-1} and I^{-1} with inverse of absolute temperature for the PDEG₈₁-*b*-PCH₇₅-*b*-PDEG₈₁ triblock copolymer: (a) first heating, (b) cooling and (c) second heating. Bottom curves: variation of their corresponding derivatives ($d(I^{-1})/dT$ and $d(I^{-1})/dT$) with temperature of PDEG₈₁-*b*-PCH₇₅-*b*-PDEG₈₁ triblock copolymer: (a) first heating, (b) cooling and (c) second heating.

scale in these triblock copolymers, the first order peak undergoes a broadening and a significant decrease in intensity, practically disappearing, at high temperatures, indicating a transition from a partially ordered initial state to another completely disordered state in the PDEG₈₁-*b*-PCH₇₅-*b*-PDEG₈₁ copolymer and the rest of the copolymers with PCH as the inner blocks. The invariant associated with this first order peak gives an idea of the existing macroscopic electron density fluctuations.^[27] The invariant is defined as:

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

where q is the scattering vector and $I(q)$ is the measured scattering intensity. Therefore, the precise location of the order-to-disorder transition can be easily estimated from different parameters of this invariant for each SAXS profile. The upper curves in Figure 5 depict either the inverse of their maximum peak intensity (I^{-1}) or their full width at half height (I^{-1}) as a function of the inverse of the absolute temperature. The discontinuity observed in these plots is related to this order-to-disorder transition upon heating and to the corresponding disorder-to-order transi-

tion upon cooling. T_{ODT} and T_{DOT} might be also determined from the subsequent derivative of these invariant parameters, as plotted in the lower part of Figure 5. It has to be said that although the calorimetry technique, in the form of DSC used in this research, is commonly utilised to determine the melting point in semi-crystalline copolymers, the regular method has not, to our knowledge, been applied to locate the ODT, since it would be necessary to use a micro-DSC^[28] capable of measuring to mJ resolution or an adiabatic scanning calorimeter with an order of magnitude better precision^[29] because of the small enthalpy jump associated with the weak first order ODT in block copolymers.

The absence of higher orders together with the existence of the order-to-disorder transition seems to indicate that an ordered structure, a lamellar one, has been developed for these PDEG-*b*-PCH-*b*-PDEG amphiphilic triblock copolymers. The maximum peak position, q^* , allows estimation of the Bragg spacing, d , using Bragg's law:

$$q^* = \frac{2\pi}{d} \quad (3)$$

where d is the periodicity or spacing. The values obtained for the different copolymers are listed in Table 2. An

Table 2. Bragg spacing of the first order estimated at 25 °C, type of morphology and T_{ODT} of PDEG-*b*-PCH-*b*-PDEG triblock copolymers on second heating.

Copolymer	d	Morphology	T_{ODT}
	nm		°C
PDEG ₂₈ - <i>b</i> -PCH ₇₅ - <i>b</i> -PDEG ₂₈	13.4	LAM	82
PDEG ₆₂ - <i>b</i> -PCH ₇₅ - <i>b</i> -PDEG ₆₂	17.1	LAM	140
PDEG ₇₃ - <i>b</i> -PCH ₇₅ - <i>b</i> -PDEG ₇₃	17.8	LAM	143
PDEG ₈₀ - <i>b</i> -PCH ₇₅ - <i>b</i> -PDEG ₈₀	18.2	LAM	145
PDEG ₈₁ - <i>b</i> -PCH ₇₅ - <i>b</i> -PDEG ₈₁	18.4	LAM	150

increase of d and a shift of T_{ODT} were observed as the length of outer segments increased, pointing to an enlargement of the PDEG lamellae thickness with augmentation of the molecular weight within the outer blocks.

Complementary information was obtained from AFM measurements. The experiments were performed on two different substrates: silicon (a neutral wafer) and mica (a hydrophilic one). In the bulk, the morphologies and phase transitions observed result from a balance between the energy associated with interactions between unlike segments at the microdomain interfaces and the entropy associated with chain stretching and the restriction of the junction points to the interfaces. However, when the bulk ordered arrays are lamellar, as in the current triblock copolymers, the final lamellar orientation for thin films on a supported substrate is determined by two additional factors that come into play:^[30–32] the interactions between blocks with the air and substrate (wetting effects) and

the relationship between the film thickness and the natural period of the bulk microphase separated structure (commensurability effects). Figure 6 shows an AFM image of a spin-coated and annealed PDEG₈₁-*b*-PCH₇₅-*b*-PDEG₈₁ film on a silicon wafer. A perpendicular lamellar nanostructure is observed, due to the non-preferential interactions of the two types of existing blocks with the air surface and the neutral substrate. This perpendicular lamellar structure is more favourable at a neutral interface because of higher conformational freedom that provides more ways to arrange the microdomain interfaces.^[33,34] However, the lamellar microdomain structure, bounded by flat non-neutral substrate and air interfaces, assumes a so-called parallel orientation, i.e., the interfaces of the microphase separated blocks are arranged parallel to the substrate plane. This orientation arises because the bounding surfaces induce an attractive field for one component of the block copolymer, which promotes growth of the composition fluctuations normal to the surface. Accordingly, the segments with lower surface energy wet the air interface and the block with a preferential interaction to the substrate wetting the substrate. These features are observed when mica is used instead of silicon, and favourable interactions are generated between the substrate and the PDEG blocks. The appearance of relief structures of islands or holes is characteristic of this parallel lamellar orientation when the initial film thickness is not commensurate with the bulk period, as clearly seen in Figure 7.

The subsequent cooling of the different PDEG-*b*-PCH-*b*-PDEG copolymers showed a scattering emergent peak. Therefore, a disorder-order transition (DOT) upon cooling was observed, located at slightly lower temperatures than the ODT on heating. This difference in temperature is common in block copolymers during the heating/cooling processes.^[35] It could be possible to obtain better development of this nanostructure if the cooling rate had been slower. However, our interest was focused on the existence or non-existence of reversible ordering of these copolymers

Figure 6. AFM height image in tapping mode for PDEG₈₁-*b*-PCH₇₅-*b*-PDEG₈₁ triblock copolymer on silicon wafer.

Figure 7. AFM height image in tapping mode for $\text{PDEG}_{81}\text{-}b\text{-PCH}_{75}\text{-}b\text{-PDEG}_{81}$ triblock copolymer on mica wafer.

under cooling in a short time cycle due to their feasible applications. On the other hand, the same deficient morphology was obtained, due to the diffuseness of the phase boundaries and the polydispersities found. The second heating SAXS profiles show a better defined and more intense first order peak, although higher orders were not exhibited for a given triblock copolymer, indicating that the initial nanostructure could be improved a bit under some other empirical conditions, for example, a higher annealing temperature at a given time and/or a longer annealing time at a constant temperature in the cast films, or at a slower cooling rate in films prepared from a disordered state. However, the ODT in the second heating was observed for a given copolymer at the same temperature as that found during its first heating, pointing

out that the ordering enhancement of these materials, for their use as interface agents in mixture of solvents,^[22] is not significant enough to justify an increase in time or energy requirements.

All the $\text{PDEG-}b\text{-PCH-}b\text{-PDEG}$ triblock copolymers presented similar behaviour to that just described, although differences were observed in the spacing and in the temperature value of the order-disorder transition, as listed in Table 2 and mentioned previously. The Bragg spacing increased with the polymerisation grade of the outer blocks of PDEG and the ODT moved to higher temperatures.

The copolymers of $\text{PCH-}b\text{-PDEG-}b\text{-PCH}$ with PDEG as the inner block were also analysed. The $\text{PCH}_{61}\text{-}b\text{-PDEG}_{77}\text{-}b\text{-PCH}_{61}$ triblock copolymer was taken as representative of this copolymer family and, therefore, its behaviour is described here in detail. Figure 8 shows SAXS profiles for the different cycles. A single defective first order maximum of scattering was observed at low temperature. This practically disappeared as the temperature increased, when the order-disorder transition takes place. It seems that the ordered arrangements were hindered and slightly more imperfect with PDEG as the inner block in these triblock copolymers, as deduced from the lower T_g^{PCH} and T_{ODT} values for analogous overall molecular weights. There is no evidence of high order reflections for any of them, independent of their relative composition. Similar to discussion for the $\text{PDEG-}b\text{-PCH-}b\text{-PDEG}$ copolymers, the development of ordering from an isotropic state, characterised by the disorder to order transition on cooling, is represented through the variation of either I^{-1} or Γ^{-1} as a function of the inverse of the absolute temperature in Figure 9. It can again be seen that this ordering occurs at slightly lower temperatures compared with that observed upon heating. The same results can be deduced from the derivative values. Identical features, the diffuseness of phase boundaries and polydispersity values seem to once more be responsible for difficulties with better ordering development. AFM micrographs present similar character-

Figure 8. SAXS profiles of $\text{PCH}_{61}\text{-}b\text{-PDEG}_{77}\text{-}b\text{-PCH}_{61}$ triblock copolymer as a function of spacing inverse: (a) first heating, (b) cooling and (c) second heating.

Figure 9. Variation of I^{-1} and I^{-1} with temperature for $\text{PCH}_{61}\text{-}b\text{-PDEG}_{77}\text{-}b\text{-PCH}_{61}$ triblock copolymer: (a) first heating, (b) cooling and (c) second heating.

istics to those observed for $\text{PDEG-}b\text{-PCH-}b\text{-PDEG}$ copolymers when supported on a neutral substrate. Therefore, a perpendicular lamellar nanostructure seems to be developed due to the non-preferential interactions between both blocks with the neutral silicon support, as exhibited in Figure 10. It has to be said that the rest of $\text{PCH-}b\text{-PDEG-}b\text{-PCH}$ triblock copolymers showed a similar morphology, as listed in Table 3, with the exception of the one involving the lowest polymerisation degree, in which no diffraction peak was observed. This finding agrees with the existence of a unique T_g in the DSC results located close to that corresponding to the PDEG, but shifted to higher temperatures due to the mixing of both types of blocks because of the small length of the PCH segments. Consequently, the $\text{PCH}_{17}\text{-}b\text{-PDEG}_{77}\text{-}b\text{-PCH}_{17}$ copolymer is not able to arrange itself into an ordered morphology either from solution or its condensed state. On the other

hand, although diffraction in the $\text{PCH}_{40}\text{-}b\text{-PDEG}_{77}\text{-}b\text{-PCH}_{40}$ triblock copolymer was noticeable, its intensity was small. Accordingly, it is not possible to provide an accurate value for the Bragg spacing. The remaining copolymers with PDEG as the inner block exhibit what was undoubtedly a first order peak. The spacing and the ODT temperature in the heating experiments increased as the outer PCH block molecular weight increased. However, the ODT was not observed for the $\text{PCH}_{62}\text{-}b\text{-PDEG}_{77}\text{-}b\text{-PCH}_{62}$ copolymer with the highest molecular weight in the outer blocks, even at temperatures as high as 230 °C.

The DSC thermal characterisation demonstrated the amorphous nature of these copolymers. Therefore, the glass transition temperatures of the inner and outer blocks were the unique thermal events observed. Accordingly, the corresponding WAXS profiles exhibited by these triblock copolymers, independent of whether PDEG or PCH was the macroinitiator, consisted of a single amorphous halo with an absence of other diffraction peaks, as seen in the left plot of Figure 11 for the $\text{PDEG}_{73}\text{-}b\text{-PCH}_{75}\text{-}b\text{-PDEG}_{73}$ copolymer. In spite of the relative simplicity of the WAXS region, a detailed assessment of variation with temperature of the amorphous halo peak, whose position in the

Figure 10. AFM height image in tapping mode for $\text{PCH}_{61}\text{-}b\text{-PDEG}_{77}\text{-}b\text{-PCH}_{61}$ triblock copolymer.

Table 3. Bragg spacing of the first order estimated at 25 °C, type of morphology and T_{ODT} of $\text{PCH-}b\text{-PDEG-}b\text{-PCH}$ triblock copolymers on second heating.

Copolymer	d	Morphology	T_{ODT} °C
	nm		
$\text{PCH}_{17}\text{-}b\text{-PDEG}_{77}\text{-}b\text{-PCH}_{17}$	—	—	—
$\text{PCH}_{40}\text{-}b\text{-PDEG}_{77}\text{-}b\text{-PCH}_{40}$	15.6	—	—
$\text{PCH}_{51}\text{-}b\text{-PDEG}_{77}\text{-}b\text{-PCH}_{51}$	18.1	LAM	95
$\text{PCH}_{58}\text{-}b\text{-PDEG}_{77}\text{-}b\text{-PCH}_{58}$	18.6	LAM	105
$\text{PCH}_{61}\text{-}b\text{-PDEG}_{77}\text{-}b\text{-PCH}_{61}$	18.7	LAM	130
$\text{PCH}_{62}\text{-}b\text{-PDEG}_{77}\text{-}b\text{-PCH}_{62}$	19.0	LAM	—

Figure 11. (a) Time resolved WAXS profiles for PDEG₇₃-*b*-PCH₇₅-*b*-PDEG₇₃ triblock copolymer during its first heating process. (b) Dependence of amorphous halo spacing on temperature.

maximum (d^{halo}) is directly ascribed to the most probable intermolecular distance between macromolecular chains,^[36] can also provide information on the existence of microphase separation in these copolymers. However, the T_g of the PDEG block was found at sub-ambient temperatures in these particular triblock copolymers, independent of which one was the inner block, and these were impossible to reach with the set-up used for these diffraction experiments. Accordingly, from 25 °C (the lowest accessible temperature and above the T_g of the inner segments) to around 75 °C, the location of the amorphous halo maximum varied in a lesser extension than at temperatures higher than 75 °C, as depicted in Figure 11(b) for PDEG₇₃-*b*-PCH₇₅-*b*-PDEG₇₃. This fact is due to the reduced motion capability of the rigid PCH blocks within this temperature range, since they are still in their glassy state, i.e., below their corresponding glass transition temperature, contrary to the PDEG segments. Once these CH blocks undergo their glass transition (independently of their position within the macrochains as inner or outer blocks, PDEG-*b*-PCH-*b*-PDEG or PCH-*b*-PDEG-*b*-PCH respectively), the whole block copolymer gains mobility at temperatures higher than about 75 °C and the position of the most probable intermolecular distance between macromolecules undergoes a shift to higher d^{halo} values in the same way that the d^{halo} thermal expansion coefficient increases. This displacement is ascribed to the existence of cooperative and generalised motions within macromolecules because of their global elastomeric state at those high temperatures. Accordingly, the glass transition temperature of the rigid PCH blocks could be estimated from the intersections of these two different slopes (fits to straight lines are represented in Figure 11(b)) associated with the change in thermal expansion coefficients and, thus, to the variation of the copolymer mobility. The agreement with those T_g values obtained by DSC for the PCH blocks was quite good, the calorimetric

value being 81 °C for the copolymer shown in Figure 11. In addition, a subtle change in the slope seemed to take place at the highest temperatures, which can be ascribed to the mobility increase once the overall disorder is reached after the order-disorder transition occurs.

Conclusion

In summary, the existence of microphase separation within PDEG-*b*-PCH-*b*-PDEG and PCH-*b*-PDEG-*b*-PCH amphiphilic triblock copolymers has been determined by differential scanning calorimetry. The corresponding glass transitions of the inner and outer blocks were shifted compared with those of the pure homopolymers, as a result of the formation of statistical copolymers between the pure blocks because of the synthetic protocol used. Due to the feasible applicability of these triblock copolymers as interface agents in mixtures of solvents, this method is rather interesting from an industrial point of view because the isolation of the inner block is not a requirement for obtaining them. However, the ordered morphology developed in the different triblock copolymers was quite imperfect, as revealed by time resolved SAXS measurements with synchrotron radiation and AFM results, because of the diffuseness of phase boundaries associated with the existing statistical copolymers between the pure blocks. Most of the triblock copolymers, independent of the inner or outer position of the rigid PCH blocks, developed a lamellar structure characterised by a clear first order scattering peak. Moreover, the Bragg spacing was considerably dependent on the molecular weight of the outer segments, its value increasing as their length did. The typical order-disorder and disorder-order transitions were also observed and determined, shifting at higher temperatures as the polymerisation degree increased. Finally, the analysis of the amorphous halo spacing with

temperature in real time temperature variable WAXS experiments was probed to estimate the glass transition of hard and rigid PCH blocks and, tentatively, ODT temperatures. The results found were in good agreement with those obtained by DSC and SAXS, respectively.

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