Investigation by combined solid-state NMR and SAXS methods of the morphology and domain size in polystyrene-b-polyethylene oxide-b-polystyrene triblock copolymers

http://www.producao.usp.br/handle/BDPI/50073

Downloaded from: Biblioteca Digital da Produção Intelectual - BDPI, Universidade de São Paulo
Investigation by Combined Solid-State NMR and SAXS Methods of the Morphology and Domain Size in Polystyrene-b-Polyethylene Oxide-b-Polystyrene Triblock Copolymers

FÁBIO A. BONK,† STEFANO CALDARELLI,† TRANG PHAN,‡ DENIS BERTIN,‡ EDUARDO R. DEAZEVEDO,‡ GERSON LUIZ MANTOVANI,§ TITO J. BONAGAMBA,§ TOMÁS S. PLIVELIC,∥ IRIS L. TORRIANI∥

1Aix-Marseille Université ISm2 UMR 6263, Sede de Saint Jérôme, 13397 Cedex 20, Marseille, France  
2LCP UMR6264, Université de Provence, Sede de Saint Jérôme, 13397, Marseille, France  
3Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos SP, Brasil  
4Laboratório Nacional de Luz Síncrotron, Campinas SP, Brasil  
5Instituto de Física “Gleb Wataghin”, Universidade Estadual de Campinas, and Laboratório Nacional de Luz Síncrotron, Campinas SP, Brasil

Received 15 May 2009; revised 24 August 2009; accepted 26 August 2009  
DOI: 10.1002/polb.21843  
Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: The microphase structure of a series of polystyrene-b-polyethylene oxide-b-polystyrene (SEOS) triblock copolymers with different compositions and molecular weights has been studied by solid-state NMR, DSC, wide and small angle X-ray scattering (WAXS and SAXS). WAXS and DSC measurements were used to detect the presence of crystalline domains of polyethylene-oxide (PEO) blocks at room temperature as a function of the copolymer chemical composition. Furthermore, DSC experiments allowed the determination of the melting temperatures of the PEO blocks. SAXS measurements, performed above and below the melting temperature of the PEO blocks, revealed the formation of periodic structures, but the absence or the weakness of high order reflections peaks did not allow a clear assessment of the morphological structure of the copolymers. This information was inferred by combining the results obtained by SAXS and 1H NMR spin diffusion experiments, which also provided an estimation of the size of the dispersed phases of the nanostructured copolymers. © 2009 Wiley Periodicals, Inc. J Polym Sci Part B: Polym Phys 48: 55–64, 2010

KEYWORDS: ABA triblock-copolymers; block copolymers; NMR; SAXS

INTRODUCTION The preparation of novel polymeric materials with well-defined architectures is a challenge of high interest, giving rise materials with superior combinations of properties.1,2 These polymeric materials can be obtained by blending distinct polymers, for example adding rubber to polystyrene, or by preparing block copolymers. The latter have received considerable attention due to the periodic ordering of their microphase separated domains as a consequence of the general thermodynamic incompatibility of the blocks. The properties exhibited by these materials allow their use in various applications, e.g. as polymeric surfactants, compatibilizers in polymer blending, dispersions, solid polymer electrolytes,3–5 and as templates for the preparation of inorganic nanoparticles.3–5 Such a span of potential applications is strongly related to the size of its characteristic nanodomains and to the thickness of the interphase regions. Among various possible materials that can be used to prepare block copolymers, poly(styrene) (PS) and poly(ethylene oxide) (PEO) can form interesting phase-separated structures, mainly because of block dissimilarity and incompatibility.3,6 Furthermore, as PEO blocks could crystallize, the number of structures and morphologies frequently obtained in block copolymers could exhibit interesting physicochemical properties arising from the competition between microphase separation and crystallization.6 Despite the structural richness of these materials, the morphological characterizations of triblock copolymers with these components are scarce.9,10

Additional Supporting Information may be found in the online version of this article.

*Present address: Instituto de Química, Universidade Estadual de Campinas, CP 6154, CEP 13083-970 Campinas, SP, Brasil.  
†Present address: Centro de Engenharia, Modelagem e Ciências Sociais Aplicadas – Universidade Federal do ABC, Santo André, SP, Brasil.  
‡Present address: MAXLab, Lund University, P.O. Box 118, SE-22100 Lund, Sweden.  
∥Present address: MAXLab, Lund University, P.O. Box 118, SE-22100 Lund, Sweden.  
Correspondence to: S. Caldarelli (E-mail: s.caldarelli@univ-cezanne.fr)

In this work, we studied a series of ABA triblock copolymers polystyrene-b-polyethyleneoxide-b-polystyrene (SEOS), in which the number-average molecular weight of the PEO blocks was kept constant at 10.0 kg.mol⁻¹ and those of the PS blocks were varied in an extended range. Due to the individual thermodynamic properties of the block components, commonly four regions with different mobilities are expected: a mobile region (PEO), a more rigid region (PS and eventually crystalline PEO) and an interphase region. This latter is loosely defined and owing to the immiscibility of the blocks, it is normally expected to be thin in comparison with the size of the PS and PEO domains.

In this work, solid-state ¹H NMR spin diffusion and SAXS analysis were used as complementary techniques to gain information on the domain size and morphology in amorphous and semicrystalline SEOS triblock copolymers. ¹H spin-diffusion NMR and SAXS¹¹,¹² are two common experimental approaches for investigating the sizes of the different regions in phase-separated systems. NMR does not require the formation of periodical domains and is sensitive to domain sizes ranging from nanometers to hundred of nanometers,¹³ but it is not able to yield morphological information directly. SAXS, in contrast, can provide morphological information, but in partially disordered systems it shows strong limitations in obtaining details on the domain sizes of the dispersed phases and interphases. We show in this article that, conversely, precise structural information on the nanostructure of the ABA block copolymers investigated can be obtained by interlacing SAXS and ¹H NMR spin diffusion analysis, overcoming the intrinsic limitations of the two techniques.

EXPERIMENTAL

Materials and Samples Preparation

The PS-b-PEO-b-PS triblock copolymers were prepared by the Nitroxide Mediated Polymerization (NMP) method of styrene using a dysfunctional PEO macroalkoxysamine. Experimental details of the block copolymer synthesis are described elsewhere⁶ and the scheme of the chemical structure of the SEOS samples is shown in Figure 1. The terminating N-tert-butyl-N(1-diethylphosphono-2,2-dimethylpropyl)-N-oxyl groups stem from the NMP synthesis procedure.

The weight ratios of the PS-b-PEO-b-PS samples were determined by solution NMR in CDCl₃ and their values are given in Table 1. The volumetric fractions were obtained from the weight ratios using the known densities of PS and PEO,¹¹,¹⁴ ρₚₛ = 1.05 g.cm⁻³ and ρₚₑₒ = 1.13 g.cm⁻³, respectively. The nomenclature SEOS-n (n = 1, 2, 3 and 4) will be used to discriminate the four concentrations studied.

SEOS as-cast films used for NMR, SAXS, WAXS, and DSC measurements were prepared as thick films by solvent casting. Samples were first dissolved in toluene at room temperature at concentrations of roughly 10 wt %. Solutions were then cast on a clean aluminium substrate. The toluene was allowed to evaporate slowly at room temperature over a period of several days. To ensure the total removal of the solvent, the films were placed in a vacuum oven at 90 °C for 48 h and then stored in a desiccator at room temperature. The thickness of the films obtained was of about 0.1 to 0.5 mm. For SAXS and WAXS measurements, the samples were cut into pieces of 1 cm², whereas for NMR, the samples were cut in small pieces of 1 mm² for SEOS-1 and 2, and powdered for SEOS-3 and 4, because in this case, the films were brittle due to increased crystallinity.

Differential Scanning Calorimetry Measurements

Specimens of the as-cast films samples (about 8–12 mg) were compressed into aluminum sample pans and then scanned from 10 to 120 °C at a rate of 10 °C/min. The experiments were carried out on a TA Instruments Q1000 differential scanning calorimeter to obtain values for the melting temperature (T_m), and the heat of fusion of the PEO block (ΔH_m^PEO) and the glass transition temperatures of the PS block (T_g).

Simultaneous SAXS/WAXS Measurements

Simultaneous SAXS and WAXS measurements were performed at the D11A-SAXS1 beamline of the Brazilian Synchrotron Light Laboratory (LNLS). The X-ray experiments were recorded simultaneously in two linear position sensitive detectors.¹⁵,¹⁶ The wavelength used was 1.608 Å. The range of the scattering vector q = (4π/λ) sin(θ), (2θ = scattering angle) was 0.008 ≤ q ≤ 0.2 Å⁻¹ for SAXS and 15 ≤ 2θ ≤ 32° for WAXS. X-ray data were taken from room

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight Ratio (PS/PEO)</th>
<th>% vol of PS</th>
<th>Total Mₚ (kg/mol)</th>
<th>Mₚ of PS Block (kg/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEOS-1</td>
<td>84.5/15.5</td>
<td>0.85</td>
<td>64.5</td>
<td>54.5</td>
</tr>
<tr>
<td>SEOS-2</td>
<td>63/37</td>
<td>0.65</td>
<td>27.8</td>
<td>17.8</td>
</tr>
<tr>
<td>SEOS-3</td>
<td>52/48</td>
<td>0.53</td>
<td>20.9</td>
<td>10.9</td>
</tr>
<tr>
<td>SEOS-4</td>
<td>29/71</td>
<td>0.30</td>
<td>14.2</td>
<td>4.2</td>
</tr>
</tbody>
</table>
temperature to 60 °C varying the temperature of a THM Linkam hot stage in steps of 5 °C.

NMR Measurements

1H solid-state NMR experiments were carried out using a Bruker Avance-400 spectrometer operating at a proton frequency of 400.3 MHz. The 1H π/2 pulse length was 3.5 μs. 1H longitudinal relaxation times T₁ were measured using the saturation recovery method in static samples at room temperature. Saturation was achieved by a sequence of 15–20 π/2 pulses. The same 1H T₁ value was observed for both components (PS and PEO) in all compositions. A recycle delay of 6 s was sufficient to avoid T₂ saturation effects. Spin diffusion measurements were performed using a multiple pulse 1H dipolar filter (discussed below) with 12 cycles and interpulse delays time τ of 5 μs. The typical mixing times used in these experiments vary between 100 μs and 1 s. All experiments were performed on static samples.

1H Spin-Diffusion NMR

1H spin-diffusion experiments are the standard NMR methods used to characterize the morphology of multi-component phase separated polymeric systems like the ABA triblock copolymers SEOS-n studied here. This section intends to provide a self-contained explanation of the NMR procedures and data analysis used in the following.

The Goldman-Shen (or T₂) filter is the methodology of choice when a considerable mobility difference among the phases exists, i.e., when the systems are constituted by both rigid and mobile phases. In this method, the signal from the mobile region is selectively excited, and then the diffusion of the magnetization from the mobile to the rigid region is monitored as a function of a mixing time tₘ. This spin diffusion process can be modeled to provide specific information such as domain sizes, interdomain distances, and interface dimensions.

In this article, we used the standard dipolar filtered 1H spin diffusion pulse sequence. The selection of the magnetization from the mobile component is achieved by a π/2 pulse followed by a dipolar filter (Fig. 2). Subsequently, a second π/2 pulse stores the selected mobile phase magnetization along the z direction for the mixing time tₘ. When magnetization diffusion back into the rigid phase can occur. After the mixing time, a read-out π/2 pulse is applied and the signal detected. At short tₘ values, the detected signal has only contributions from the mobile phase and thus a single sharp line (with a long T₂) is observed. As tₘ increases, the spin diffusion into the rigid phase causes the appearance of a second broad component in the detected signal. Thus, to monitor the tₘ dependence of the mobile phase signal is necessary somehow to separate it from the sharp component. In our case, this was achieved by decomposing the resulting 1H spectra for each value of tₘ using mixed Lorentzian and Gaussian lineshapes for the mobile phase and a single broader Gaussian lineshape for the rigid phase signal. At longer tₘ values, the spectra of the mobile region could be fitted with a pure Lorentzian lineshape.

Once the tₘ dependence of the mobile phase magnetization is obtained, the domain sizes can be estimated from the mixing time dependent diffusion curves and the diffusion model proposed, considering Fick’s second law

\[
\frac{\partial m(\vec{r}, t_m)}{\partial t} = \nabla \cdot \left( D(\vec{r}) \nabla m(\vec{r}, t_m) \right),
\]

where D is the diffusion coefficient and m(\vec{r}, t) is the physical quantity that diffuses. Particularly, for NMR, m(\vec{r}, t) is the density of magnetization along z direction after application of the dipolar filter. An analytical solution for the case of one-dimensional diffusion in polymers has been proposed, which could be used to fit the whole spin-diffusion process. However, the spin-diffusion coefficient D could be scale dependent hindering the search for a general solution of eq 1. As discussed by Claus et al., a simpler approach makes use of the initial rate approximation, which is valid for systems where the interfacial thickness is small with respect to the domain sizes. This approach is robust with respect to the variation of the diffusion constants, as it concentrates on a well-defined time window of the diffusion process. The average size of the mobile phase, dₘob, can be obtained using the following equation:

\[
dₘob = \frac{4ε}{π} \times \frac{\sqrt{Dₘob}}{\sqrt{Dₘob + Drig}} \times \sqrt{tₘ},
\]

where ε is the number of orthogonal directions relevant for the spin diffusion process, being 1 for one dimensional diffusion geometries (e.g., lamellar blocks copolymers), 2 for two-dimensional geometries (e.g., cylinder-like morphologies), and 3 for discrete phases (e.g., spheres in a matrix). Dₘob and Drig are, respectively, the mobile and rigid phase 1H spin diffusion coefficients, and \(\sqrt{tₘ} \) is determined in a plot of the mobile phase signal intensity vs. \(\sqrt{tₘ} \) by extrapolating the linear portion of the curve to the abscissas axis. The interdomain distance, dᵢ, is determined by the relationship

\[
dᵢ = \frac{dₘob}{\sqrt{φₘob}}.
\]

where the φₘob is the volumetric fraction of the mobile phase. In most of our analysis, the dispersed mobile phase is PEO (which can assume the three kinds of morphology cited above) and the rigid matrix corresponds to PS. Then, φₘob can be estimated from the SEOS composition (Table 1).
An important feature of eq 2 is its dependence on the \(^1\text{H}\) spin diffusion coefficients \(D_{\text{mob}}\) and \(D_{\text{rig}}\) which must be known for evaluating the domain sizes of the system. According to Demco et al.,\(^{14}\) the diffusion coefficients are related to the Van Vleck second moment of the NMR resonance through its full-line-width-at-half-height \(\Delta(v)_{1/2}\), which in the case of Gaussian lines is given by

\[
D_{\text{matrix}} = \frac{1}{12} \sqrt{\frac{\pi}{2 \ln(2)}} (r^2) \Delta(v)_{1/2}
\]  

and for Lorentzian lines by

\[
D_{\text{dis}} = \frac{1}{6} (r^2) \sqrt{\frac{x \Delta(v)_{1/2}}{}}
\]

where \((r^2)\) is the mean square distance between the nearest \(^1\text{H}\) spins. For PEO \((r^2)_{\text{PEO}} = 5.032\ \text{Å}^2\) and for PS \((r^2)_{\text{PS}} = 5.83\ \text{Å}^2\), \(x\) is a cutoff parameter for the Lorentzian line shape (i.e., the value for which the absorption spectrum intensity for the frequency range \(|\Delta v| > x\) can be neglected). In this work \(x\) was taken as 10 times \(\Delta(v)_{1/2}\).

**RESULTS AND DISCUSSION**

**Differential Scanning Calorimetry and WAXS Analyses**

The thermograms obtained for the four samples under study during the heating scan are shown in Figure 3. Changes in the heat capacity can be clearly seen for SEOS-1 and SEOS-2 between 60 and 80 °C. The glass transition temperatures of the PS block, \(T_g^{\text{PS}}\), determined by the 50% heat capacity change, are listed in Table 2. Their values decrease proportionally with the molecular weight of the PS block, as expected. In fact, the glass transition becomes not detectable for lower PS concentrations, as it probably overlaps with the principal endothermic peak. Furthermore, the \(T_g\) values obtained are lower than the expected values for the PS homopolymers with the same molecular weight. This may be the result of interface effects of the PS glass domains located between the molten PEO domains.\(^{21}\)

The PEO melting temperature, \(T_m^{\text{PEO}}\), and the PEO mass degree of crystallinity, \(X_c\), obtained from DSC are shown in Table 2. The second quantity was calculated from the measured heat of fusion \(\Delta H_f^{\text{PEO}}\) using the equation:

\[
X_c = \frac{\Delta H_f^{\text{PEO}}}{w_{\text{PEO}}} \cdot \Delta H_f
\]

where \(w_{\text{PEO}}\) and \(\Delta H_f\) is the weight fraction of the PEO block and the fusion enthalpy of perfect PEO crystals and equal to 207 J g\(^{-1}\) respectively.\(^{22}\)

\(X_c\) values show a linear increase with the PEO concentration in the block copolymer. In the extreme case of SEOS-1 no detectable crystallinity was observed. This behavior is coherent with the idea proposed by Xie et al.\(^{23}\) that higher quantities of PS could limit the folding of the central block. \(T_m^{\text{PEO}}\) values are almost the same in all semicrystalline copolymer samples under study.

WAXS data from all SEOS samples and pure PEO (for comparison) at room temperature are shown in Figure 4. The diffractogram recorded for SEOS-1 shows only a large amorphous halo, indicating a completely amorphous morphology.

No changes in the position of the main reflections are observed from SEOS-n samples compared with the homopolymer. This indicates that the crystal structure of the PEO block is not affected by the block copolymer composition.

The degree of crystallinity can be obtained from WAXS data using the equation:

\[
x_{c}^{\text{WAXS}} = \frac{1}{w_{\text{PEO}}} \cdot \left( \frac{I_c}{I_a + I_c} \right)
\]

where \(I_c\) is the integrated intensity due to the crystalline PEO and \(I_a\) the integrated intensity corresponding to the amorphous scattering. The values obtained, following these

<table>
<thead>
<tr>
<th>Sample</th>
<th>(T_g^{\text{PS}}) (°C)</th>
<th>(T_m^{\text{PEO}}) (°C)</th>
<th>Heat of Fusion (\Delta H_f) (J.g(^{-1}))</th>
<th>(X_c^{\text{DSC}})</th>
<th>(X_c^{\text{WAXS}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEOS-1</td>
<td>70</td>
<td>–</td>
<td>–</td>
<td>&lt;5(^{a})</td>
<td>&lt;5(^{a})</td>
</tr>
<tr>
<td>SEOS-2</td>
<td>65</td>
<td>47</td>
<td>18</td>
<td>24</td>
<td>29</td>
</tr>
<tr>
<td>SEOS-3</td>
<td>–</td>
<td>48</td>
<td>50</td>
<td>50</td>
<td>55</td>
</tr>
<tr>
<td>SEOS-4</td>
<td>–</td>
<td>51</td>
<td>95</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>PEO(^{b})</td>
<td>–</td>
<td>67</td>
<td>172</td>
<td>83</td>
<td>82</td>
</tr>
</tbody>
</table>

\(^{a}\) PEO Crystallinity under the detection limit.
\(^{b}\) Values from the homopolymer PEO were obtained for a sample prepared in the same way as for SEOS samples.
procedures, are indicated in Table 2, showing a very good correspondence with those obtained by DSC.

Since the microphase separated amorphous state is the point of comparison of the morphological characterization by X-ray and solid state NMR (see below), the melting of the PEO phase was confirmed in temperature dependent WAXS experiments. The temperatures observed for complete melting of the crystalline PEO were of 50 °C for SEOS-2 and SEOS-3, and 55 °C for SEOS-4.

**SAXS Analyses**

SAXS results are summarized in Figure 5. In some of the block copolymer compositions, the structure factor contribution can be detected in the SAXS intensity curves obtained at room temperature (black line in Fig. 5a–d), and the first correlation peak can be clearly identified for all patterns. However, this peak broadens along the series with decreasing PS content, which testifies of increased structural disorder.

Poor statistics in the SEOS-1 data does not allow precise identification of the higher order peaks indicated by the numbers in the Figure. This is probably due to a weak electron density contrast between amorphous PEO and PS domains.\textsuperscript{25}

**FIGURE 4** WAXS curves at room temperature for PEO and the SEOS as cast films. The fitted amorphous halos are indicated in each case as a dotted line.

**FIGURE 5** SAXS measurements for SEOS samples at room temperature (black curves), 50 °C (green curves) and 60 °C (red curves). The arrows indicate the position of higher order correlation peaks for expected morphologies based on the blocks volume fractions\textsuperscript{24}: (a) SEOS-1; (b) SEOS-2; (c) SEOS-3; (d) SEOS-4.
The scattering SAXS patterns of the SEOS-2 and SEOS-3 samples contain some indication of the higher order peaks of the structure, but the intensity is also very low and the peaks are poorly defined, preventing a decisive confirmation of the morphology expected for these samples based on other similar systems (hexagonal PEO cylinders in a PS matrix for sample SEOS-2 and PEO-PS lamellas for sample SEOS-3, which would correspond to peaks indicated with an arrow in Fig. 526).

In the case of sample SEOS-4, a second maximum can be detected in a position suggesting a contribution from the semicrystalline lamellar morphology of the PEO matrix.

Other details of the domain structure of the samples can be obtained from SAXS patterns corresponding to temperatures above the melting point of the PEO blocks. As shown in Figure 5a–c, similar SAXS curves are obtained at 60 °C (red lines) and room temperature (black lines) for the three samples SEOS-1, 2 and 3. This fact indicates that the microphase morphology is preserved after melting, and the crystallization of the PEO block occurred in restricted phase morphology (confined crystallization). For the higher temperature patterns, the decrease in the scattered intensity may be due to the loss of order and/or of electron density contrast.

A completely different behavior is observed for SEOS-4, in which the correlation peak is lost at 60 °C (red line). This fact suggests a matrix inversion, the PEO providing the overall morphology. At the intermediate temperature of 50 °C (green line) the shift of this maximum towards lower q values suggests that the fusion of the PEO lamellae and the increased mobility of the short PS blocks lead to a complete loss of the correlation peak at 60 °C. It is important to note that in this sample, the PEO volumetric fraction is 70%, being the major component of the system.

This behavior is characteristic of unconfined crystallization, in which the semi-crystalline lamellar structure overrides the pre-existing phase separation morphology. This is expected due to the low molecular weight of the PS block and its reduced viscosity in this sample.

When PEO is amorphous (T ≥ 60 °C), the increasing broadening of the main SAXS peak for lower PS concentration reflects the loss of organization in the morphology. This fact is consistent with the expected increasing loss of rigidity of the end blocks. The extreme case is SEOS-4, in which heating above the PEO melting point results in the loss of the correlation peak. Due to this fact we did not investigate further this sample. The noisy signal observed for higher q values is due to weak scattering of the samples and a smoothing of the end of the curves no longer shows high order peaks.

In the SAXS spectra, the coordinate corresponding to the maximum of the main correlation peak (q_m), can be associated with the interdomain distances, d_i. In cases in which the morphology of the sample is known, the d_i values can be calculated as follows24,26:

\[
\text{Lamellar} \quad d_i = \frac{2 \cdot \pi}{q_m} \quad (8)
\]

**TABLE 3** Interdomain Distances, d_i (nm), Obtained from SAXS Experiments at T = 60 °C for Different Hypothetical Morphologies

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lamellar</th>
<th>HCP</th>
<th>BCC</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEOS-1</td>
<td>21.7</td>
<td>25.1</td>
<td>26.6</td>
</tr>
<tr>
<td>SEOS-2</td>
<td>21.3</td>
<td>24.6</td>
<td>26.1</td>
</tr>
<tr>
<td>SEOS-3</td>
<td>15.0</td>
<td>17.3</td>
<td>18.4</td>
</tr>
</tbody>
</table>

Table 3 summarizes the interdomain distances calculated using equations (8, 9 and 10) for all possible morphologies of the SEOS-1, 2, 3 samples. Due to the modest resolution of the existing data, the possible existence of a gyroid structure was not postulated, as was the case in similar experiments reported in the literature.27

The interfacial thickness, \(L_{\text{INTER}}\), can also be estimated from the SAXS profiles. The analysis of the experimental data that allows calculation of the interphase region is based on Porod’s theory. For the ideal case in which there is a sharp boundary separating the two phases involved, the scattered intensity falls as \(q^{-4}\) for the tail end region of the scattering curve according to the expression \(I(q) = P q^{-4}\) (where \(P\) is the Porod constant). In polymeric materials, possible phase intermixing and the presence of heterogeneities of length scale significantly smaller than the domain size in the system, may be the source of diffuse background scattering, producing deviations from the \(q^{-4}\) behavior. In this case, the \(l q^4\) vs \(q^4\) plot exhibits a systematic deviation from Porod’s law and the straight line of the observed intensity data presents a positive slope \(C_0\) [Fig. 6(a)]. Considering that electron density fluctuations in polymers are generally three dimensional and the contribution of the scattering is a constant, independent of \(q\), the expression \(I(q) = C_0 + Pq^{-4}\) can be used to describe the observed intensity. The value of \(C_0\) can be obtained from the \(l q^4\) vs \(q^4\) plot and used to correct the intensity due to the aforementioned electron density fluctuations \((I(q) - C_0)\) as shown in Figure 6(a) for the SEOS-2 sample. The analysis of the background corrected intensity in the Porod region still contains information on the interphase region.

In the case of a finite interfacial thickness, the plot \(\ln[(I - C_0)q^4]\) vs \(q^2\) will show a negative deviation from the ideal constant value at high q as can be observed in Figure 6(b). The interfacial thickness, \(L_{\text{INTER}}\), can then be estimated from this plot by assuming a convolution of the ideal electron density profile (sharp interfaces) with a Gaussian smoothing function of the form \(\exp(-r^2/2\sigma^2)\), \(\sigma\) being the standard deviation and a measure of the interfacial
This value is given by \( L_{\text{INTER}} = (2\pi)^{1/2} \sigma \). The steps outlined for this procedure are exemplified in Figure 6 (a and b) for the SEOS-2 sample. The results are summarized in Table 4.

**NMR Analyses**

The DSC and WAXS results showed that in the case of SEOS-2 and 3, the PEO block is semicrystalline at room temperature. Hence, it is expected that the observed \(^1\)H spin-diffusion process, going from mobile to rigid regions, would occur from amorphous PEO to crystalline PEO first, and only then to the amorphous PS. To avoid this double diffusion process and examine only the transfer process from amorphous PEO to PS, the NMR spin diffusion measurements were performed over the melting temperature of the PEO blocks at 55 °C. As the sample SEOS-1 was already essentially completely amorphous at 22 °C, the spin-diffusion analysis can be performed without heating of the sample.

The \(^1\)H NMR spectra for samples SEOS-1,2,3, and 4 are shown in Figure 7. In the case of SEOS-4, the spectrum is composed by two lines of comparable widths. In this condition, as the second moments of the two lines are very similar, it is not possible to filter out the PS signal, and spin-diffusion experiments are not accessible. Nonetheless, this demonstrates that in SEOS-4, the molecular segments in the PS block have a degree of mobility that is, from the NMR point of view, similar to those in the PEO matrix, implying fast reorientation of the PS blocks molecules. In other words, the softening of the PS block \((T_g)\) occurs below 55 °C. This confirms our explanation of the absence the observation of the glass transition in the DSC thermograms as a result of overlap with the principal endothermic peak due to fusion of the PEO block. This behavior also nicely agrees with the SAXS results for SEOS-4 that point to the absence of phase separation after the fusion of the crystalline PEO at 60 °C.

Contrary to SEOS-4, the \(^1\)H spectra of samples SEOS-1,2, and 3 are clearly composed of a narrow and a broad line, which are assigned to the mobile PEO and the rigid PS phase, respectively. A first analysis of the spectra was achieved by deconvolution with a narrower lorentzian lineshape.

**TABLE 4** Estimation of Interphase Size for SEOS Samples from SAXS Results

<table>
<thead>
<tr>
<th>Sample</th>
<th>( L_{\text{INTER}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEOS-1</td>
<td>0.7 ± 0.3</td>
</tr>
<tr>
<td>SEOS-2</td>
<td>1.4 ± 0.3</td>
</tr>
<tr>
<td>SEOS-3</td>
<td>1.0 ± 0.2</td>
</tr>
</tbody>
</table>

**FIGURE 6** The steps outlined for the interphase calculation are exemplified in a and b for the SEOS-2 sample. (a) a \( I(q) \) vs \( q^4 \) plot used for the determination of the background corrected intensity \( I(q) = C_0 \) (b) plot \( \ln[I(q)-C_0]q^4 \) vs \( q^2 \) of the corrected scattering intensity used for the estimation of the interphase thickness using a sigmoidal gradient model for the electron density profile. (Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.)

**FIGURE 7** Line shape deconvolution of the 1 NMR spectra for SEOS samples. The temperature was of 22 °C for SEOS-1 and of 55 °C for the other cases. The width of the broad lines (corresponding to the rigid material) are a) 33.53 kHz, b) 30.37 kHz, c) 29.93 kHz, and d) 2.80 kHz. The reduction in linewidth corresponds to increased mobility of the PS copolymer block.
associated to the mobile PEO phase and a broader Gaussian lineshape, corresponding to the rigid PS phase (Table 5 and Fig. 7). The values obtained are shown in Table 5 and are in fair agreement with the chemical composition of the copolymer, as the PS component is shown to decrease along the series. An exception to the trend is observed for SEOS-3, which can be explained by the very low intensity of the broad line and the associated expected large error. For SEOS-4, both signals become considerably narrower and well visible, so that the guess of the relative percentage is again good. It is noteworthy that the line corresponding to the PS phase becomes narrower upon decreasing the PS concentration, which corresponds to the increased mobility in this phase. This is again in qualitative agreement with the SAXS results that show increasingly disordered structures upon PS concentration. At any rate, the incertitude on the determination of the broad signal is too large to provide reliable quantitative results. In the following our analysis has thus been performed exclusively following the intensity variations of narrow $^1$H signal.

The width of the NMR lines corresponding to the rigid and mobile phase were used to determine the spin diffusion coefficients $D_{mob}$ and $D_{rig}$ respectively, using eqs (4) and (5). The calculated values are shown in Table 6. The results obtained for the rigid PS block are very similar to those obtained by Chen and Schmidt-Rohr, whereas the coefficients relative to the mobile PEO block are in agreement with those reported in the literature for mobile domains.

Figure 8 shows a plot of the sharp Lorentzian peak area as a function of the square root of the mixing time, $\sqrt{t_m}$, describing the spin diffusion process. The error in the evaluation of the areas is estimated to be about 3%. Following the procedure described above (solid lines in Fig. 8), these curves provided the parameter $\sqrt{t_m}$, which will be used below to calculate $d_{mob}$ and $d_i$ using eqs (2) and (3) for the three possible morphologies ($\varepsilon = 1$ to 3) (Table 7).

As discussed, SAXS results were not conclusive in determining the exact phase morphologies for samples SEOS-1, 2, and 3, for the lack of higher-order correlation peaks. Thus, in an attempt to overcome this limitation, we applied the same methodology of Spiess group to compare interdomain distances calculated from the NMR spin diffusion data using $\varepsilon = 1$, 2, and 3 ($d_i$ NMR in Table 8) with the outcome of the SAXS analysis (in Table 3). The sample morphology (actually the $\varepsilon$

### Table 5: Results of the Deconvolution of the NMR Spectra in Figure 6, Using the Sum of a Lorentzian (L) and a Gaussian (G) Line

<table>
<thead>
<tr>
<th>Sample</th>
<th>SEOS-1 (22 °C)</th>
<th>SEOS-2 (55 °C)</th>
<th>SEOS-3 (55 °C)</th>
<th>SEOS-4 (55 °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>L(%)</td>
<td>26.5</td>
<td>38.0</td>
<td>75.0</td>
<td>61.6</td>
</tr>
<tr>
<td>G(%)</td>
<td>73.5</td>
<td>62.0</td>
<td>25.0</td>
<td>38.4</td>
</tr>
</tbody>
</table>

### Table 6: Diffusion Coefficients Calculated Using eqs (4) and (5)

<table>
<thead>
<tr>
<th>Sample</th>
<th>$D_{rigid\ matrix}$ (nm$^2$/ms)</th>
<th>$D_{disp\ mobile}$ (nm$^2$/ms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEOS-1 (22 °C)</td>
<td>0.246</td>
<td>0.050</td>
</tr>
<tr>
<td>SEOS-2 (55 °C)</td>
<td>0.228</td>
<td>0.040</td>
</tr>
<tr>
<td>SEOS-3 (55 °C)</td>
<td>0.218</td>
<td>0.036</td>
</tr>
</tbody>
</table>
value) was taken as the one that provided the best agreement between the NMR and SAXS data.

At first inspection, comparison of Tables 3 and 8 suggests that the best agreement between SAXS and $^1$H spin-diffusion NMR data points out definitely for a lamellar morphology for SEOS-3, hints toward a BCC one for SEOS-1, whereas for SEOS-2 essentially the same probability is found for a lamellar or a hexagonal spatial arrangement. This corresponds to an interdomain length of 26.7, between 21.9 and 25.6, and of 15.2 nm, for samples SEOS-1, -2, and -3, respectively.

The matrix volume fraction can be estimated from the calculated values for $d_i$ (Table 3, SAXS data) and $d_{mob}$ (Table 6, NMR data) and for volumetric consideration of the possible microdomain structures (lamellar, HCP, or BCC). The results obtained are shown in Table 9 and confirms, by comparison with Table 1, the proposed morphologies. The analysis above is prone to error propagation on the SAXS, NMR, and composition parameters. In particular, the error in the position of the first SAXS maximum appears to be of most impact. Interestingly, good agreement between SAXS and NMR data cannot be achieved if $q$ values differ by more than a few percent from the ones reported in Table 3.

Thus, the combined NMR and SAXS analysis confirms the expected morphologies for SEOS-1 and SEOS-3, but it cannot be conclusive on SEOS-2.

Further structural information can be obtained by detailed inspection of the NMR results. The $^1$H spin-diffusion decays plotted in Figure 8 present marked differences for the three copolymers, namely regarding the length of the linear decay region and the level of the equilibrium plateau attained for long mixing times. The later behavior depends on the relative PEO and PS concentrations, which determines the amount of signal transferable from the mobile to the rigid part after the dipolar filter. Considering the values for the weight % ratios in Table 1, and the number of $^1$H nuclei per repetitive unit in PEO and PS blocks, the plateau values for all samples are higher than they would be expected from the stoichiometry. This is an indication of the presence of segments with intermediate mobility, probably in the PS-PEO interface. Another interesting feature among the decays is the length of the initial delay before the beginning of the linear decay, $t_{LAG}$. Although this parameter has a difficult interpretation, a link can be drawn between its presence and the existence of a region in the copolymers where the spin diffusion behaves in an intermediate way between a rigid and mobile phase.

In fact, it is well established that block copolymers have a thin interphase between two blocks with different compatibility, defining a gradient of the mobilities between them. It is not an easy task to define the spin-diffusion coefficient of the interphases, $D_{INTER}$, but as a first approximation it can be assumed as the mean value of the mobile and less mobile phases spin diffusion coefficients. In this case, the width of the interphase region, $L_{INTER}$, can be linked to the time lag before the beginning of the linear decay of the spin diffusion curves as $^{12}$:

$$L_{INTER} = \sqrt{\frac{4 \cdot D_{INTER} \cdot t_{LAG}}{3}} \quad (11)$$

Table 10 summarizes the calculated diffusion coefficients and the sizes of the interfacial region for SEOS 1, 2, and 3.

However, the interpretation of $L_{INTER}$ values requires some care. In fact, while in the case of the SEOS-1 and SEOS-2 well-defined lags can be seen and expected on the basis of the clear role played by the abundant PS as a matrix, the situation for SEOS-3 is less well defined. In the first two cases, the interface width is found to increase in reducing the PS concentration, which can be justified as an overall softening of the matrix. In the latter case, PS and PEO are in comparable concentrations and the mobility difference between the two phases is also smaller. This low contrast situation may

**Table 7** Calculated $\sqrt{D_{mob}}$ Values

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sqrt{D_{mob}}$ (ms$^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEOS-1 (22 °C)</td>
<td>13.5</td>
</tr>
<tr>
<td>SEOS-2 (55 °C)</td>
<td>23.6</td>
</tr>
<tr>
<td>SEOS-3 (55 °C)</td>
<td>22.9</td>
</tr>
</tbody>
</table>

**Table 8** Domain Sizes, $d_{mob}$ (nm), and Interdomain Sizes, $d_i$ (nm), from NMR Spin-Diffusion Analysis for Different Hypothetical Morphologies

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d_{mob}$ (NMR)/nm</th>
<th>$d_i$ (NMR)/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>SEOS-1</td>
<td>4.7</td>
<td>9.4</td>
</tr>
<tr>
<td>SEOS-2</td>
<td>7.5</td>
<td>15.0</td>
</tr>
<tr>
<td>SEOS-3</td>
<td>7.0</td>
<td>13.9</td>
</tr>
</tbody>
</table>

* Best agreement with SAXS (Table 3) in bold italics.

**Table 9** Matrix Volume Fraction Calculated from SAXS ($d_i$) and NMR ($d_{mob}$) Data for Different Hypothetical Morphologies

<table>
<thead>
<tr>
<th>Sample</th>
<th>% Matrix</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEOS-1</td>
<td>0.78</td>
<td>0.87</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>SEOS-2</td>
<td>0.65</td>
<td>0.66</td>
<td>0.56</td>
<td></td>
</tr>
<tr>
<td>SEOS-3</td>
<td>0.53</td>
<td>0.42</td>
<td>0.99</td>
<td></td>
</tr>
</tbody>
</table>

**Table 10** Estimation of Interphase Size Characteristics for SEOS Samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>$D_{INTER}$ (nm$^2$/ms)</th>
<th>$\sqrt{t_{LAG}}$ (ms$^{1/2}$)</th>
<th>$L_{INTER}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEOS-1</td>
<td>0.147</td>
<td>0.81</td>
<td>0.38</td>
</tr>
<tr>
<td>SEOS-2</td>
<td>0.134</td>
<td>2.48</td>
<td>1.05</td>
</tr>
<tr>
<td>SEOS-3</td>
<td>0.127</td>
<td>1.12</td>
<td>0.46</td>
</tr>
</tbody>
</table>
bias the determination of the interface thickness from eq (11). The spin-diffusion decay curve [Fig. 8(c)] is also confirming this point by showing a rather smooth decay behavior. The reduced interphase region width calculated for the SEOS-3 case can be thus hypothetically described rather as a characteristic length of an almost continuous gradient of concentrations, more than as a discontinuity region.

Finally, from a comparison of the interphase thicknesses calculated from spin diffusion decays and SAXS data, we note a difference in the individual values, but similar trends. It may be interesting to mention that the negative deviation from the Porod law for large q-values of the background corrected intensity, is attributed to fluctuations in electron density in the interdomain region, and for this reason, the width of the diffuse boundary may correspond to the real interphase region.

CONCLUSION

The combination of temperature dependent SAXS experiments and solid-state NMR measurements has proved effective in characterizing the morphology of a series of four samples of PS-b-PEO-b-PS triblock copolymers with variable composition. For the as-cast samples, WAXS and DSC techniques revealed the effect of the relative block concentration on the degree of crystallization of PEO. Higher concentrations of PS hinder the crystallization of the PEO blocks. SAXS results showed microphase segregation in all cases, but failed to provide conclusive evidence in most cases on the sample morphology for the lack of high order correlation peaks. However, it was shown that a triblock copolymer with only 30% of PS volume fraction had a lamellar morphology due to the semi-crystalline characteristics of the PEO matrix.

An analysis of the samples above the melting temperature of the PEO block enabled a direct comparison between SAXS and spin-diffusion NMR results, which allowed an estimation of the sample spatial morphology, and concurrently of the size of the domains, of the interphase and of the interdomain distances. Furthermore, both techniques (SAXS and NMR) probed an increasing degree of microstructural disorder upon decreasing the PS content in the samples. This result seems to be correlated with a size of the interphase region inversely proportional to the PS block concentration.

The authors acknowledge the Region Provence Alpes Côte d’Azur (PACA) – France (post-doctoral scholarship), ARKEMA, ARCUS PACA-Brésil, and the FAPESP for financial support. WAXS/SAXS data were collected under the proposals D11A-SAXS1 5428 and 4816 of the Brazilian Synchrotron Light Laboratory (LNLS) and at the 711 beamline of the MAXLab synchrotron facility using beamtime granted to TSP.

REFERENCES AND NOTES