Immiscible Polydiene Blocks in Linear Copolymer and Terpolymer Sequences

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ABSTRACT: Synthesis, molecular, and morphological characterization of two linear diblock copolymers consisting of two polydienes with specific geometric isomerisms and two triblock terpolymers with a combination of the same polydienes with polystyrene are investigated for both lower and very high molecular weights. This work is inspired from a previous research study which demonstrated that linear ABC terpolymers consisting of polystyrene, poly(butadiene), and poly(isoprene), with specific geometric isomerisms for the polydienes, lead to 3-phase microphase separated systems. We report also the coexistence of the core-shell double gyroid and the 3-phase 4-layer alternating lamellae morphologies with the majority fraction being the lamellar structure.

KEYWORDS: anionic polymerization; diblock copolymers; differential scanning calorimetry (DSC); lamellar; SAXS; self-assembly; TEM

INTRODUCTION Block copolymers (BCPs) have the potential to generate a variety of well-defined and precisely controlled microdomain morphologies with very small dimensions since the molecular characteristics can be very well handled, especially through the use of anionic polymerization for the synthesis of the corresponding materials.1 The uniqueness of BCPs lies on their ability to self-assemble without the application of external fields, specific modification reactions and so forth compared to other materials. This property has contributed to the understanding of how a simple linear diBCP (A-b-B) microphase separates depending on the volume fraction of one segment (e.g., $\phi_A$) and the Flory-Huggins interaction parameter between the two chemically different chains ($\chi_{AB}$). Since increased values of $\chi_{AB}$ may lead to microphase separation of BCPs exhibiting low total molecular weight ($\chi_{AB}N$ is the value governing the self-assembly, $N$ is the total degree of polymerization for both chains), lower dimensions for the characteristic pattern involved in each case may be adopted. DiBCPs have been studied extensively and their behavior in bulk is rather well understood, with notable exception being the precise volume fraction limits upon which the transition from one phase to another occurs in different segment combinations and chain architectures. It should be noted that the phase behavior in such systems is a result of minimizing the free energy due to asymmetric chain stretching and packing frustration.3,4 BCPs have been applied in lithographic applications in which well-ordered and periodic microdomains can be transferred into suitable substrates.1,5,6

Periodic three-dimensional (3D) cubic network structures have only been identified for BCPs in rather narrow volume fraction regimes.7 The double gyroid (DG) structure with a glassy network phase in a rubbery matrix is mechanically much tougher than the classic glassy sphere/cylinder/lamellae morphologies requiring higher stresses for yield and exhibiting large elongation to break.8,9 The phase diagram $\chi_{AB}N$ versus $\phi_A$ is described by Bates and Fredrickson10 for the strong segregation regime for corresponding PS-b-PI diBCPs.

The addition of a third chemically different segment allows the existence of more complex microdomain geometries
which are difficult to predict. Microphase separation is more complicated for multiblock, multicomponent systems such as linear triblock terpolymers consisting of three chemically different segments. Depending on the type of segments used, the structures identified via morphological characterization are very different than simple diblocks since, if all blocks are immiscible, a three-phase system must occur. Two volume fractions are involved (e.g., $f_A, f_B$), three interaction parameters must be considered ($\chi_{AB}, \chi_{BC}, \chi_{AC}$), and in addition the block sequence (ABC vs. BAC or ACB) contributes significantly to the observed morphologies.\textsuperscript{11} In the case of asymmetric linear triblock terpolymers, various types of 3-phase morphologies have been observed.\textsuperscript{12} Theoretical predictions have provided substantial information for the morphologies adopted by ABC linear triblock systems leading to a phase diagram which is affected by variations in composition, molecular weight, and block sequence.\textsuperscript{13}

Ternary systems, such as core–shell structures have been demonstrated in binary blends of ABC and BC terpolymers leading to a phase diagram which is affected by variations in composition, molecular weight, and block sequence.\textsuperscript{13}

Linear terpolymers of PS-b-PI-b-P2VP\textsuperscript{14} and PS-b-PI-b-P2VP\textsuperscript{15} sequence, respectively [where P2VP is poly(2-vinylpyridine)] have been studied leading to the ordered tricontinuous double diamond which remained stable even after the block sequence alteration (from ISP to SIP). Furthermore, the alternation of PI with PB [poly(butadiene) with ~90% 1,2-microstructure] led to the existence of a new type of 3D structure for PS-b-PB-b-P2VP\textsuperscript{16} and PI-b-PS-b-PDMS\textsuperscript{6} systems [where PDMS is poly(dimethylsiloxane)], which was characterized as a core-shell gyroid where the minority component forms the core of the networks surrounded by the midblock while the remaining end block is the matrix.\textsuperscript{13}

In this study, we report the controlled synthesis, molecular, and morphological characterization of two $\text{PB}_{1,4}$-$\text{b}$-$\text{P}_{1,4}$ diBCPs and two PS-$\text{b}$-$\text{PB}_{1,4}$-$\text{b}$-$\text{PI}_{3,4}$ (SBI) linear terpolymers where the two polydienes exhibit chemically different microstructures corresponding to their geometric isomerism. The PB block in all samples exhibits the usual ~92% 1,4 geometric isomerism whereas the PI block contains 3,4-(~55%), ~15% 1,2, and ~30% 1,4. The results on the diene/diene diBCPs show well-ordered structures in exclusively polydiene samples for the first time. A previous study by our group involving nonlinear architectures of the specific polydienes demonstrated microphase separation.\textsuperscript{20} In order to obtain core-shell morphologies it is necessary to have: $\gamma_{AC} > \gamma_{AB} > \gamma_{BC}$, where A is PS, B is PB, and C is PI in our case.\textsuperscript{21,22} Successful synthesis is demonstrated through the results from size exclusion chromatography (SEC), proton nuclear magnetic resonance spectroscopy ($^1$H NMR), and membrane osmometry (MO). The morphological characterization is supported by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS) experiments. The long range order of the investigated films are evident in the increased number of peaks on the In $I(q)$ versus $q$ plots in the SAXS data for the triblock terpolymers only. Since the electron densities of the two polydiene chains are approximately equal, the SAXS patterns did not lead to significant scattering and, therefore, no SAXS results are given for the diBCPs. The coexistence of cubic and lamellar microphases has been reported previously for neat linear and non-linear (star) macromolecules but only for the case of two component systems.\textsuperscript{23–25}

### EXPERIMENTAL

#### Materials

The purification methods of all reagents involved as well as the detailed handling of the polymerization have been described elsewhere.\textsuperscript{26–28} The molecular characteristics for all samples are given in Table 1.

#### Characterization Instrumentation

The molecular characterization was carried out via SEC and MO. More details are given elsewhere.\textsuperscript{26} A size exclusion chromatograph, equipped with an isocratic pump (SpectraSystem P1000), column oven (LabAlliance) heated at 30 °C, three columns in series (PLgel 5 mm Mixed-C, 300 × 7.5 mm), refractive index (RI, Shodex RI-101) and two-angle laser light scattering detectors, and tetrahydrofuran (THF) as the eluent, was calibrated with eight PS standards ($M_\text{w}$: 4300–3,000,000 g/mol). The number-average molecular weights ($M_\text{n}$) (values higher than

### Table 1: Molecular Characteristics of the Precursors and the Final Samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\langle M_\text{n}\rangle_{\text{PS}}$ a (kg/mol)</th>
<th>$\langle M_\text{n}\rangle_{\text{PB}}$ a (kg/mol)</th>
<th>$\langle M_\text{n}\rangle_{\text{PI}}$ a (kg/mol)</th>
<th>$\langle M_\text{w}\rangle_{\text{tot}}$ b (kg/mol)</th>
<th>$\langle M_\text{w}\rangle_{\text{PS}}$ c (w/w)</th>
<th>$\langle M_\text{w}\rangle_{\text{PB}}$ d (w/w)</th>
<th>$\langle M_\text{w}\rangle_{\text{PI}}$ d (w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BI-1</td>
<td>–</td>
<td>32.5 a</td>
<td>33.0 b</td>
<td>66.0 b</td>
<td>1.06</td>
<td>70.0 d</td>
<td>0.26</td>
</tr>
<tr>
<td>BI-2</td>
<td>–</td>
<td>590.0 a</td>
<td>420.0 d</td>
<td>1,010.0 d</td>
<td>1.10</td>
<td>1,111.1 d</td>
<td>0.58</td>
</tr>
<tr>
<td>SBI-1</td>
<td>27.3</td>
<td>15.7 b</td>
<td>50.0 e</td>
<td>103.0 e</td>
<td>1.03</td>
<td>106.1 f</td>
<td>0.26</td>
</tr>
<tr>
<td>SBI-2</td>
<td>28.5</td>
<td>17.9 b</td>
<td>33.8 f</td>
<td>80.0 f</td>
<td>1.05</td>
<td>84.0 g</td>
<td>0.35</td>
</tr>
</tbody>
</table>

a MO in toluene at 35 °C.  
b SEC in THF at 30 °C.  
c From combination of SEC and MO measurements.  
d From $^1$H NMR in CDCl$_3$ at 25 °C.  

SCHEME 1 Synthesis reactions for the preparation of the linear triblock terpolymer of the required PS-b-PB₁,₄-b-PI₃,₄ sequence.

15,000 g/mol were measured with a Gonotec membrane osmometer Osmomat 090 at 35 °C. Toluene, dried with CaH₂, was used as the solvent for the measurements.

¹H NMR determination of the composition and the geometric isomerism or microstructure of the materials were carried out in CDCl₃ at 25 °C using a Bruker AVANCE II spectrometer (resonance frequency of ¹H 250 MHz). Data were processed using UXNMR (Bruker) software.

For the poly(butadiene) block, the typical microstructure observed was characteristic of anionic polymerization of butadiene in benzene (92 wt % 1,4 and 8 wt % 1,2). The small quantity of polar solvent (THF, < 1 mL) leads to a microstructure of PI of approximately 55 wt % 3,4, 15 wt % 1,2, and 30 wt % 1,4.

Differential scanning calorimetry (DSC) measurements were accomplished with a Q20 TA instrument. The heating ramp was 5 °C/min and the temperature ranged from −120 to 150 °C. Two heating and one cooling cycles were performed and the results of the second heating were reported and analyzed using Advantage v5.4.0 (TA instruments) software.

TEM and SAXS were employed for the morphological characterization of the final copolymers and terpolymers. More details are given elsewhere.²⁰,²⁹,³⁰ Approximately 1.0 mm thick films of the material were cast from a dilute solution (~4–5 wt %) in toluene and chloroform over a period of 7 days at ambient conditions. The selectivity of the solvent can be estimated by using the solubility parameters, δ. The literature values³⁰ of δ for polystyrene and 1,4-polybutadiene (92% 1–4 content) are 9.1 and 8.4 (cal/cm³)¹/², respectively, and those of toluene and chloroform are 8.9 (cal/cm³)¹/² and 9.2 (cal/cm³)¹/², respectively. The high 3,4-microstructure of PI suggests a solubility parameter larger than that for cis-1,4-PI (90 wt %) [δ = 8.2 (cal/cm³)¹/²]. From the values of solubility parameters, the two polydiene are slightly less soluble in both chosen solvents when compared to the PS segments.

In order to obtain near-equilibrium microstructures after casting, the films were annealed for 7 days at 130 °C and 5 days at 150 °C under vacuum. For TEM investigation, 50–70 nm thick sections were cryo-micromotomed at −100 °C (below the lowest Tg) and the sections were picked up on 600-mesh copper grids. The grids were then placed in the vapors of a 4% OsO₄—water solution for selective staining of the two polydiene domains for 30–45 min, depending on the quality of the stainer solution and in order to avoid overstaining.

The SAXS diffraction patterns were obtained at room temperature on the Time-Resolved Diffraction Facility (station X12B) at the National Synchrotron Light Source at Brookhaven National Laboratory using a custom-built two-dimensional detector (10 × 10 cm, 512 × 512 pixels) interfaced to a real-time histogramming memory system.

FIGURE 1 SEC chromatograms for the precursors and the final products for samples BI-1 and SBI-2.
(~0.5 g) were taken after the formation of the first block for SEC, MO and \(^1\)H NMR studies.

**Synthesis of PS-b-PB\(_{1,4}\)-b-PI\(_{3,4}\)**

The synthesis of the SBI type linear triblock terpolymers was accomplished as well by sequential anionic polymerization of styrene (4 g, 38.46 mmol), butadiene (1.95 g, 36.10 mmol), and isoprene (4.6 g, 67.65 mmol) in benzene, using sec-BuLi as initiator (0.147 mmol). After the polymerization of styrene in benzene (300 mL) at room temperature conditions, appropriate amount of butadiene is distilled in the apparatus in order to successfully prepare the necessary
Results and discussion

In Figure 1 SEC chromatographs for BI-1 and SBI-2 samples are given. It should be mentioned that in the SEC chromatographs for both samples the initial precursor (PB and PS for the diblock and the triblock sample, respectively), intermediate product (PS-b-PB for the triblock sample) and final sample results are exhibited. The good agreement between the molecular characteristics (Table 1) from different characterization methods (SEC, MO, and 1H NMR) confirms the high degree of homogeneity in molecular weight and composition for the final samples. The absence of termination reactions, verifies the correct practice of all the procedures involved (e.g., purification of the reagents and thorough cleaning of the polymerization reactor from any impurities). Through the 1HN MR spectra (Fig. 2) we calculated not only the weight fractions per segment but also the characteristic ratios of the stereochemical microstructures involved for both polydienes. The results for the different microstructures are exhibited in Table 2 together with the corresponding volume fractions.

Among all the possible combinations of microstructures for polydiene blocks experimentally synthesized [PB: 1,4-, and 1,2-, PI: 1,4- (cis & trans), 3,4- and 1,2-], there is only one combination reported in the literature which exclusively leads to microphase separation, either for the two polydienes,20,31–34 or through their combination with a third microstructure involved for both polydienes. The correct practice of all the procedures involved (e.g., purification of the reagents and thorough cleaning of the polymerization reactor from any impurities). Through the 1HN MR spectra (Fig. 2) we calculated not only the weight fractions per segment but also the characteristic ratios of the stereochemical microstructures involved for both polydienes. The results for the different microstructures are exhibited in Table 2 together with the corresponding volume fractions.

Structural Characterization

The two dibCPs of the PB1,4-b-PI3,4 sequence vary in molecular weight. This is evident from the TEM images shown in Figure 3.

The TEM results suggest that both samples exhibit alternating lamellar morphology as expected from the almost identical volume fraction between the two blocks. The darker domains correspond to the heavily stained with vapors of OsO4 PB1,4 chains while the lighter domains correspond to slightly stained PI3,4 segments as explained thoroughly already in the literature.24 Since the electron densities of the two polydiene chains are approximately equal no SAXS results are given for the dibCPs. The d10 spacing of the alternating lamellae in both samples can be calculated approximately by the TEM images and is equal to 28 and 130 nm for the lower and the higher molecular weight diblock samples, respectively. Therefore, it is evident from the TEM images of the dibCPs that the sequence of the polydiene blocks with the specific microstructures leads to well-defined microdomain structures almost identical to those reported for PS/PI dibCPs in the literature.10

DSC measurements clearly indicate 2 and 3 distinct TgS, respectively, for the dibCPs and the triblock terpolymers, suggesting 2-phase and 3-phase microdomain structures, respectively. All Tg values correspond quite well to those expected for the corresponding homopolymers even for the polydienes with the different stereochemical microstructures (Supporting Information Figs. S1 and S2). Selected bright field TEM micrographs of both terpolymer samples (SBI-1 and SBI-2, respectively) exhibit grains with alternating 3-phase 4-layer lamellar and ordered patterns typical of core-shell gyroid can be seen in Figure 4.

From the TEM results it is clear that staining with OsO4 allows the observation of a 3-phase system, where the lightest areas correspond to the PS blocks, gray to the PI and black to the PB domains, respectively. Furthermore, it is evident from the TEM images that there is coexistence between core-shell gyroid and alternating lamellae domains, an observation which could be due to either that the specific sample is right on the boundary between the two morphologies, thus indicating that longer annealing and/or differentiation of the annealing temperature may transform the system to one of the two different structures, or that the two morphologies coexist due to thermodynamic factors in order for the system to reach equilibrium.

Similar results were observed when the samples were cast from chloroform (Supporting Information Fig. S3) and even when the annealing temperature increased to 150 °C for 5 days (Supporting Information Fig. S4). Furthermore, it should be taken into account that the two triblock
terpolymers vary in total molecular weight and block volume fraction sequence since for both samples (SBI-1 and SBI-2) the ratio between the three blocks is approximately 2/1/4 and 2/1/2, respectively, but the observed morphology is identical, leading to the conclusion that this coexistence may be attributed to the specific chemical structure of the polydienes and the block sequence in the final terpolymers. Therefore, the observed morphology is likely not a metastable structure.

Taking into consideration theoretical approaches concerning such systems it is reasonable to expect a core-shell morphology with PB segments exhibiting an intermediate layer between the inner PS core and outer PI matrix since such a topology allows the PB/PI interface to be significantly smaller compared to the corresponding PS/PI interface. However, the aforementioned statement can be verified since the PI segments are not the usual linear ones used for all theoretical studies but they exhibit only a maximum of ~30% 1,4-microstructure, therefore, they are behaving mostly as grafted chains with small ligands (double bonds) per monomeric unit.

The SAXS plots of log \( I(q) \) versus \( q \) on the films used to obtain the microtomed sections of the triblock terpolymers for the TEM studies are shown in Figure 5.

It is clearly evident that only the 3-phase 4-layer alternating lamellar structure can be seen in both samples, since no other reflections are observed from the SAXS plot corresponding directly to the DG structure. Additionally, it should be pointed out that the observation of five peaks in the specific plots leads to the fact that the terpolymers are rather well ordered in bulk.

Through TEM analytical observation, the lamellae phase is most prominent as verified by the SAXS pattern. The first reflection from the SAXS plots leads to a \( d \)-spacing value \( (d_{01}) \) equal to 45 nm (sample SBI-1) and 38 nm (sample SBI-2) which is in good agreement with the values calculated from the TEM images (~43 nm and 37 nm, respectively).

This morphology (core-shell DG) was reported for the first time more than a decade ago by the Bates group in a PI-b-PS-b-PDMS (ISD) linear triblock terpolymer with ratios in volume fractions approximately equal to 2/2/1. These ratios are completely different when compared to our terpolymers ratios.

In the former sample (ISD) the unit cell comprises of two D cores forming the two lattices of three fold connectors in a gyroid network, where each of the D domains is covered with an S shell and the matrix is formed by the I blocks, resulting in five independent, three-dimensionally continuous domains. This triply periodic cubic structure is also called the pentacontinuous core-shell gyroid phase. In the present system, the sequence of interaction parameters is: \( \chi_{SD} >> \chi_{ID} > \chi_{IS} \) and the structure formed is such that the D domain is the core and the S domain completely separates I and D blocks.

In our case, PS which is the intermediate block in molecular weight and volume fraction but still an end block (as D in the ISD sequence reported in the literature) forms the core of the two networks and the middle block (PB in our case and PS in the ISD sequence) forms the periphery of the networks. Furthermore, the matrix consists by the remaining

**FIGURE 3** Bright-field TEM images for: (a) low molecular weight diBCP (BI-1) and (b) high molecular weight diBCP (BI-2). Special notation should be given to the scale bars of the TEM images which despite being almost identical in length they correspond to 100 nm and 500 nm for sample BI-1 and BI-2, respectively, indicating the difference in molecular weight for the two samples.
end block which is the largest in terms of volume fraction and molecular weight, being the PI.

It should be noted that in our case we have two differences compared to the ISD sample. The first one involves the fact that the interaction parameter between PS and PI in our system is based on the values for the usual PI segments which are more than 90% with 1,4-microstructure and the second depends on the Flory-Huggins interaction parameters inequalities, therefore, we can only assume that our \( \chi \) values are somewhat different from those reported for the ISD system by the Bates group.\(^4\)

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**FIGURE 4** Bright-field TEM images exhibiting grains with coexistence of a two fold projection for a core-shell DG with three-phase 4-layer lamellae domains where PS is the core, PB is surrounding the core of the networks and PI is the matrix. (a) TEM images for sample SBI-1 and (b) TEM images for sample SBI-2. A blow-up in a distinct area of both morphologies is shown where each block is assigned directly to the TEM image color differences (white, gray, black). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
The inner S-B interface has a significantly higher interfacial curvature, while the outer B-I interface is probably less curved. Increasing gradually the inner component compatibility, \( v_{SB} \) against that of the outer, \( v_{BI} \), creates a tendency of enlarging the overall interfacial curvature. These materials will be of great interest for nanopatterning applications since it has been already reported\(^3\)\(^5\)\(^6\)\(^7\)\(^8\)\(^9\)\(^10\) that polydienes and especially PI can be easily removed with various methods (ozonolysis and reactive-ion etching) leading to nanoporous or nanorelief materials.

**CONCLUSIONS**

The successful synthesis of linear diBCPs of the PB\(_{1,4}\)-b-PI\(_{3,4}\) type and triblock terpolymers consisting of PS and the two polydienes (PB and PI) with relatively different microstructures is reported. The molecular characterization results led to well-defined final materials. DSC studies showed immiscibility between the two different polydienes with specific percentages of geometric isomerisms or microstructures as well as for the three chemically different segments in the terpolymers since 2 and 3 \( T_g \) values were observed, respectively. Furthermore, the TEM images indicate microphase separation as well as the coexistence of 3-phase systems corresponding to alternating lamellae and a cubic structure identified as the core-shell DG regardless the solvent used for the casting and the annealing temperature and duration. SAXS experiments for the triblock terpolymers verified the lamellar phase probably due to the higher percentage that it holds throughout the microtomed sections on the TEM grid compared with the core-shell cubic morphology.

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**REFERENCES AND NOTES**


