# Utility of Interaction Chromatography for Probing Structural Purity of Model Branched Copolymers: 4-Miktoarm Star Copolymer

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ABSTRACT: A miktoarm star-shaped copolymer, with one polystyrene arm ($M_w$ = 198 kg/mol) and three polyisoprene arms ($M_w$ = 51 kg/mol) ($PSPI_3$), was rigorously characterized by temperature gradient interaction chromatography (TGIC). The polymer was prepared by linking active chain ends of precursor polymers to tetrachlorosilane as the linking agent, and the precursor polymers were prepared by anionic polymerization. The crude product was purified by fractional precipitation to remove the byproducts and the excess reagents. Size exclusion chromatography (SEC) analysis shows a narrow single elution peak whose molecular weight and composition are in good agreement with the predicted values in experimental precision. Therefore, it appears on the basis of conventional characterization using SEC, light scattering, and NMR that the fractionated mother represents a high-purity $PSPI_3$ miktoarm star copolymer. However, TGIC analysis reveals the presence of significant amount of byproducts, most significantly $PSPI_2$, which amounts to about 20% of the fractionated sample. This result clearly indicates that the analysis results utilizing conventional polymer characterization tools such as SEC, light scattering, osmometry, and viscometry are insufficient to establish the purity of polymers with complex architecture. It seems preferable to carry out a more detailed analysis such as that described in this work, in particular for polymers with complex architectures, if rigorous proof of structural purity is required.

## Introduction

Star-shaped polymers prepared by linking one end of linear chains to a multifunctional linking agent are interesting as the simplest and most well-defined model system for branched polymers. Such star polymers have been synthesized mainly by linking active anionic chains with multifunctional chlorosilanes.[1−5] Recently, the synthesis of stars with chemically different arms, miktoarm stars, has been achieved.[6−11] Miktoarm stars are block copolymers with branched structures, and they have been studied extensively, in particular in terms of their self-assembled morphologies.[12−18]

The conventional characterization of the purity of star-shaped polymers has been based on size exclusion chromatography (SEC) analysis. Although SEC coupled with various detection methods still constitutes a powerful tool for such analyses, SEC results alone are usually not sufficient to verify structural purity. SEC separates polymer molecules according to their hydrodynamic volume, which changes little with the number of arms in star-shaped polymers. Therefore, often SEC cannot resolve byproducts that do not differ much in hydrodynamic volume from the major products. Other characterization methods determining the average molecular weight such as membrane osmometry or light scattering also cannot verify structural purity due to errors associated with these measurements and since average molecular weights may not greatly affected by the presence of certain impurities.

An alternative characterization method employs interaction chromatography (IC). IC separation is driven by enthalpic interactions of the solute molecules with the stationary phase, and these interactions are, to a first approximation, proportional to the molecular weight. As already demonstrated with linear homopolymers,[19−22] branched homopolymers,[23−25] and diblock copolymers,[26] the resolution power of IC is far superior to that of SEC. Even with use of the anionic polymerization method, it is often difficult to synthesize branched polymers with a uniform chain structure, and usually byproducts are formed. The product mixture is commonly purified by fractional precipitation, and the structural uniformity of the isolated products is examined by conventional characterization methods including SEC, membrane osmometry, and NMR. Although conventional characterization results may suggest a high degree of structural homogeneity, IC analysis usually reveals the significant presence of differently branched byproducts, mainly of lower branching number.[23−25]

In this study, we extend the characterization by temperature gradient interaction chromatography (TGIC),[19,27] a form of interaction chromatography, to the case of a complex miktoarm star copolymer with one polystyrene (PS) arm and three polyisoprene (PI) arms, $PSPI_3$. Such star polymers are more difficult to characterize than branched homopolymers since the byprod-

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ucts, typically polymers with missing arm(s) or coupled products, have not only different molecular weight but also different compositions. Unlike star-shaped homopolymers, both the composition and the molecular weight of each copolymer species must be determined to identify the molecular species in each elution peak.

## Experimental Section

**Synthesis.** High-vacuum line techniques and all glass reactors with break-seals were used in conducting the anionic polymerization. The reaction scheme used for the synthesis of the 4-miktoarm star copolymer is as follows:

$$\text{styrene} + \textit{sec}\text{-BuLi} \rightarrow \text{PSLi} \quad \text{(PS arm)}$$

$$\text{isoprene} + \textit{sec}\text{-BuLi} \rightarrow \text{PILi} \quad \text{(PI arm)}$$

$$\text{PSLi} + \text{(excess) } SiCl_4 \rightarrow PSSiCl_3 + \text{LiCl} + \text{excess } SiCl_4\uparrow$$

$$PSSiCl_3 + \text{(excess) PILi} \rightarrow PSPI_3Si + 3\text{LiCl} + \text{PILi}\downarrow \quad \text{(fractionation)}$$

The initial step of the synthesis involved the reaction of a solution (∼5% w/v) of PSLi in benzene with a 100-fold excess of $SiCl_4$ for preferential formation of $PSSiCl_3$. Excess $SiCl_4$ was removed by repeated sequential out-distillation of volatile contents and in-distillation of fresh dry benzene; after three out-distillations, the stripped polymer was pumped on the vacuum line for 1 week at 50 °C. Subsequently, benzene was distilled into the reactor to make a ∼5% w/v solution of $PSSiCl_3$, and then a ∼5% w/v solution of PILi (20% excess) in benzene was added. After 1 week, a small amount of THF was added (∼0.5% v/v) to expedite the final linking reactions. The progress of linking was monitored by removing samples from the reactor and analyzing them with SEC.

The final product of $PSPI_3$ was purified by using fractional precipitation. The crude polymer product was dissolved in toluene to make a ∼1% w/v solution: Methanol was added slowly until a cloud point was obtained, and slightly more methanol was added to cause partial precipitation. Warming was carried out to homogenize the solution, followed by gradual cooling overnight. This resulted in a separation of the complex mixture into two distinct phases: a lower high-molecular-weight enriched syrup and an upper high-molecular-weight depleted dilute solution. Through iterative fractionation, the higher MW star products were thus isolated.

**SEC Analysis.** For the SEC analysis, two mixed bed columns (Polymer Lab. Mixed C, 300 × 8.0 mm i.d.) were used. SEC chromatograms were recorded with a multiangle laser light scattering (MALLS, Wyatt, mini-DAWN) and a refractive index detector (Wyatt, Optilab DSP) using tetrahydrofuran (THF, Duksan, HPLC grade) as the mobile phase. Polymer samples for the SEC analysis were dissolved in THF at an appropriate concentration (∼1.0 mg/mL), and the injection volume was 100 μL. The flow rate of the mobile phase was 0.8 mL/min. The column temperature was kept at 40 °C using a column oven (Eppendorf, TC-50). Chromatograms were recorded and processed by Astra software. To obtain the absolute molecular weight by light scattering detection, the refractive index increment, d*n*/d*c*, was determined separately with an interferometric refractometer (Wyatt, Optilab DSP) at 690 nm.

**TGIC Analysis and Fractionation.** TGIC experiments were carried out with a C18 bonded silica column (Zorbax, 100 Å pore, 250 × 9.4 mm i.d., 5 μm particle size). The mobile phase was a $CH_2Cl_2/CH_3CN$ mixture (75/25, v/v, Duksan, HPLC grade) at a flow rate of 0.9 mL/min. The polymer sample was dissolved in a portion of the elution solvent at a concentration of 30 mg/mL, and the injection volume was 100 μL. The column temperature was controlled in a preprogrammed manner by circulating water from a bath/circulator (Neslab, RTE-111) through a homemade column jacket. To obtain chemical composition for the sample corresponding to each TGIC elution peak, the chromatogram was recorded with a UV absorption detector (TSP, UV 100) operating at a wavelength of 260 and 235 nm. At 260 nm wavelength only PS absorbs the light while both PS and PI show absorptions at 235 nm. From the relative signal intensities, one can estimate the PI content in the elution peak. Unfractionated miktoarm star polymers were separated using TGIC, and the fractionated polymer species in each elution peak were analyzed in detail to determine molecular weight, composition, and morphology.

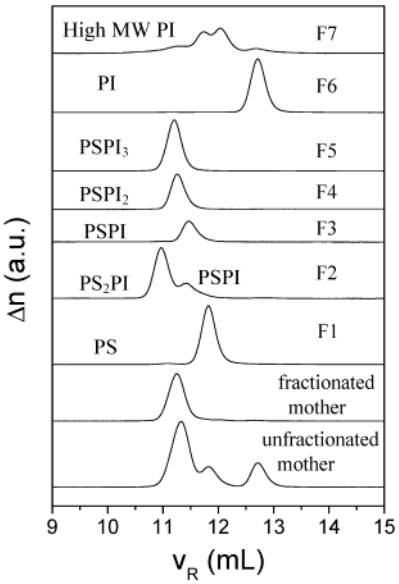


**Figure 1.** SEC chromatograms of the unfractionated mother, fractionated mother (via solvent/nonsolvent fractionation), and seven TGIC fractions (F1−F7) recorded by an RI detector. Column: two mixed bed columns (Polymer Lab, PL-mixed C, 300 × 8 mm i.d.); eluent: THF; temperature: 40 °C.

**Small-Angle X-ray Scattering (SAXS).** SAXS measurements were carried out at the synchrotron SAXS facility in the Pohang Light Source, Korea.[28] The wavelength ($\lambda$) of the X-ray beam was 1.608 Å, and the energy resolution ($\Delta\lambda/\lambda$) was $1.5 \times 10^{-2}$. All specimens contain 0.3 wt % 2,6-di-*tert*-butyl-4-methylphenol. This antioxidant was added to the toluene solution of the polymers, and the solvent was slowly evaporated for 1 day at room temperature and further evaporated under vacuum at 50 °C for 1 day. Then the polymer samples were annealed in the 1 mm thick spacer at 140 °C for 1 month under vacuum and cooled to room temperature. SAXS profiles were obtained at room temperature. The obtained SAXS intensities were corrected for absorption and air scattering.

**Transmission Electron Microscopy (TEM).** Transmission electron micrographs were obtained to identify the morphology of the samples annealed at 140 °C for 1 month. Electron transparent films of the mother and the fractionated copolymers were cryo-microtomed (RMC Ultracut) to a nominal thickness of 50−80 nm at −120 °C and transferred to Cu grids. The specimens were stained by exposure for 1 h to $OsO_4$ (Polysciences, 0.4% in water) vapor before taking bright-field TEM (Hitachi-7600) micrographs.

## Results and Discussion

**Chromatographic Characterization.** In Figure 1, SEC chromatograms of the mother polymers before and after fractionation are displayed at the bottom, together with those of TGIC fractions (F1−F7), which will be discussed later. The unfractionated "mother polymer" shows multiple elution peaks indicating the presence of significant amount of byproducts and the excess PI arm precursors. After the fractionation, however, the SEC chromatogram shows a single elution peak of $M_w/M_n = 1.04$.

The $M_w$ of the elution peak was measured as 332 kg/mol and the PS content was 44.8 wt %, which favorably

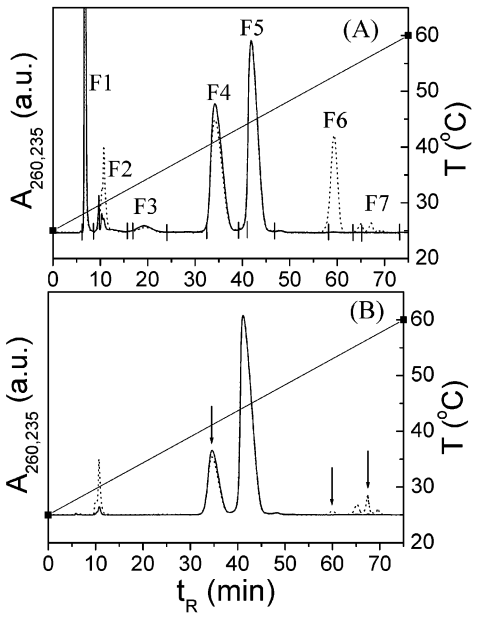


**Figure 2.** TGIC chromatograms of the unfractionated (A) and fractionated (B) mother miktoarm copolymer by miktoarm copolymer by a UV absorption detector operated at 260 nm (solid line) and 235 nm (dotted line). Unfractionated mother (A) shows a number of peaks indicating the presence of various byproducts and even the fractionated mother (B) still contains significant amounts of a few byproducts indicated by arrows. Small vertical bars at the baseline of the chromatogram (A) indicate the regions where these fractions were collected. Column: Zorbax C18, 100 Å, 250 × 9.4 mm i.d., eluent: $CH_2Cl_2/CH_3CN$ = 75/ 25 (v/v). The temperature program is shown in the plot.

compare with the predicted values, $M_w$ of 350 kg/mol and PS content of 42.9%, taking into account experimental errors. Therefore, it appears on the basis of conventional characterization using SEC, light scattering, and NMR that the fractionated mother represents a high-purity $PSPI_3$ miktoarm star copolymer. Until now, this strategy epitomizes the characterization of such complex nonlinear block copolymers.

The mother polymer was analyzed by TGIC, and Figure 2 displays the chromatograms of the unfractionated (A) and the fractionated mother polymer (B). Figure 2A shows that there exist a number of peaks, indicating the presence of various byproducts and excess PI arm. The number of peaks observed in TGIC is much greater than that observed in the SEC analysis, demonstrating the high resolution of TGIC. The solid trace is the chromatogram reflecting the absorbance at 260 nm; the dotted trace reflects the absorbance at 235 nm. The chromatograms recorded at these two wavelengths were superimposed and normalized with respect to intensity of the most abundant peak (F5). Therefore, the peaks other than F5 showing a higher intensity in the solid trace (260 nm) than the dotted trace (235 nm) contain less PI than the major peak, since PI does not absorb at 260 nm. It is thus clear that all the peaks eluting before the major peak have higher PS content while the peaks eluting after the major peak have less PS content than the major peak. This finding is expected from the TGIC separation conditions used, under which the interaction strength of PI with the reversed phase stationary phase is stronger than the interaction strength of PS.[21] An exception is the peak appearing at $t_R \approx 11$ min, which is the injection solvent peak; the relative intensity of this peak has no relationship with the polymer composition.

The mother polymer was fractionated into seven fractions (F1−F7), as shown in Figure 2A for a more detailed analysis. Small vertical bars at the baseline of the chromatogram indicate the regions where these fractions were collected. Among the fractions, F6 and F7 were not detected at 260 nm, which indicates that they do not contain PS. Many of the byproducts detected in the unfractionated mother polymer were absent in the fractionated mother polymer, as shown in Figure 2B. However, a significant amount of F4 and detectable amounts of F6 and F7 were still present in the fractionated mother polymer. This is discussed later in more detail. The fractions collected from the mother polymer were characterized by $^1$H NMR for composition and by SEC-MALLS for $M_w$ and $M_w/M_n$. Although the molecular weight determination can be accomplished by combining TGIC and MALLS, SEC-MALLS analysis was used to avoid the complication from preferential sorption due to the use of a mixed solvent in TGIC analysis.[23] The top seven chromatograms in Figure 1 display the SEC analysis results of the seven fractions. The characterization results are summarized in Table 1. The molecular weights were determined using d$n$/d$c$ values calculated by the following formula:

$$\mathrm{d}n/\mathrm{d}c = (\mathrm{d}n/\mathrm{d}c)_{PS} w_{PS} + (\mathrm{d}n/\mathrm{d}c)_{PI} w_{PI}$$

The composition, $w_{PS}$ and $w_{PI}$, in each fraction of the polymer species was determined by NMR for F1, F4, F5, and F6. For F2 and F3, NMR analysis was not done due to the limited amount of the TGIC fractions. For these samples, a reasonable estimate of the structure was made, and the self-consistency of the calculated molecular weight to the estimated structure was used as the criterion for the validity of the analysis. As can be seen in Table 1, the measured and predicted molecular weights are in excellent agreement with each other.

Fraction F1 contains homo-PS that contributes to the SEC chromatogram of the unfractionated mother as the middle elution peak among the conspicuous three resolved peaks. It also shows a trace amount of higher molecular weight species, the retention time of which corresponds to $PS_2$. Among the various possibilities, impurities in $SiCl_4$ or incomplete linking could be responsible for the $PS_2$ homopolymer. The presence of substantial amounts of impurities in the chlorosilane is highly unlikely, however, as the purity of the material used was 99.9%. Thus, steric hindrance to linking is the most likely cause of this byproduct. The F2 fraction contains $PS_2PI$ and PSPI. The PSPI seems to be a contaminant from F3 in the TGIC fractionation process as expected from the wide fractionation range of F2 shown in Figure 2A. Again, the incomplete chain structure is most likely due to incomplete linking. There are strong steric effects present which hinder complete linking when $SiCl_4$ is used as a linking agent. The use of butadiene end-capping of the PI chains could partially overcome this effect, but end-capping was not pursued in this work. The fractions F4 and F5 are $PSPI_2$ and $PSPI_3$, respectively. $PSPI_3$ (F5) and $PSPI_2$ (F4) elute practically at the same SEC retention volume, and they elute together as the most intense peak in the SEC chromatogram of the unfractionated mother polymer. The formation of a significant amount of $PSPI_2$ could best be attributed to steric hindrance and/or insufficient linking reaction time. It was previously reported that

**Table 1. Characterization of Miktoarm Star Copolymer by SEC-MALLS and $^1$H NMR**

| fraction | $w_{PI}$ | $M_w$ (kg/mol) measured[b] | $M_w$ (kg/mol) calculated[d] | relative abundance[h] (unfractionated mother) | relative abundance[h] (fractionated mother) |
|---|---|---|---|---|---|
| F1 (PS) | 0[a] | 198 | | 38.9 | 0.1 |
| F2 ($PS_2PI$) | 0.115[e] | 443[c] | 447 | 1.4 | |
| F3 (PSPI) | 0.206[e] | 255 | 249 | 3.6 | |
| F4 ($PSPI_2$) | 0.347[a] | 303 | 300 | 60.4 | 23.2 |
| F5 ($PSPI_3$) | 0.439[a] | 347 | 351 | 100 | 100 |
| F6 (PI) | 1[a] | 51 | | 55.6 | 0.8 |
| F7 (PI)[f] | 1[a] | | | 6.7 | 6.9 |
| mother[g] | 0.448[a] | 332 | | | |

[a] Determined by $^1$H NMR. [b] Determined by SEC-MALLS. [c] Peak MW determined by SEC-MALLS. [d] Calculated from MW of PS (F1) and PI (F6) determined by SEC-MALLS. [e] Calculated from the structure and the MW of PS (F1) and PI (F6) determined by SEC-MALLS. [f] High MW PI. [g] Fractionated mother. [h] Relative abundance in weight.

it takes many weeks to complete similar linking reactions.[24] Fraction F6 contains homo-PI that corresponds to the last elution peak in the SEC chromatogram of the unfractionated mother. The homo-PI must be mainly from the excess PI arms that were not removed by conventional fractionation. Finally, fraction F7 consists of homo-PI having higher molecular weights. The high-molecular-weight homo-PI could have been formed from the reaction of PILi with residual $SiCl_4$, i.e., incompletely removed excess chlorosilane left over from the end-capping of PS anions.

After identifying all the byproducts, we can examine the fractionated mother polymer in more detail. Figure 2B shows six identifiable peaks of F1, F2, F4, F5, F6, and F7. F5 is the desired product ($PSPI_3$), the relative amount of which increases greatly during the fractionation process. F1 and F6 were removed well, and only a trace amount of each species is left. The large peak in the F2 fraction region is the injection solvent peak. On the other hand, there still remains a significant amount of F4 and F7. F4 elutes together with F5 as a single SEC peak, and it is impossible to detect the presence of a significant amount of $PSPI_2$ in the fractionated mother by SEC. In Table 1 the amounts of the polymer species relative to the target polymer ($PSPI_3$) are summarized. The relative abundance was calculated by determining the concentration of PS and PI in each elution peak from the absorbance at 260 and 235 nm. Most of the byproducts were removed by the fractionation process; however, the removal of F4 was not very well accomplished, and the relative amount of F7 even increased. In general, the polymers having relatively high PI molecular weight survived the fractionation process, which is understandable from the fractionation scheme.

Summarizing the characterization results, analysis results utilizing conventional polymer characterization tools such as SEC, light scattering, osmometry, and viscometry are insufficient to establish the purity of polymers with complex architecture. It seems preferable to carry out a more detailed analysis such as the one described in this study.

**Morphology of Fractionated Mother, $PSPI_2$, and $PSPI_3$.** We investigated the morphology of the fractionated mother polymer, $PSPI_2$, and $PSPI_3$ to find out how the imperfect structural intactness of the miktoarm star polymers could influence morphology. Figure 3 displays the SAXS profiles of pure $PSPI_2$, pure $PSPI_3$, and the fractionated mother polymer.

The fractionated mother polymer and $PSPI_3$ show similar SAXS patterns, resembling a bicontinuous cubic morphology; alternatively, $PSPI_2$ clearly shows a SAXS pattern corresponding to a lamellar morphology.

The lamellar phase of $PSPI_2$ was characterized by the series of the scattering peaks appearing at the integer

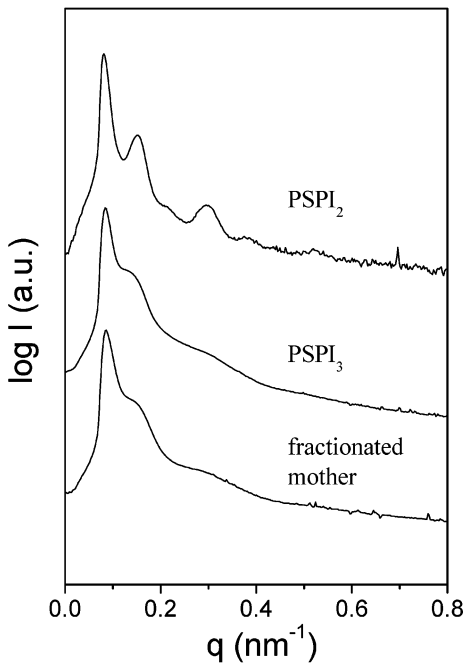


**Figure 3.** SAXS profiles of the $PSPI_2$, $PSPI_3$, and fractionated $PSPI_3$ mother from the top. The $PSPI_2$ sample exhibits LAM morphology as judged from the integer multiple peaks relative to the first-order scattering maximum peak. SAXS profiles of $PSPI_3$ and fractionated $PSPI_3$ mother are too obscure to assign the microdomain structures.

multiple $q$ position relative to the first-order scattering maximum. The first maximum peaks are partially blocked by the beam stopper since they are located in low $q$ due to the high molecular weight of the sample.

It is difficult to assign the morphology with SAXS profiles only due to the broad higher order scattering peaks. Therefore, the morphology of the polymer samples was examined by TEM, as displayed in Figure 4. In the TEM micrographs, PI domains appear dark since $OsO_4$ preferentially stains the double bond of PI. In Figure 4A, $PSPI_2$ shows a reasonably well-developed lamellar morphology. The lamellae are not extended and curved significantly, which is often observed in miktoarm star copolymers with an asymmetric branch point of different arms. On the other hand, $PSPI_3$ and the fractionated mother samples show network structures with very similar appearance as displayed in parts B and C of Figure 3, respectively. They do not show high symmetry to be categorized into any symmetry groups such as gyroid or double diamond structure. This may be due to insufficient annealing time for such high-molecular-weight samples, although the samples were annealed for 1 month at 140 °C. If we consider this morphology

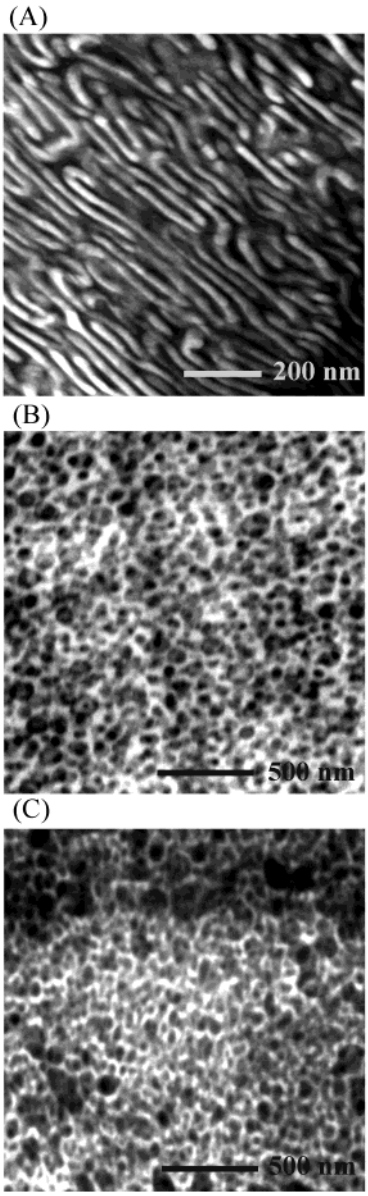


**Figure 4.** TEM micrographs of the $PSPI_2$ (A), $PSPI_3$ (B), and fractionated $PSPI_3$ mother (C). (A) displays the lamellar phase having alternating arrangement of PS and PI. (B, C) shows bicontinuous morphologies like in interpenetrating network structure.

as a bicontinuous cubic structure, the morphologies of the three polymers are in good agreement with the predictions of Milner.[29]

The fractionated mother polymer seems to show the same morphology as the purified $PSPI_3$ since it has a composition not much different from $PSPI_3$. In any event, the fact that we observed a similar morphology for the fractionated mother and the purified $PSPI_3$ should not be interpreted as suggesting that the conventional characterization methodology is adequate for this type of morphological study. In the present case, the molecular weight of PI block is small, and the residual homo-PI nicely compensates for the presence of a significant amount of remaining $PSPI_2$ in the fractionated mother to result very small change in the overall composition of the polymer from that of $PSPI_3$. However, we can imagine a much worse situation. For example, if the composition of the block copolymer of interest falls on near the phase boundary, the presence of byproducts may lead to erroneous conclusions. More detailed analysis such as that described in this work is necessary, in particular for polymers with complex architectures, if rigorous proof of structural purity is required. In the production of model polymers, the ability to scrutinize our successes (and failures) is a highly valuable asset.

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