

Synthesis, Characterization and Self-Assembly of Linear and Miktoarm Star Copolymers of Exclusively Immiscible Polydienes

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Supporting Information

The following data are given in the Supporting Information:

- A). SEC and ¹H-NMR Molecular Characterization Results
- B). DSC Thermal Characterization Results

A) SEC and $^1\text{H-NMR}$ Molecular Characterization Results

Diblock copolymers of the $\text{PB-}b\text{-PI}_{3,4}$ type

In the following SEC chromatographs, the initial PB precursors and the final diblock copolymers for the $\text{PB-}b\text{-PI}_{3,4-3}$ and $\text{PB-}b\text{-PI}_{3,4-4}$ are presented (Fig. S1 and S2 respectively).

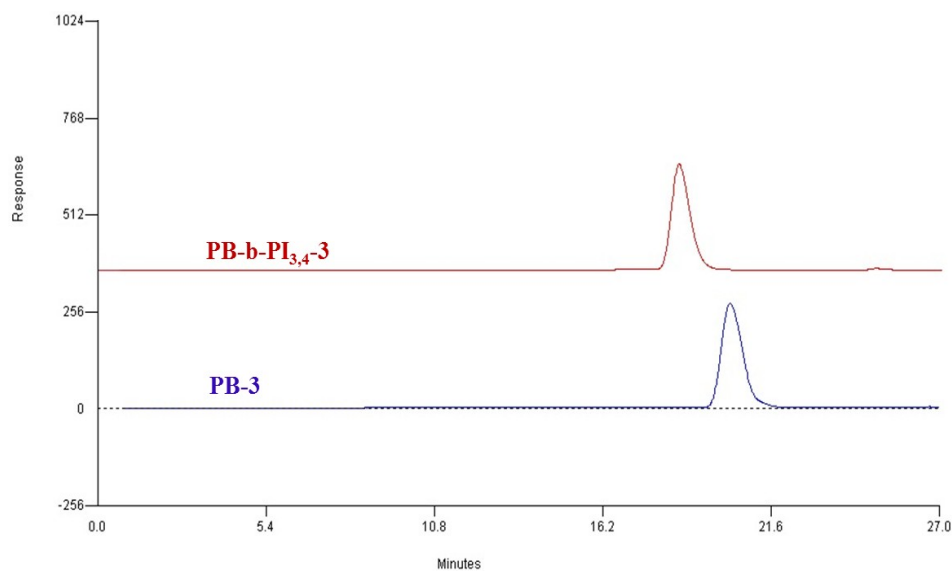


Fig. S1 SEC chromatographs of the PB-3 block (blue) and the final diblock copolymer of the $\text{PB-}b\text{-PI}_{3,4-3}$ type (red).

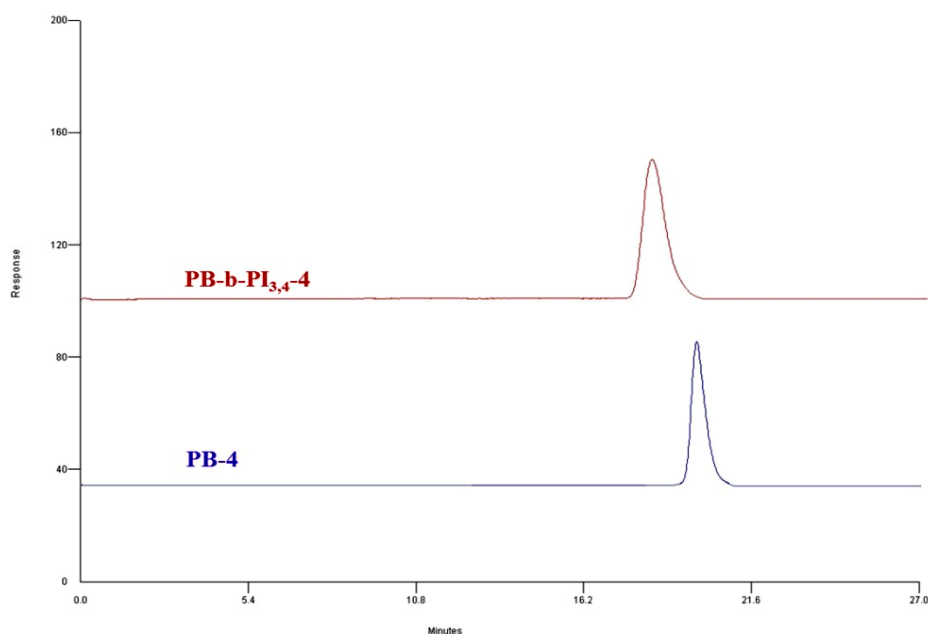


Fig. S2 SEC chromatographs of the PB-4 block (blue) and the final diblock copolymer of the $\text{PB-}b\text{-PI}_{3,4-4}$ type (red).

Miktoarm star copolymers of the $\text{PB}(\text{PI}_{3,4})_2$ and $\text{PB}(\text{PI}_{3,4})_3$ type

In Fig. S3 and S4 the initial PB and PI blocks the unfractionated miktoarm star copolymers of the $\text{PB}(\text{PI}_{3,4})_2\text{-S}_7$ and $\text{PB}(\text{PI}_{3,4})_3\text{-S}_8$ type and the final purified products are given respectively.

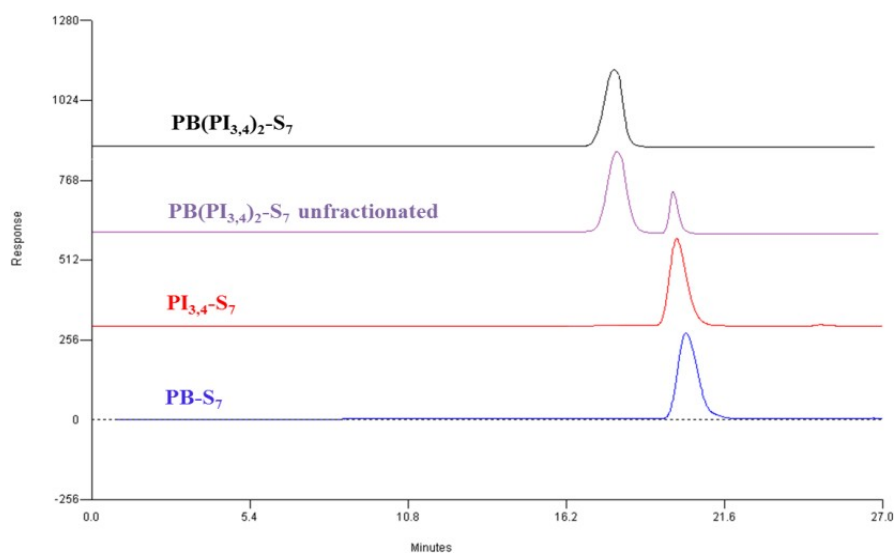


Fig. S3 SEC chromatographs of the PB-S₇ (blue) and PI_{3,4}-S₇ (red) blocks, unfractionated star copolymer of the PB(PI_{3,4})₂-S₇ (purple) and the final fractionated miktoarm star copolymer of the PB(PI_{3,4})₂-S₇ type (black).

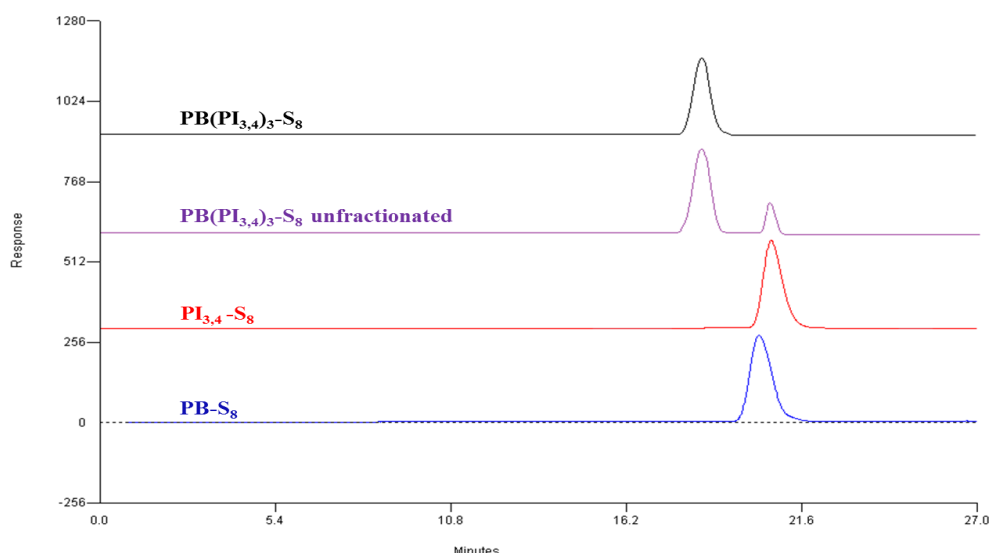


Fig. S4 SEC chromatographs of the PB-S₈ (blue) and PI_{3,4}-S₈ (red) blocks, the unfractionated star copolymer of the PB(PI_{3,4})₃-S₈ (purple) and the final fractionated miktoarm star copolymer of the PB(PI_{3,4})₃-S₈ type (black).

¹H-NMR Spectroscopy

In Table S1, the proton chemical shifts corresponding to the different geometric isomerism of the PB and PI segments are reported. As it is evident, the ratio of each microstructure can be estimated via ¹H-NMR spectroscopy since, different protons generate different chemical shifts in a corresponding ¹H-NMR spectrum.

Table S1 Type and number of protons with the corresponding chemical shifts for protons incorporated in the monomeric units of polybutadiene and polyisoprene.

Polymeric chain	Geometric Isomerism	Type and Number of Protons	Chemical shift(ppm)
PB	1,4	Olefinic(2)	5,35
		Olefinic(1)	5,60
	1,2	Olefinic(1)	5,60
PI	1,4	Olefinic(2)	4,95
		Olefinic(1)	5,12
	3,4	Olefinic(2)	4,70
		Olefinic(1)	5,82
	1,2	Olefinic(1)	5,82
	Olefinic(2)	5,00	

In Table S2, the mass fractions of both blocks as well as the characteristic microstructures of each block for all linear and miktoarm star copolymers, as calculated by $^1\text{H-NMR}$, are presented.

Table S2 Mass fractions and characteristic microstructures of each block for linear and miktoarm star copolymers, as calculated by $^1\text{H-NMR}$ spectroscopy results.

Samples	f_{PB}	f_{PI}	1,4-PB (%)	1,2-PB (%)	3,4-PI (%)	1,4-PI (%)	1,2-PI (%)
PB- <i>b</i> -PI _{3,4} -1	0,42	0,58	91	9	58	29	13
PB- <i>b</i> -PI _{3,4} -2	0,71	0,29	92	8	57	30	13
PB- <i>b</i> -PI _{3,4} -3	0,59	0,41	92	8	60	28	12
PB- <i>b</i> -PI _{3,4} -4	0,32	0,68	90	10	62	23	15
PB(PI _{3,4}) ₂ -S ₁	0,41	0,59	92	8	60	25	15
PB(PI _{3,4}) ₃ -S ₂	0,40	0,60	92	8	59	27	14
PB(PI _{3,4}) ₂ -S ₃	0,67	0,33	91	8	61	23	16
PB(PI _{3,4}) ₃ -S ₄	0,69	0,31	91	8	60	26	14
PB(PI _{3,4}) ₂ -S ₅	0,57	0,43	91	9	61	24	15
PB(PI _{3,4}) ₃ -S ₆	0,56	0,44	91	9	58	28	14
PB(PI _{3,4}) ₂ -S ₇	0,30	0,70	92	8	59	26	15
PB(PI _{3,4}) ₃ -S ₈	0,28	0,72	92	8	62	22	16

B) DSC Thermal Characterization Results

In Fig. S5-S7 the DSC thermographs for the three (3) sets comprised of the one (1) linear and the two (2) star copolymers, corresponding to PB-*b*-PI_{3,4}, PB(PI_{3,4})₂ and PB(PI_{3,4})₃ respectively, are given. The displayed thermographs correspond to the second heating cycle.

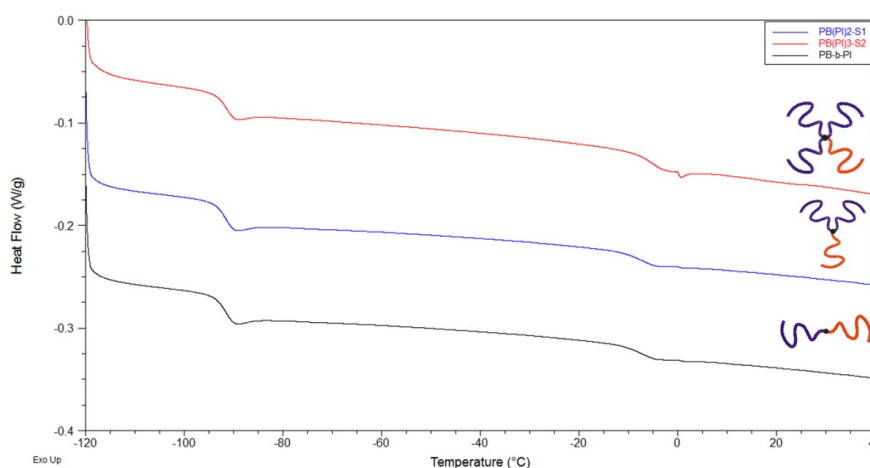


Fig. S5 DSC thermographs for samples constituting set No 1, where PB-*b*-PI_{3,4}-1, PB(PI_{3,4})₂-S₁ and PB(PI_{3,4})₃-S₂ are the black, blue and red colour curves respectively.

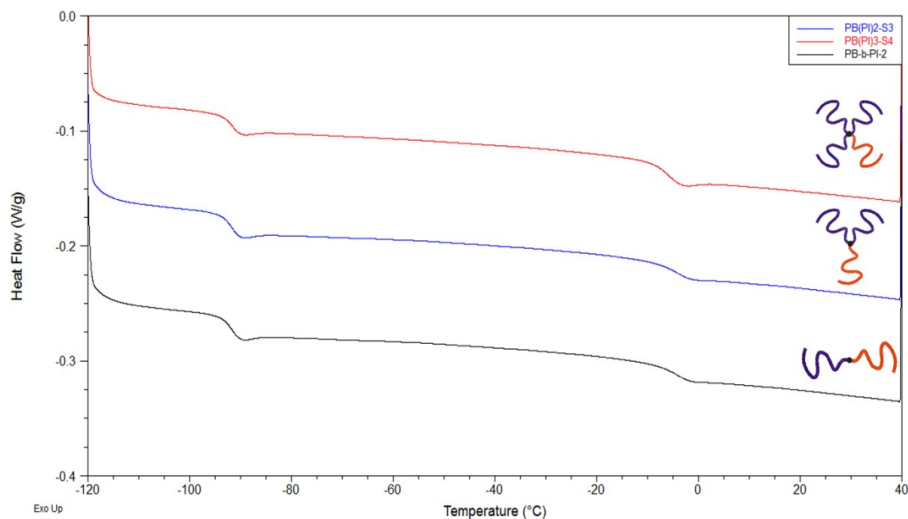


Fig. S6 DSC thermographs for samples constituting set No 2, where PB-b-PI_{3,4}-2, PB(PI_{3,4})₂-S₃ and PB(PI_{3,4})₃-S₄ are the black, blue and red colour curves respectively.

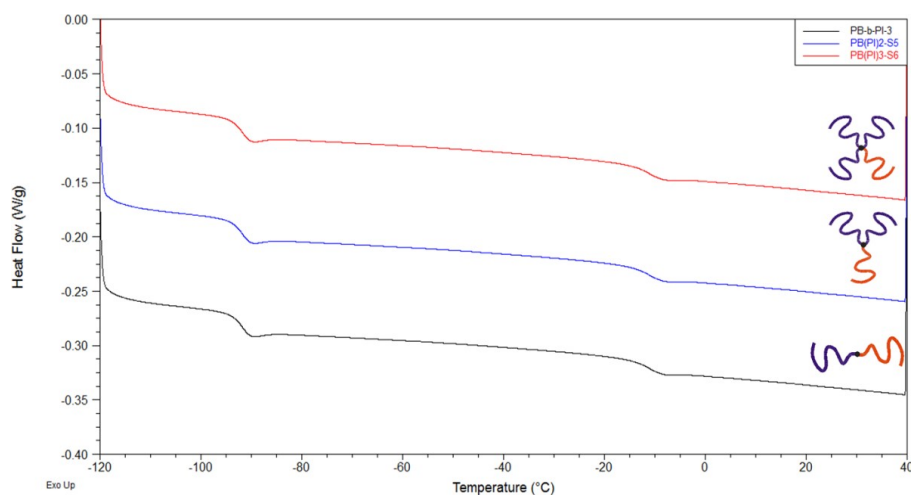


Fig. S7 DSC thermographs for samples constituting set No 3, where PB-b-PI_{3,4}-3, PB(PI_{3,4})₂-S₅ and PB(PI_{3,4})₃-S₆ are the black, blue and red colour curves respectively.