SUPPLEMENTARY INFORMATION

Hydrodynamics of Polystyrene–Polyisoprene Miktoarm Star Copolymers in a Selective and a Non-Selective Solvent

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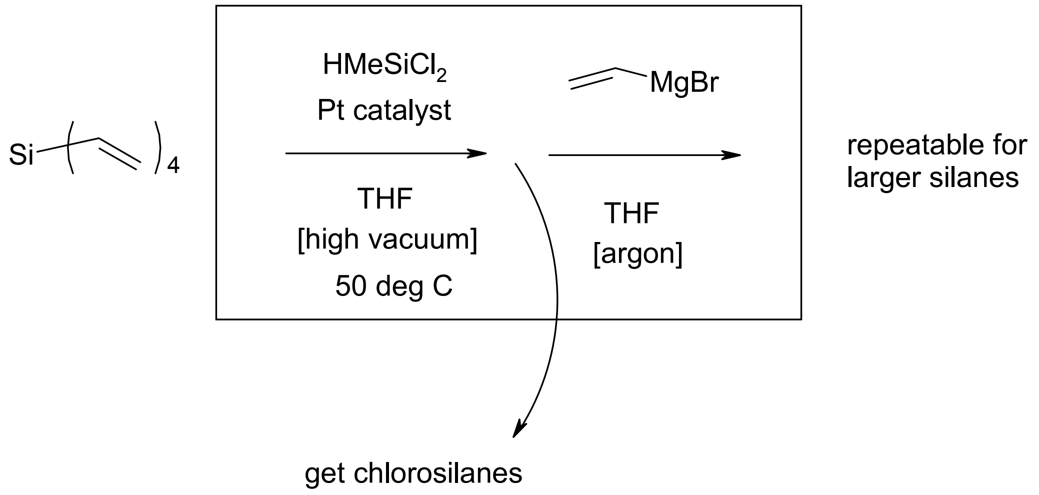
Preparation of Multichlorosilane Linking Agents

The chemistry discussed below regarding multichlorosilane syntheses is well accounted by Zhou and Roovers.[1] In preparation for the hydrosilylation reactions, tetravinylsilane (97%, Aldrich), $HSiMeCl_2$ (99%, Aldrich), and Me_3SiCl (99%, Aldrich) were dried by stirring over CaH_2 overnight and then were distilled into ampules. Hexanes were dried over BuLi, benzene was purified over PSLi, THF was purified over K/Na alloy; and these solvents were docked at the vacuum line and out-distilled as needed. Pt catalyst (Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex, solution in xylene, Aldrich) was transferred to a vacuum apparatus, diluted with benzene and distributed into ampules. For the Grignard reaction, Mg, vinyl bromide (1.0 M in tetrahydrofuran), tetrahydrofuran (99.9%, anhydrous, inhibitor-free, "Sure-seal"), and 1,2-dibromoethane (99%) were all used as received from Aldrich.

The multichlorosilanes were prepared according to the following methodology:



$Si[CH_2CH_2Si(Me)Cl_2]_4$ = "$SiCl_8$"

$Si[CH_2CH_2Si(Me)[CH_2CH_2Si(Me)Cl_2]_2]_4$ = "$SiCl_{16}$"

Scheme S1. Methodology for the preparation of multichlorosilane linking agents.

$Si[CH_2CH_2Si(CH_3)Cl_2]_4$ ("$SiCl_8$") was synthesized in a specially prepared apparatus, depicted in Figure S1. The apparatus, built with an integral condenser, was designed to have exactly one low point for effective and unambiguous turnover by reflux, and it was affixed to the high-vacuum line by means of an all-glass bridge equipped with a Teflon stopcock. The apparatus was evacuated under high-vacuum, after which 75 ml THF was in-distilled. The stopcock was closed. The break-seal of $(CH_3)_3SiCl$ was ruptured so that 0.25 g of Me_3SiCl in 1 ml hexane was added. The solution was left to stir and modestly reflux overnight from a 45 °C bath to the 20 °C apparatus and 15 °C condenser. The following morning, ampules of Pt catalyst (0.1% in benzene, 1 ml) and tetravinylsilane (2.69 g, 19.7 mmol) were opened and the contents were allowed to reflux under the same conditions for 1 additional hour. $HSiMeCl_2$ (10.9 g, 94.8 mmol; 20% excess) was then added to the solution to commence the hydrosilylation reaction; the ampule was slightly chilled, the seal broken, the contents allowed to mix. The temperature of the external water bath was noticed to rise by a couple of degrees, indicating an exothermic event inside the reactor. The reaction was allowed to progress for 24 h at 45-50 °C. The majority of volatile contents were out-distilled from the apparatus and collected to a waste reservoir docked elsewhere on the vacuum line. 75 mL of benzene were in-distilled, the contents stirred well, and the volatile contents were again stripped by out-distilling to the waste reservoir. The reactor was then purged overnight under high vacuum, and the following day the manifold was basically silent according to the Tesla coil. Hexanes were in-distilled, and although the multichlorosilane is sparingly soluble, 150 mL was enough to dissolve the product at RT. The apparatus was taken off the high vacuum line by sealing the constriction above the condenser. All of the solution was poured to the collection appendage and distributed to the ampules. One small simple ampule was broken open and hydrolyzed into water, whence a cursory titration with 0.1 M NaOH solution indicated a 97% yield. Another small ampule was derivatized by reaction with MeLi in THF for characterization purposes. $Si[CH_2CH_2Si(CH_3)_3]_4$ was found by ^1H NMR ($C\underline{H_2}C\underline{H_2}$: multiplet, area 4.00 H's, δ 0.35-0.50 ppm; $C\underline{H_3}$: singlet, area 9.09 H's, at δ 0.00 ppm) and ^{13}C NMR (3 $Si\underline{C}$ peaks, δ -3, 2, and 8 ppm). One further small ampule was diluted to a usable concentration in hexanes to use as linking agent for macromolecular anions. A majority quantity was collected into the largest ampule to be used for the subsequent synthesis of the larger multichlorosilane.

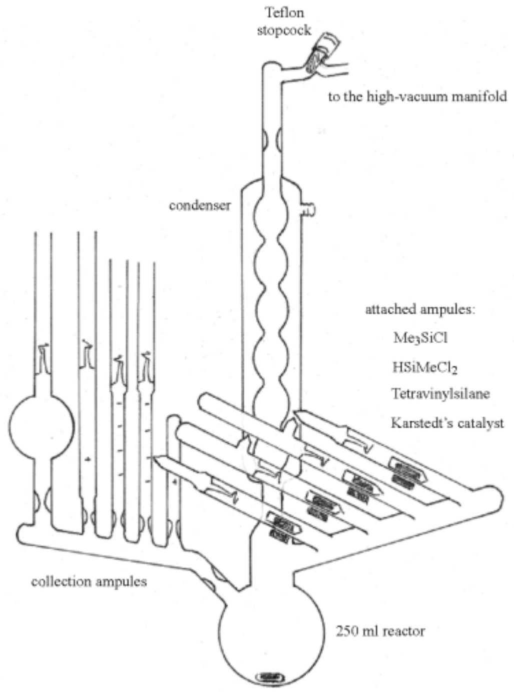


Figure S1. Hydrosilylation apparatus.

$Si[CH_2CH_2Si(CH_3)(CH{=}CH_2)_2]_4$ ("Octavinylsilane") was prepared by the reaction of $SiCl_8$ with $CH_2{=}CHMgBr$. In a dry, argon-filled 500 mL 2-neck RB flask equipped with a condenser and an addition funnel, 3.52 g Mg (145 mmol) was stirred in 30 ml THF. Vinyl bromide (161 mL at 1 M in THF, 161 mmol) was transferred to the addition funnel by cannula. After adding a 10-15 mL of this reagent to the reactor flask, 0.2 mL $BrCH_2CH_2Br$ (2 mmol) was injected. The reaction started as evidenced by warming discernible by hand and evolution of ethylene gas. The remaining vinyl bromide solution was added dropwise over a 45 min interval in a manner that maintained a gentle rate of reflux in the reactor. The reactor was kept warm for an additional hour, after which it appeared that all of the Mg had been consumed. The reactor flask was then cooled to a temperature slightly below room temperature by using an external water bath. $SiCl_8$ (14.4 mmol, limiting reagent) was re-ampulized into a suitable addition funnel of its own, still under vacuum as a more concentrated THF solution. This solution of $SiCl_8$ was affixed to the Grignard reaction flask in place of the condenser. This reagent was added dropwise over 1 h, and the reaction left to progress overnight. After hydrolysis and work-up, the crude product was chromatographed on silica with 0.4% ethyl acetate in hexane. ^1H NMR ($C\underline{H}{=}C\underline{H}_2$: 3 doubled doublets, area 6.00 H's, δ 5.68-6.22 ppm; $C\underline{H}_2C\underline{H}_2$: broad singlet, area 3.94 H's, δ 0.40-0.65 ppm; $C\underline{H}_3$: sharper singlet, area 3.01 H's, δ 0.10-0.20 ppm) and ^{13}C NMR (3 *sp3* Si$\underline{C}$ peaks, δ -6, 3, and 6 ppm; and 2 *vinyl* $\underline{C}$ peaks, δ 133, 142 ppm) indicated the isolation of clean octavinylsilane 2.80 g of this compound was stripped on the vacuum line, scrubbed with in/out distillation of purified benzene, vacuumed overnight, dissolved into 20 mL purified in-distilled hexanes, and ampulized for the next hydrosilylation.

$Si[CH_2CH_2Si(CH_3)[CH_2CH_2Si(CH_3)Cl_2]_2]_4$ ("$SiCl_{16}$") was synthesized in a manner analogous to $SiCl_8$. The same apparatus and technique as described in the above hydrosilylation reaction were used. 85 mL THF, 0.25 g Me_3SiCl, 1 mL 0.1% Pt catalyst solution, 2.80 g octavinylsilane (5.29 mmol, limiting reagent) and 11.0 g $HSiMeCl_2$ (96 mmol; i.e., 125 % excess) were used. After collecting the large flask of $SiCl_8$, it was affixed to a transfer apparatus, depicted in Figure S2, to prepare it for the subsequent Grignard reaction. This apparatus was fitted with a dropping ampule, the inner body of which was sealed with 2 breakable membranes. The apparatus was dried under high vacuum. The small ampule of Me_3SiCl in hexanes was ruptured and this reagent was used to rinse and silanize the interior of the apparatus and dropping ampule by means of a towel strip and liquid nitrogen. These reagents were then evacuated to a 0°C collection flask elsewhere on the vacuum manifold. The break-seal to the flask containing $SiCl_8$ in solution was ruptured and hexanes were stripped from the apparatus by using a 25°C to 0°C temperature differential in order to gently evaporate the solvent. Finally the apparatus was opened to the main vacuum for ~10 min. Purified THF was then in-distilled, and the apparatus was sealed and detached. The THF solution of $SiCl_8$ was then collected to the addition ampule by pouring, and this ampule was rinsed and detached from the apparatus at its entry constriction. (Although the $SiCl_8$ had been originally nearly saturated in 110 mL hexanes, this reagent dissolved quite easily in 50 mL of THF.) On the day of use, the addition ampule was prepared through some final glassblowing and docked to the vacuum line. (See Figure S3.) The ampule was vacuumed until dry and the Tesla coil was silent. About 0.1 g of Me_3SiCl was collected to the ampule compartments, distributed above and below. The ampule was then repressurized with Argon, taken from the vacuum line, and at once inverted and fit to the vessel containing the in-progress Grignard reaction. (See Figure S4.) After waiting a moment, the membrane seals above and below the $SiCl_8$ solution were ruptured, allowing this reagent to be delivered slowly by gravity.

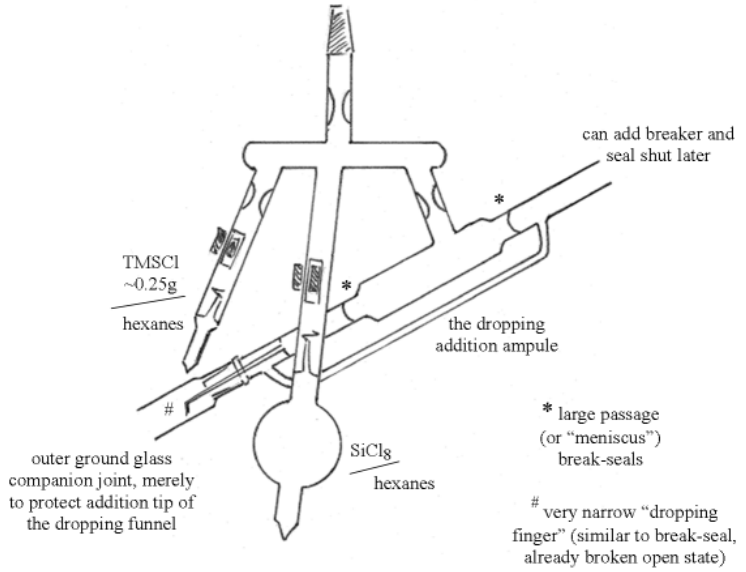


Figure S2. Chlorosilane transfer technique, scene 1.

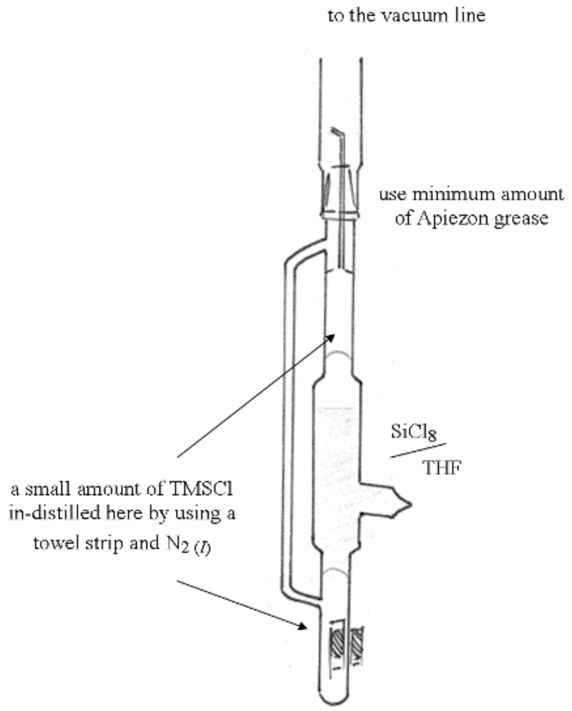


Figure S3. Chlorosilane transfer technique, scene 2.

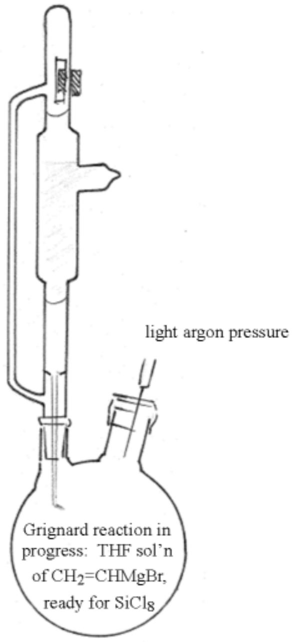


Figure S4. Chlorosilane transfer technique, scene 3.

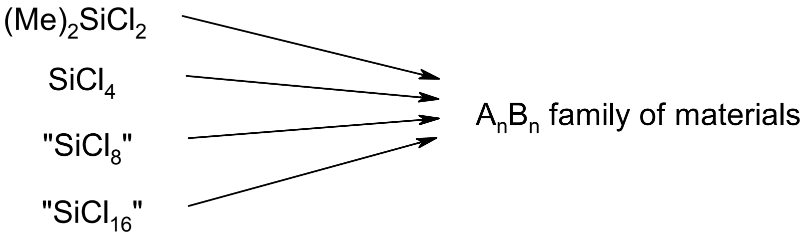
Preparation of PS_nPI_n Miktoarm Stars

In preparation for the polymerization and linking reactions, isoprene (99%, Aldrich) was purified from BuLi, styrene (99%, Aldrich) was purified from dibutylmagnesium; and these monomers were ampulized until needed. *sec*-BuLi was synthesized under vacuum from the reduction of sec-BuCl with excess Li metal. 1,2-Dimethoxyethane (DME) was purified from K/Na alloy and ampulized. Isoprene and styrene were each polymerized in large batches from sec-BuLi in benzene and distributed to many ampules and reserved for subsequent preparation of families of PI_nPS_n in which, even with variance of n, the PI and PS arms would match each other exactly.

The star copolymers were then assembled according to the reaction:

$$\mathrm{SiCl_{2n}} \xrightarrow{\text{n PSLi}} \xrightarrow{\text{n PILi}} \mathrm{(PS)_n(PI)_n}\ \text{star copolymer}$$

To make miktoarm stars having n = 1, 2, 4, and 8 different arms (multisilanes) were employed:



PS_1PI_1 diblock. A solution of polyisoprenyllithium (PILi, 143 μmol) in benzene was first added to a 100-fold excess of $(CH_3)_2SiCl_2$ (~2 mL) in 50 mL benzene, and then the excess silane was stripped away by repeated out-distillations and 4 days open vacuum, and then redissolved in benzene. Polystyryllithium (PSLi, 167 μmol, i.e., in excess) in benzene was then added to the $(PI)(CH_3)_2SiCl$. Fractionation with toluene-methanol was required to isolate the PS_1PI_1 diblock. It was noticed that PILi has a greater tendency to couple with $(CH_3)_2SiCl_2$ than does PSLi, and there was a small amount of PI_2 dimer in the final product that was removed through the fractionation process. There also seems to be a small amount of PI homopolymer in the final PI_1PS_1 diblock that cannot be removed by fractionation.

PS_2PI_2 star. A benzene solution of 75.5 μmol $SiCl_4$ was prepared in a linking reactor. A benzene solution of 169 μmol PSLi was added incrementally. Next, a benzene solution of 190 μmol PILi was added. After several days, a small amount of 1,2-dimethoxyethane (DME) (0.5% v/v) was added to expedite the final linking reaction. After 2 weeks the reaction was quenched and precipitated into methanol, followed by fractionation with toluene-methanol. An SEC eluogram is shown for both the crude reaction product and finally fractionated PS_2PI_2 star copolymer in **Figure S5**.

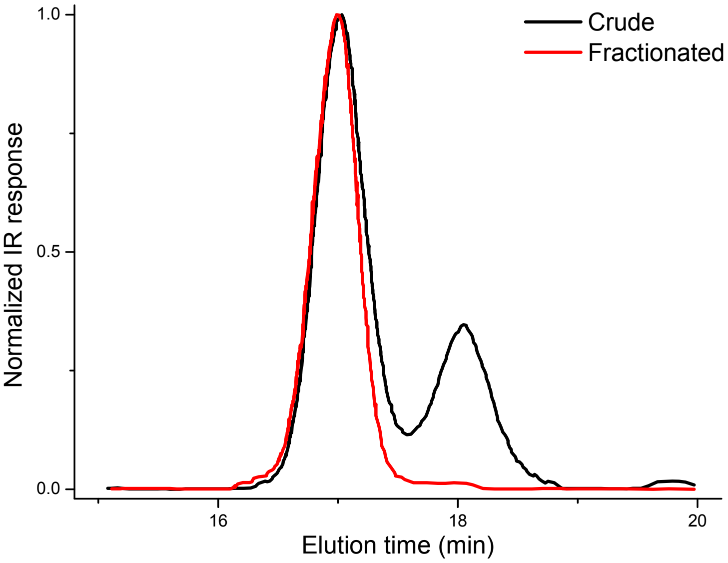


Figure S5. SEC eluograms for PS_2PI_2 copolymer.

PS_4PI_4 star. A benzene solution of 38.4 μmol $SiCl_8$ was prepared in a linking reactor. A benzene solution of 169 μmol PSLi was added incrementally. Next, a benzene solution of 189 μmol PILi was then added. After several days a small amount of DME (0.5% v/v) was added to expedite the final linking reaction. After 2 weeks the reaction was quenched and precipitated into methanol, followed by fractionation with toluene-methanol.

PS_8PI_8 star. A benzene solution of 18.7 μmol $SiCl_{16}$ was prepared in a linking reactor. A benzene solution of 159 μmol PSLi was added incrementally. Next, a benzene solution of 186 μmol PILi was then added. After several days, a small amount of DME (0.5% v/v) was added to expedite the final linking reaction. After 2 weeks the reaction was quenched and precipitated into methanol, followed by fractionation with toluene-methanol.

Static and Dynamic Light Scattering of PS_nPI_n Miktoarm Star Copolymers

Figure S6 shows a comparison of the normalized light intensity autocorrelation functions, $[g_2(q,\tau)\text{-}1]^{1/2}$, (see Equation 1 in the Article) for the PS_nPI_n miktoarm star block copolymers in n-hexane at all of the concentrations studied. It is seen clearly that as concentration increases, the values of $[g_2(q,\tau)\text{-}1]^{1/2}$ increase because there is less incoherent scattering from the solutions. This pattern of behavior is most striking in the smaller miktoarm star copolymers, PS_1PI_1 and PS_2PI_2.

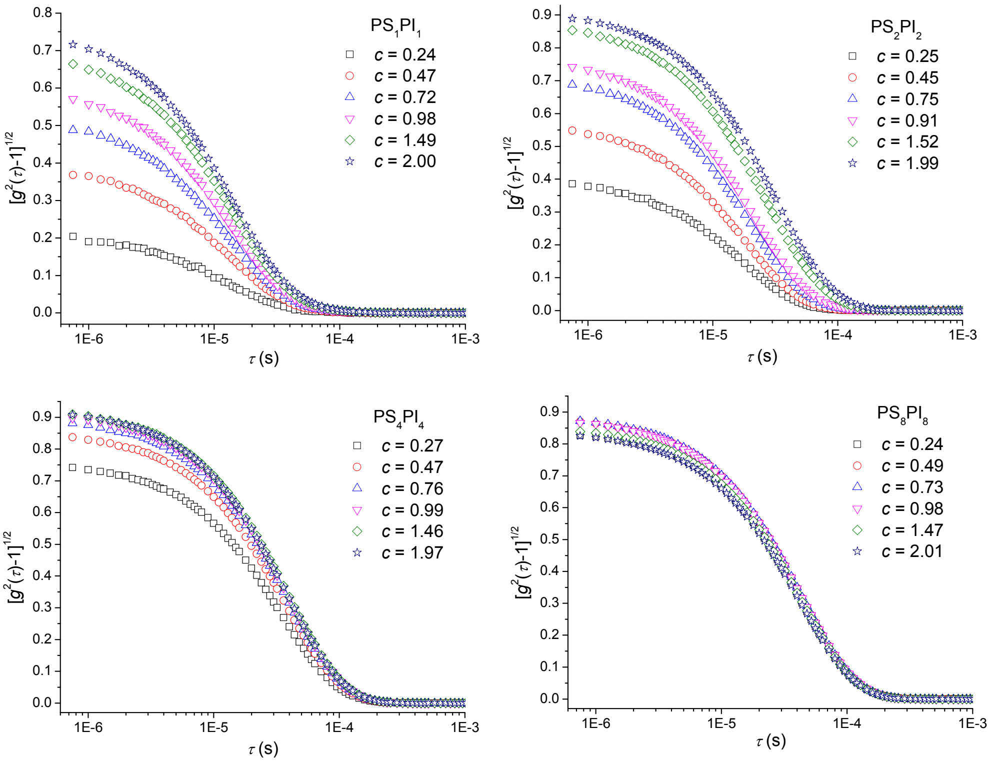


Figure S6. Autocorrelation functions for PS_nPI_n miktoarm star copolymers at the six concentrations studied in n-hexane ($\theta = 96°$). Concentrations given in the legends are in units of mg/mL.

The following tables provide the solution diffusion coefficient, D_s, and the hydrodynamic radius, R_h, determined for each of the PS_nPI_n miktoarm stars in n-hexane (Tables S1-S4) and in THF (Tables S5-S8). R_h values were calculated using the Stokes-Einstein equation. As described in the Article, fast modes observed in dynamic light scattering measurements of samples PS_1PI_1 and PS_2PI_2 correspond to the population of scatterers having smaller R_h, and these are ascribed to single PS_1PI_1 and PS_2PI_2 miktoarm stars. The slow mode observed arises from aggregation of the PS_1PI_1 and PS_2PI_2 miktoarm stars, which explains the larger R_h (smaller D_s values). For the PS_4PI_4 and PS_8PI_8 copolymers, only single stars are observed over the concentration range studied; thus, no labeling of fast or slow modes is needed.

Table S1. Hydrodynamic properties of PS_1PI_1 miktoarm star copolymers in n-hexane.

Sample ID	*c* (mg/mL)	D_s (cm^2/s)	R_h (nm)
PS_1PI_1	0.24	8.97×10^{-7}	8.3
PS_1PI_1	0.47	8.60×10^{-7}	8.7
PS_1PI_1 fast	0.72	1.06×10^{-6}	7.1
PS_1PI_1 slow	0.72	2.46×10^{-7}	30.4
PS_1PI_1 fast	0.98	9.85×10^{-7}	7.6
PS_1PI_1 slow	0.98	1.69×10^{-7}	44.1
PS_1PI_1 fast	1.49	1.02×10^{-6}	7.3
PS_1PI_1 slow	1.49	1.96×10^{-7}	38.0
PS_1PI_1 fast	2.00	1.01×10^{-6}	7.4
PS_1PI_1 slow	2.00	1.95×10^{-7}	38.3
PS_1PI_1 fast	5.88	9.91×10^{-7}	7.5
PS_1PI_1 slow	5.88	1.71×10^{-7}	43.8

Table S2. Hydrodynamic properties of PS_2PI_2 miktoarm star copolymers in n-hexane.

Sample ID	c (mg/mL)	D_s (cm^2/s)	R_h (nm)
PS_2PI_2	0.25	6.93×10^{-7}	10.8
PS_2PI_2	0.45	6.69×10^{-7}	11.1
PS_2PI_2	0.75	6.01×10^{-7}	12.4
PS_2PI_2	0.91	5.61×10^{-7}	13.3
PS_2PI_2 fast	1.52	6.61×10^{-7}	11.3
PS_2PI_2 slow	1.52	2.63×10^{-7}	28.3
PS_2PI_2 fast	1.99	6.36×10^{-7}	11.7
PS_2PI_2 slow	1.99	2.72×10^{-7}	27.4
PS_2PI_2 fast	5.88	8.36×10^{-7}	8.0
PS_2PI_2 slow	5.88	3.09×10^{-7}	23.5

Table S3. Hydrodynamic properties of PS_4PI_4 miktoarm star copolymers in n-hexane.

Sample ID	c (mg/mL)	D_s (cm^2/s)	R_h (nm)
PS_4PI_4	0.27	3.49×10^{-7}	21.4
PS_4PI_4	0.47	3.26×10^{-7}	22.9
PS_4PI_4	0.76	3.16×10^{-7}	23.6
PS_4PI_4	0.99	3.11×10^{-7}	23.9
PS_4PI_4	1.46	3.08×10^{-7}	24.2
PS_4PI_4	1.97	3.10×10^{-6}	24.0
PS_4PI_4	5.89	3.28×10^{-6}	22.7

Table S4. Hydrodynamic properties of PS_8PI_8 miktoarm star copolymers in n-hexane.

Sample ID	c (mg/mL)	D_s (cm^2/s)	R_h (nm)
PS_8PI_8	0.24	2.86×10^{-7}	26.1
PS_8PI_8	0.49	2.84×10^{-7}	26.3
PS_8PI_8	0.73	2.83×10^{-7}	26.3
PS_8PI_8	0.98	2.83×10^{-7}	26.3
PS_8PI_8	1.47	2.87×10^{-7}	26.0
PS_8PI_8	2.01	2.90×10^{-6}	25.7
PS_8PI_8	5.83	3.05×10^{-6}	24.4

Table S5. Hydrodynamic properties of PS_1PI_1 miktoarm star copolymers in THF.

Sample ID	c (mg/mL)	D_s (cm^2/s)	R_h (nm)
PS_1PI_1	0.96	6.19×10^{-7}	7.8
PS_1PI_1	3.94	6.67×10^{-7}	7.2
PS_1PI_1	6.91	7.24×10^{-7}	6.6

Table S6. Hydrodynamic properties of PS_2PI_2 miktoarm star copolymers in THF.

Sample ID	*c* (mg/mL)	D_s (cm^2/s)	R_h (nm)
PS_2PI_2	0.98	4.18×10^{-7}	11.5
PS_2PI_2	1.41	4.29×10^{-7}	11.2
PS_2PI_2	2.42	4.53×10^{-7}	10.6
PS_2PI_2	4.30	5.02×10^{-7}	9.7

Table S7. Hydrodynamic properties of PS_4PI_4 miktoarm star copolymers in THF.

Sample ID	*c* (mg/mL)	D_s (cm^2/s)	R_h (nm)
PS_4PI_4	1.02	3.05×10^{-7}	15.7
PS_4PI_4	1.98	3.27×10^{-7}	14.7
PS_4PI_4	3.92	3.81×10^{-7}	12.6
PS_4PI_4	9.48	5.28×10^{-7}	9.1

Table S8. Hydrodynamic properties of PS_8PI_8 miktoarm star copolymers in THF.

Sample ID	*c* (mg/mL)	D_s (cm^2/s)	R_h (nm)
PS_8PI_8	0.99	2.43×10^{-7}	19.8
PS_8PI_8	2.05	2.68×10^{-7}	17.9
PS_8PI_8	3.93	3.11×10^{-7}	15.3
PS_8PI_8	6.33	3.64×10^{-7}	13.2

The analysis of SLS data requires the knowledge of the value for refractive index increment, *dn/dc*, for the miktoarm stars in each solvent. As stated in the Article, the *dn/dc* for the PS_nPI_n copolymers in THF can be calculated from the mass percentage contribution of each constituent. On the other hand, for the stars in n-hexane the *dn*/*dc* values were obtained from measurements of differential refractive index from a pure n-hexane solvent and the results are shown in Figure S7. The SLS results, presented via the Zimm plots, for stars PS_4PI_4, and PS_8PI_8 in n-hexane and for PS_2PI_2, PS_8PI_8 in THF are shown in Figures S8 to S11. The Zimm plot for miktoarm star PS_4PI_4 in THF is shown as Figure 9 in the Article.

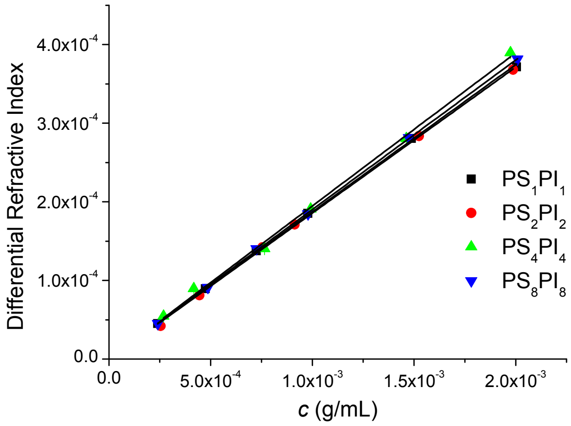


Figure S7. Differential refractive index versus concentration for PS_nPI_n miktoarm stars in n-hexane. The *dn*/*dc* values are obtained from the slope of each line.

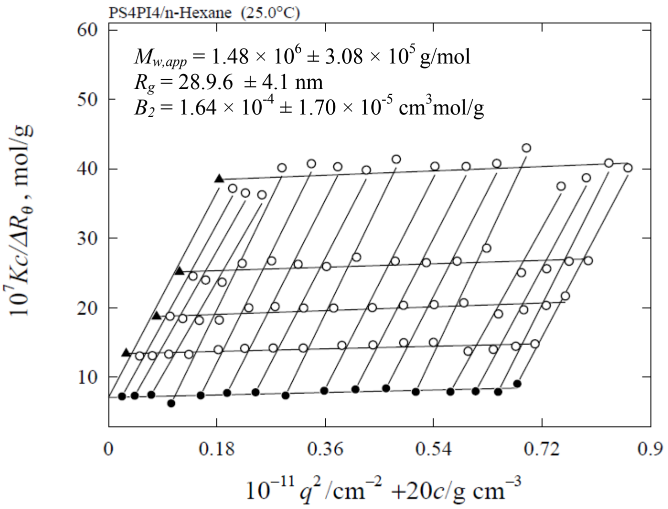


Figure S8. Zimm plot for star PS_4PI_4 in n-hexane with results from fittings the lines extrapolated to $c = 0$ and to $q^2 = 0$.

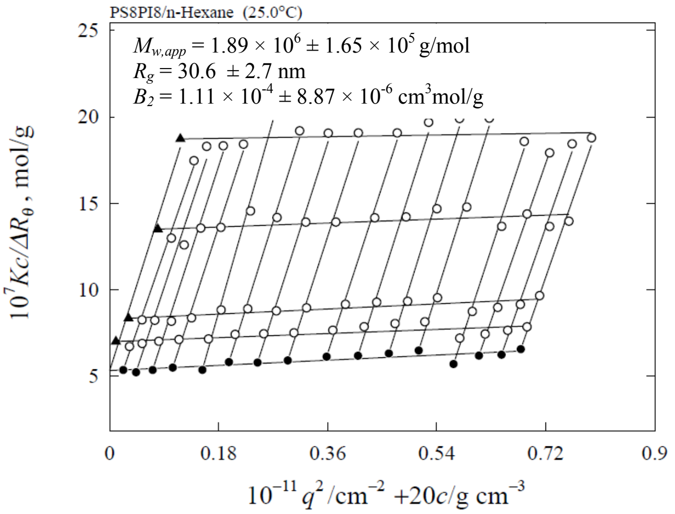


Figure S9. Zimm plot for star PS_8PI_8 in n-hexane with results from fittings the lines extrapolated to $c = 0$ and to $q^2 = 0$.

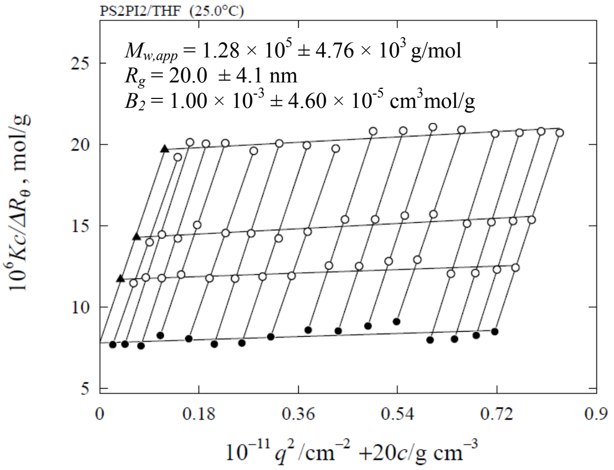


Figure S10. Zimm plot for star PS_2PI_2 in THF with results from fittings the lines extrapolated to $c = 0$ and to $q^2 = 0$.

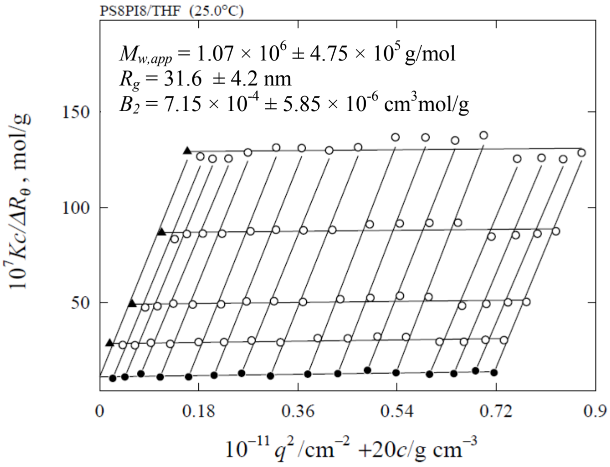


Figure S11. Zimm plot for star PS_8PI_8 in n-hexane with results from fittings the lines extrapolated to $c = 0$ and to $q^2 = 0$.

Reference

S1. Zhou, L.L.; Roovers, J. *Macromolecules*, 1993, **26**, 963.