

Supporting Information
for
**Reversible Cross-linking of Polyisoprene Coronas in Micelles, Block
Comicelles, and Hierarchical Micelle Architectures using Pt(0)-
Olefin Coordination**

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Experimental Section

Monomer purifications were performed under an atmosphere of purified N₂. Anionic polymerizations were carried out in an inert atmosphere glovebox. All other manipulations were carried out under an open atmosphere unless otherwise stated. PFS block copolymers were prepared by previously reported methods.¹ 1,2- and 1,4-polybutadiene and PI₅₁₄-*b*-PEO₂₅₀ were purchased from PolymerSource. All polymers used in this study, together with their properties, are listed in Table S1. *n*-Butyllithium (1.6 M) in *n*-hexanes, *sec*-butyllithium (1.4 M) in cyclohexane, isoprene, hexamethylcyclotrisiloxane (D₃), and 2-bis(diphenylphosphino)ethane were purchased from Aldrich. Platinum-divinyltetramethyldisiloxane complex in xylenes (Karstedt's Catalyst) with a Pt wt % of 2.1-2.4 was purchased from ABCR (Karlsruhe,

Germany); the concentration of Karstedt's Catalyst was assumed to be 2.4 wt % Pt for stoichiometric calculations. Isoprene was first distilled from CaH_2 followed by distillation from *n*-butyllithium and stored at $-40\text{ }^\circ\text{C}$. Hexamethylcyclotrisiloxane (D_3) was dissolved in pentane and stirred over CaH_2 for 48 hours. Subsequently, the pentane was distilled off and the D_3 was consecutively sublimed under reduced pressure 3 times. THF was distilled from Na/benzophenone immediately before use.

The air sensitivity of Karstedt's Catalyst requires that all of the $\text{Pt}(0)$ cross-linking procedures are performed under an inert atmosphere. However, after the addition of Karstedt's Catalyst, the cross-linked micelle solutions are stable to air and show no property changes over months. Sonications were performed using a Bandelin Sonorex Digitec DT 255H ultrasonic bath operating at 35 kHz with an average output of 160 watts.

Polymer Characterization Gel permeation chromatography was carried out on diblock copolymers and aliquots of the first block using a Viscotek VE 2001 Triple-Detector Gel Permeation Chromatograph equipped with an automatic sampler, a pump, an injector, an inline degasser, and a column oven ($30\text{ }^\circ\text{C}$). The elution columns consist of styrene/divinyl benzene gels with pore sizes of $500\text{ }\text{\AA}$ and $100,000\text{ }\text{\AA}$. Detection was conducted by means of a VE 3580 refractometer, a four-capillary differential viscometer, and a 90° and low angle (7°) laser light ($\lambda_0 = 670\text{ nm}$) scattering detectors, VE 3210 & VE 270. THF (Fisher) was used as the eluent, with a flow rate of 1.0 mL/min . Samples were dissolved in the eluent (2 mg/mL) and filtered with a Ministart SRP 15 filter (polytetrafluoroethylene membrane of $0.45\text{ }\mu\text{m}$ pore size) before analysis. The calibration was conducted using a PolyCALTM polystyrene standard (PS115K) from

Viscotek. To determine the molecular mass of the block copolymers, aliquots of the first block were taken and the molecular mass of the first block was determined by GPC. The molecular weights of the diblocks were then determined by combining the molecular weight M_n of the first block from GPC measurements with the block ratio of the diblock copolymer, which was obtained by integrating the ^1H NMR spectroscopic signal intensities of the respective blocks.

Transmission Electron Microscopy (TEM) Copper grids from Agar Scientific, mesh 400, were coated with a carbon film. Carbon coating was done using an Agar TEM Turbo Carbon Coater where carbon was sputtered onto mica sheets before deposition on the grids via flotation on water. The samples for electron microscopy were prepared by drop casting one drop (*ca.* 10 μL) of the micelle colloidal solution onto a carbon coated copper grid which was then placed on a piece of filter paper to remove excess solvent. Bright field TEM micrographs were obtained on a JEOL1200EX II microscope operating at 120 kV and equipped with an SIS MegaViewIII digital camera. Images were analyzed using the ImageJ software package developed at the US National Institute of Health. For the statistical length analysis, 300-400 cylinders were carefully traced by hand to determine the contour length. Each TEM micrograph was analyzed completely, *i.e.* every cylindrical micelle in each image was counted in order to reduce subjectivity. From this data L_n and L_w of each sample of monodisperse cylindrical micelles was calculated as shown below (L = length of object, N = number).

$$L_n = \frac{\sum_{i=1}^n N_i L_i}{\sum_{i=1}^n N_i} \quad L_w = \frac{\sum_{i=1}^n N_i L_i^2}{\sum_{i=1}^n N_i L_i}$$

Energy-dispersive X-ray analyses (EDX) were performed using an Oxford Instruments ISIS 300 system with silicon detector and beryllium window.

Dynamic Light Scattering (DLS)

Dynamic light scattering (173°) experiments were performed using a nano series Malvern zetasizer instrument equipped with a 633 nm red laser. Samples were analyzed in 1 cm glass cuvettes at 25 °C. For the purpose of the light scattering studies the refractive index of the block copolymers involved was assumed to be 1.60. The results of dynamic light scattering studies are reported as apparent hydrodynamic radius ($R_{H,app}$), acknowledging that the particles have been modeled as spheres in the experiments conducted.²

Table S1. Polymer Characterization Data

Sample	M_n first block (g/mol) ^a	Block ratio ^b	M_n diblock ^b	PDI ^a
PI ₆₃₇ - <i>b</i> -PFS ₅₃	43,400	12:1	56300	1.01
PFS ₂₈ - <i>b</i> -PDMS ₅₆₀	6,700	1:20	48200	1.02
PFS ₁₁₄ - <i>b</i> -PDMS ₈₁	27,600	1:0.71	33600	1.03
PFS ₆₀ - <i>b</i> -PDMS ₆₆₀	14,800	1:11	63700	1.06
PI ₂₂₀₀	150,000 ^c	N/A	N/A	1.06 ^c
1,2 PB ₁₉₂₀	104,000 ^d	N/A	N/A	1.08 ^d
1,4 PB ₁₈₄₀	107,500 ^d	N/A	N/A	1.08 ^d
PI ₅₁₄ - <i>b</i> -PEO ₂₅₀	35,000 ^d	1:0.48 ^d	46,000 ^d	1.06 ^d

^aDetermined by triple detection GPC analysis. ^bDetermined by relative integration of ¹H NMR signals from each block. ^cValues determined by conventional GPC using a polystyrene standard. ^dValues provided by PolymerSource.

Preparation of Polydisperse PI₆₃₇-*b*-PFS₅₃ Cylindrical Micelles

To a 100 mL vial containing 30 mg of PI₆₃₇-*b*-PFS₅₃ was added 60 mL of hexane. The sealed vial was immersed into an oil bath and heated to 70 °C for 2 hours. The clear pale yellow solution was cooled to room temperature and allowed to age for 3 days. TEM analysis of a

small aliquot showed the formation of polydisperse, cylindrical PI₆₃₇-*b*-PFS₅₃ micelles (Figure 1A).

1,1,3,3-Tetramethyldisiloxane (TMDS) Cross-Linked PI₆₃₇-*b*-PFS₅₃ Cylindrical Micelles Using Karstedt's Catalyst

2 mL of a polydisperse PI₆₃₇-*b*-PFS₅₃ micelle solution (0.5 mg/mL in hexane) was degassed by bubbling through N_{2(g)} for 10 minutes. 10 µL of Karstedt's Catalyst solution was then added to the micelle solution, followed by the addition of 3 µL of TMDS. The reaction mixture was left undisturbed for 18 hours after which the solution was passed through a short neutral Al₂O₃ column. TEM analysis of a small aliquot of the solution showed darkening of the micellar corona (Figure 1B). EDX analysis of the PI₆₃₇-*b*-PFS₅₃ micelles showed signals attributable to Fe, Si, Pt, and Cu (Figure S1).

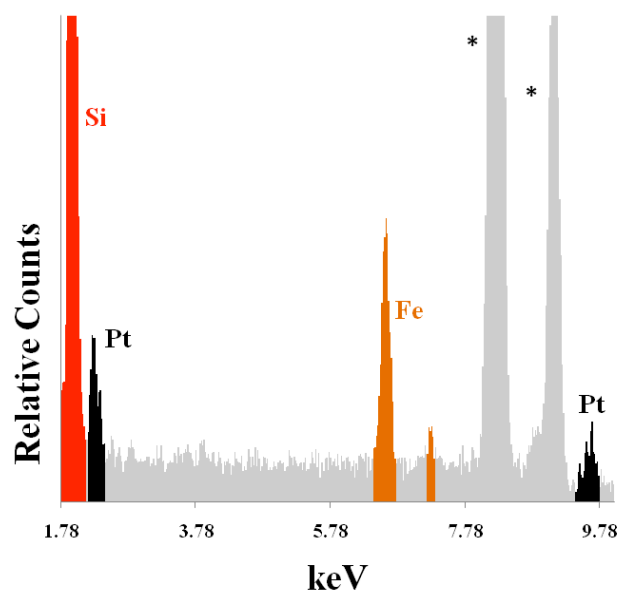


Figure S1. EDX spectrum of the TMDS/Pt cross-linked micelles showing signals attributable to Pt, Fe, and Si. The strong signals labeled with an asterisk (*) are attributed to copper from the TEM grid.

Karstedt's Catalyst-Induced Cross-Linking of Polydisperse PI₆₃₇-*b*-PFS₅₃ Cylindrical Micelles and Subsequent Cross-Linking Reversal with Dppe

To 10 mg of PI₆₃₇-*b*-PFS₅₃ polydisperse cylindrical micelles dispersed in 20 mL hexane was added 100 μ L of Karstedt's Catalyst (approx 10 mol % Pt with respect to olefin groups). The solution was allowed to age for 18 hours. TEM micrographs of a drop casted aliquot showed darkening of the corona (Figure 2A). A small aliquot (ca. 200 μ L) was dried with a N₂ stream and then resuspended in THF. TEM micrographs of a drop casted aliquot from the THF solution showed that the micelles did not dissolve in THF (Figure 2B). EDX line analysis showed the presence of Fe, Si, and Pt localized on the micelle (Figure S2).

Solid dppe (20 mg, 0.05 mmol) was added directly to the micelle dispersion in hexane. The colloidal solution was allowed to age for 2 hours. The clear solution became bright yellow in color. A small, approximately 1 mL aliquot of the yellow solution was dried and then redissolved in C₆D₆. ³¹P NMR spectroscopy showed dppe and dppe₂Pt as the only phosphorus containing compounds (Figure S5).³ The remaining yellow solution was passed through a short neutral alumina column to remove the dppe₂Pt. The pale yellow hexane solution was evaporated, leaving a yellow residue. The yellow residue was dissolved in 1 mL THF and added to stirring MeOH (20 mL). A yellow-orange precipitate was collected and dried under vacuum at 40 °C for 18 hours. The residue was identified by ¹H NMR spectroscopy and GPC as PI₆₃₇-*b*-PFS₅₃ copolymer. By ¹H NMR spectroscopy and GPC, PI₆₃₇-*b*-PFS₅₃ appeared unchanged after removal of the Pt cross-linking (Figure S3-S6). A total of 8.1 mg of PI₆₃₇-*b*-PFS₅₃ copolymer was collected. The yield was 81% based on 10 mg of PI₆₃₇-*b*-PFS₅₃ micelles.

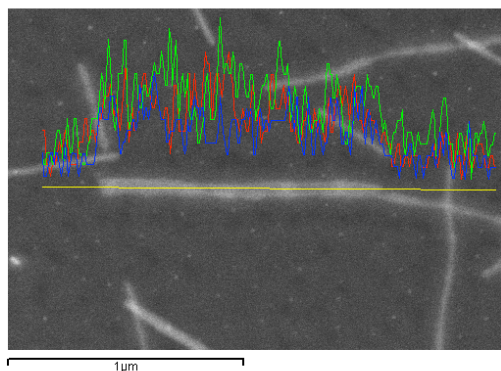


Figure S2. Dark field TEM micrograph and EDX line analysis of PI₆₃₇-*b*-PFS₅₃ cylindrical micelles after addition of Karstedt's Catalyst. For the EDX trace, silicon is red, iron is green, and platinum is blue.

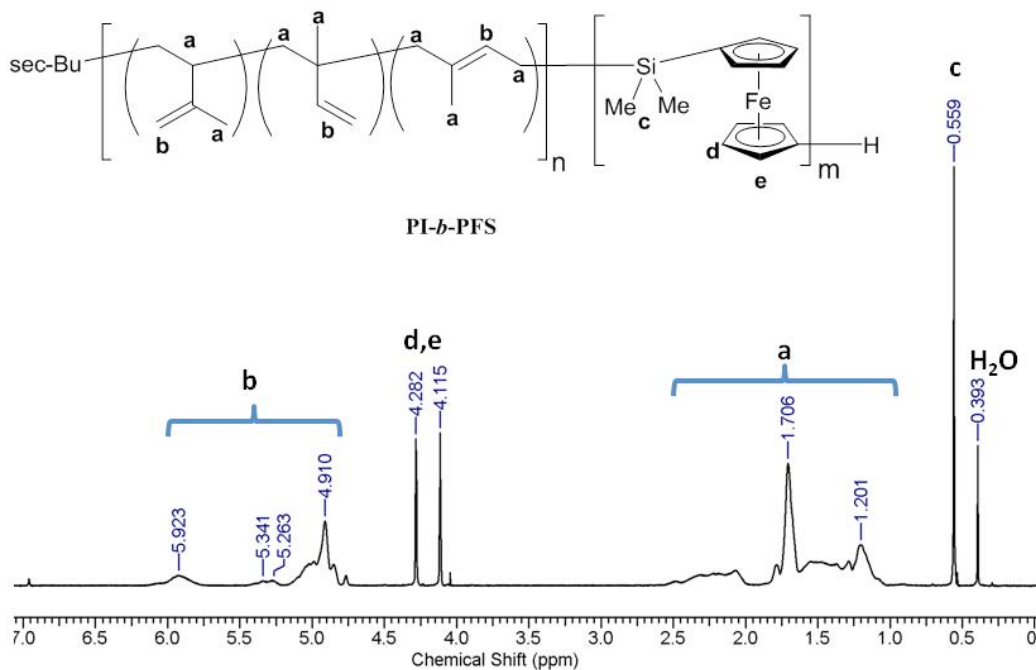


Figure S3. ¹H NMR spectrum (400 MHz, C₆D₆) of PI₆₃₇-*b*-PFS₅₃ diblock copolymer before cross-linking manipulations.

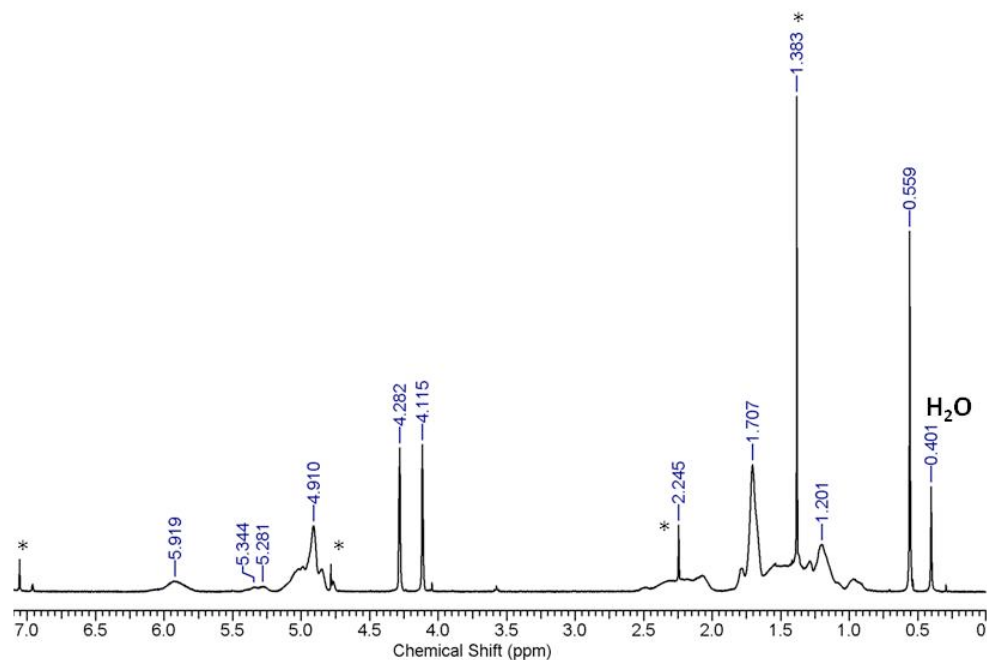


Figure S4. ^1H NMR spectrum (400 MHz, C_6D_6) of $\text{PI}_{637}\text{-}b\text{-PFS}_{53}$ diblock copolymer after removal of cross-linking. Signals marked with an asterisks (*) are attributed to butylated hydroxytoluene (BHT). BHT originates from the THF solvent used during polymer purification, where it is used as a radical stabilizer.

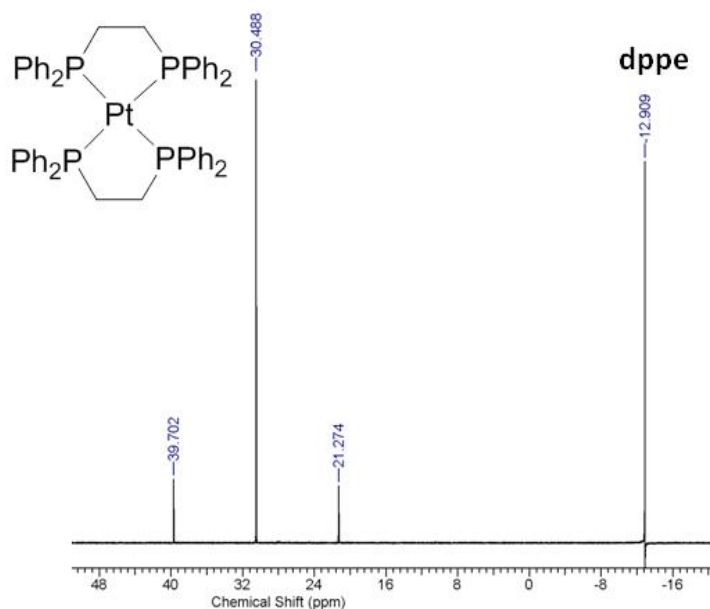


Figure S5. ^{31}P NMR spectrum (162 MHz, C_6D_6) of an aliquot of the micelle solution after the addition of dppe to Pt(0) cross-linked $\text{PI}_{637}\text{-}b\text{-PFS}_{53}$ micelles.

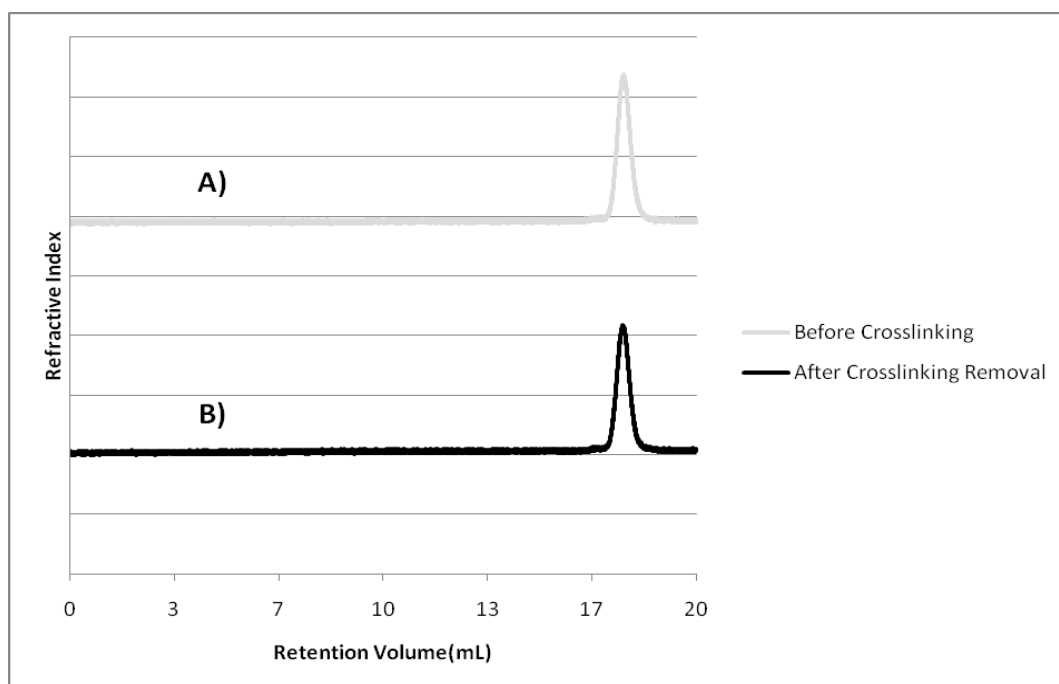


Figure S6. GPC traces of $\text{PI}_{637}\text{-}b\text{-PFS}_{53}$ diblock copolymer in THF. (A) Before cross-linking and (B) After removal of the cross-linking.

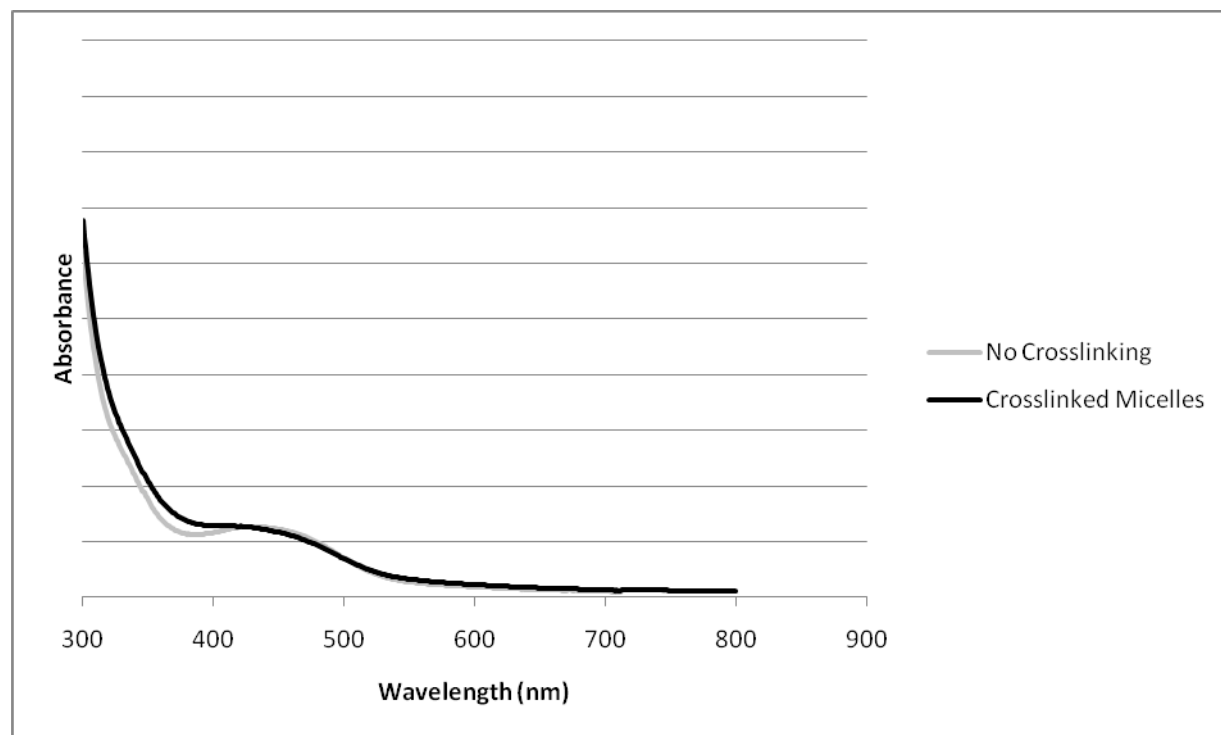


Figure S7. UV-Vis spectrum of 0.5 mg/mL $\text{PI}_{637}\text{-}b\text{-PFS}_{53}$ micelles in hexane before and after cross-linking with Karstedt's Catalyst.

Observation of Residual Vinyl Siloxane Ligands after $\text{PI}_{637}\text{-}b\text{-PFS}_{53}$ Micelle Cross-Linking with Karstedt's Catalyst

10 mg of $\text{PI}_{637}\text{-}b\text{-PFS}_{53}$ polydisperse micelles were cross-linked with Karstedt's Catalyst as described above. After cross-linking, the micelles were purified and collected as a small pellet from the hexane solution via centrifugation. The pellet was then suspended in C_6D_6 and 30 mg (0.075 mmol) of dppe was added. ^1H NMR analysis of the bright yellow solution showed signals attributable to 1,3-divinyldimethylsiloxane moieties which had originated from Karstedt's Catalyst (Figure S8).

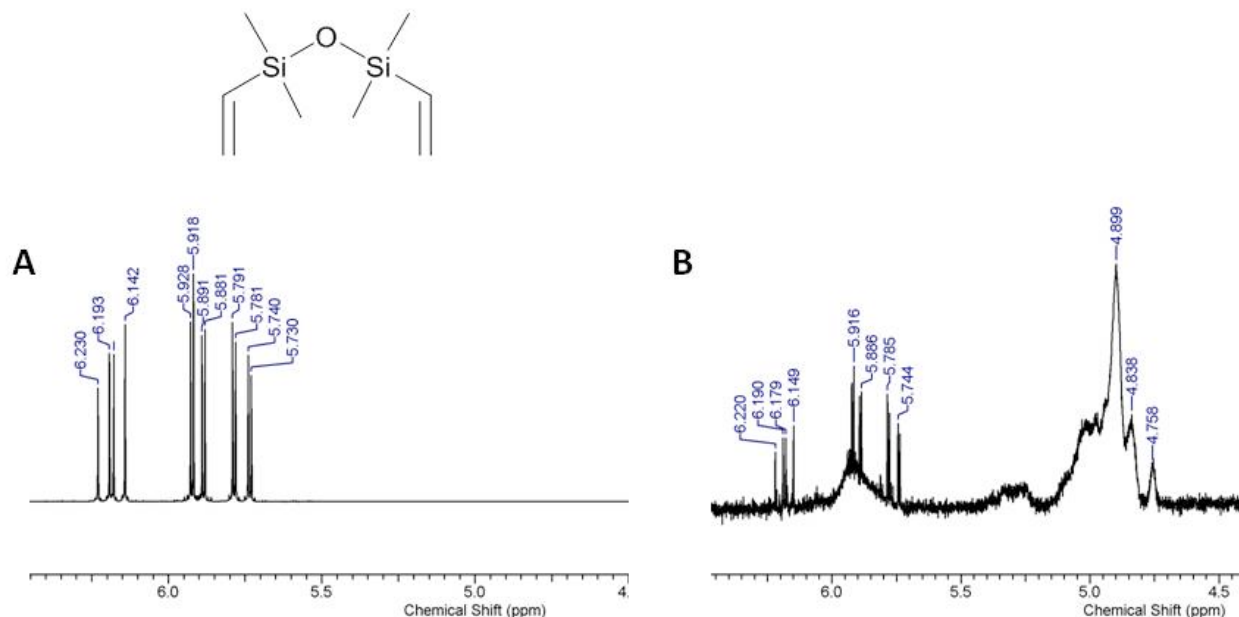
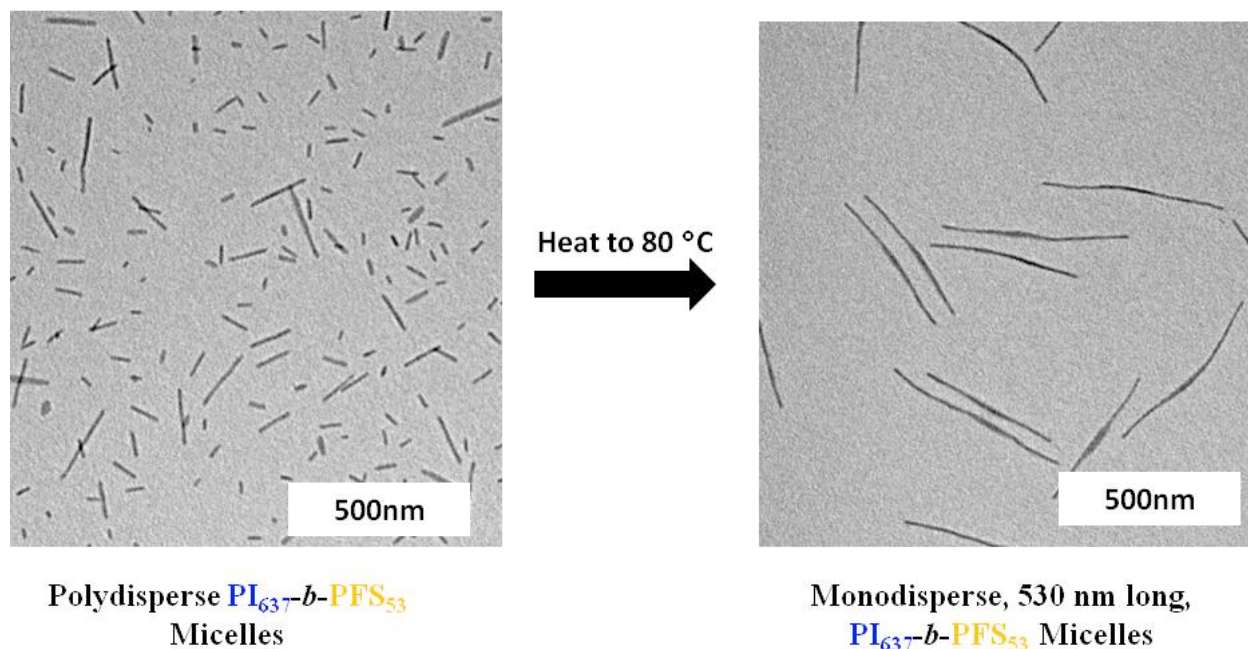


Figure S8. (A) Reference ^1H NMR spectrum (400 MHz, C_6D_6) of the vinyl region of 1,3-divinyltetramethyldisiloxane. B) ^1H NMR spectrum (400 MHz, C_6D_6) of the vinyl region of PI₆₃₇-*b*-PFS₅₃ after removal of cross-linking. Signals attributable to 1,3-divinyltetramethyldisiloxane and PI are visible.

Preparation of Monodisperse PI₆₃₇-*b*-PFS₅₃ Cylindrical Micelles with a Contour Length of 526 nm

Monodisperse PI₆₃₇-*b*-PFS₅₃ micelles were prepared following a literature procedure.⁴ First 10 mg of PI₆₃₇-*b*-PFS₅₃ was dissolved in 50 mL of decane by heating the solution to 80 °C for 2 hours. The pale yellow solution was allowed to cool to room temperature and aged for 3 days. The decane solution was sonicated for 25 minutes in a sonication bath at room temperature. After sonication, the resulting micelle dispersion consists of short, polydisperse, cylindrical micelles with a PI₆₃₇-*b*-PFS₅₃ concentration of 0.5 mg/mL in decane (Scheme S1).

A dispersion of monodisperse $\text{PI}_{637}\text{-}b\text{-PFS}_{53}$ cylindrical micelles was formed by taking a volume of the 0.5 mg/mL micelle solution, heating to 80 °C for 1 hour, and then cooling to room temperature and aging for 2 days.⁴ The resulting cylindrical micelles have an average contour length of 526 nm with a PDI of 1.03 as determined by TEM (Scheme S1, Figure 3A, and Table 1).



Scheme S1. TEM micrographs of the formation of monodisperse $\text{PI}_{637}\text{-}b\text{-PFS}_{53}$ cylindrical micelles through a self-seeding process.⁴

Pt(0) Cross-Linking of Monodisperse $\text{PI}_{637}\text{-}b\text{-PFS}_{53}$ Cylindrical Micelles

Pt(0) cross-linking of the monodisperse $\text{PI}_{637}\text{-}b\text{-PFS}_{53}$ cylindrical micelles was performed in an identical fashion to the cross-linking of polydisperse $\text{PI}_{657}\text{-}b\text{-PFS}_{53}$ micelles (see above).

Sonication of (Both Cross-Linked and Non-Cross-Linked) Monodisperse PI₆₃₇-*b*-PFS₅₃ Cylindrical Micelles

2.0 mL (0.5 mg/mL PI₆₃₇-*b*-PFS₅₃) of the monodisperse micelle solution (either cross-linked or not cross-linked) was placed in a 7 mL vial and positioned in an ultrasonic bath for 10 minutes at room temperature. TEM micrographs of non-cross-linked PI₆₃₇-*b*-PFS₅₃ cylindrical micelles after sonication showed a significant decrease in micelle contour length (Figure 3B, Table 1). DLS measurements of the non-cross-linked micelle solutions before and after sonication showed a significant decrease in the $R_{H,app}$ of the micelles (Figure S9A and Table S2). TEM micrographs of cross-linked PI₆₃₇-*b*-PFS₅₃ micelles showed very little change in micelle contour length after sonication (Figure 3D, Table 1). DLS measurements of the cross-linked micelle solutions before and after sonication showed very little change in the $R_{H,app}$ of the micelles (Figure S9B and Table S2).

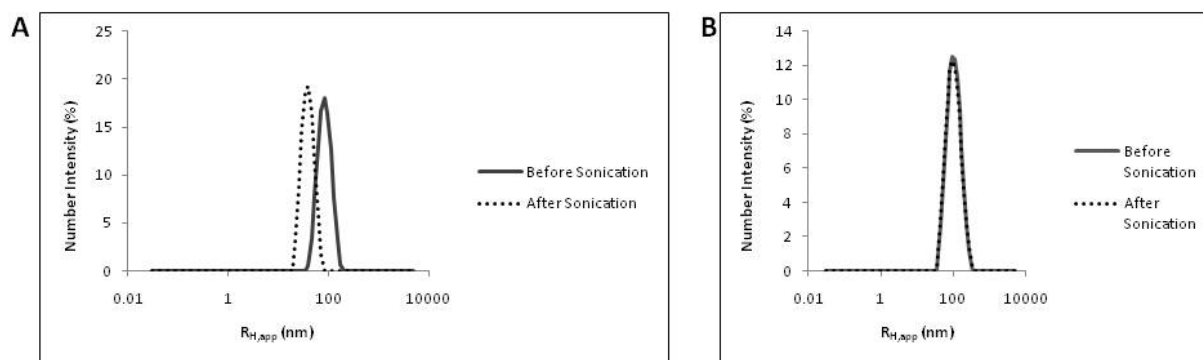


Figure S9. (A) CONTIN plots of the DLS data of non-cross-linked monodisperse PI₆₃₇-*b*-PFS₅₃ cylindrical micelles in decane before and after undergoing sonication for 10 minutes. (B) CONTIN plots of the DLS data of Pt-cross-linked monodisperse PI₆₃₇-*b*-PFS₅₃ cylindrical micelles in decane before and after undergoing sonication for 10 minutes. The $R_{H,app}$ values are determined using a hard sphere model which does not take into account the cylindrical structure of the PI₆₃₇-*b*-PFS₅₃ micelles. This led to the discrepancy between $R_{H,app}$ and the micelle contour lengths measured by TEM.²

Table S2. Results of DLS experiments for colloidal solutions of cross-linked and non-cross-linked 526 nm monodisperse PI₆₃₇-*b*-PFS₅₃ micelles before and after undergoing sonication for 10 minutes. The smaller $R_{H,app}$ compared to the micelle contour length in the TEM micrographs is a consequence of modeling the micelles as spheres in the DLS experiment.² The smaller $R_{H,app}$ of the cross-linked micelles compared to the non-cross-linked micelles is probably due to the inclusion of platinum in the corona of the cross-linked micelles.

Sample	$R_{H,app}$ (nm)	PDI
Not cross-linked, before sonication	76.1	0.06
Not cross-linked, after sonication	32.8	0.07
Cross-linked, before sonication	62.3	0.21
Cross-linked, after sonication	61	0.19

Preparation of PFS₆₀-*b*-PDMS₆₆₀ Cylindrical Micelles

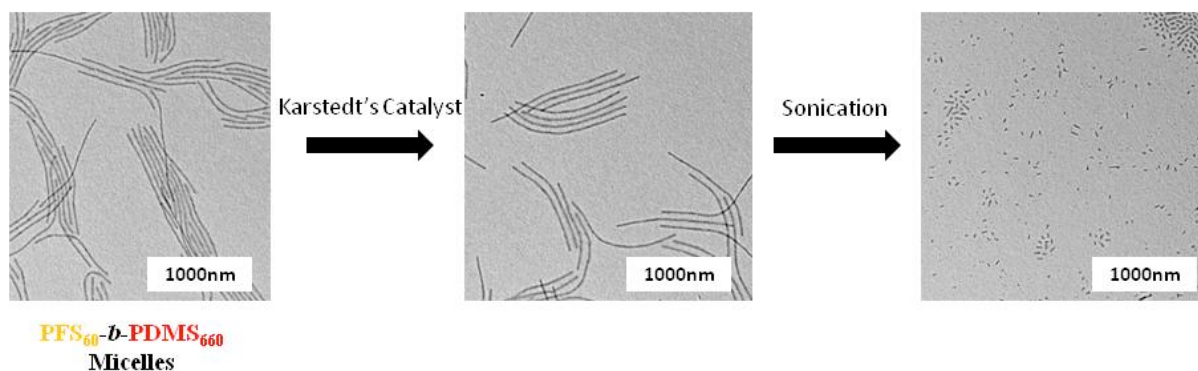
Approximately 1000 nm long PFS₆₀-*b*-PDMS₆₆₀ cylindrical micelles were formed by adding 50 μ L of a PFS₆₀-*b*-PDMS₆₆₀ THF solution (50 mg/mL) to a stirring 5 mL hexane colloidal dispersion of 0.1 mg of short, stub-like PFS₂₈-*b*-PDMS₅₆₀ cylindrical seed micelles.⁵ This solution was allowed to age for 2 days.

Attempted Pt(0)-Induced Cross-Linking and Subsequent Sonication of PFS₆₀-*b*-PDMS₆₆₀ Cylindrical Micelles

To 1 mg of PFS₆₀-*b*-PDMS₆₆₀ cylindrical micelles dissolved in 2 mL of hexane was added 15 μ L of Karstedt's Catalyst (approximately 20 mol % Pt with respect to PDMS repeat unit). The solution was allowed to age for 18 hours. Darkening of the micelle corona was not evident in TEM micrographs of drop casted aliquots from the hexane solution (See Scheme S2). A small aliquot of the micelle solution was dried with a N₂ stream and then resuspended in THF, a good solvent for both PFS and PDMS. Micelles were not observed in TEM micrographs of a drop casted aliquot from the THF solution, which was consistent with the disassembly of the PFS₆₀-*b*-PDMS₆₆₀ micelles into unimers.

The 2 mL hexane solution of PFS₆₀-*b*-PDMS₆₆₀ with Karstedt's Catalyst was placed in a 7 mL vial and positioned in an ultrasonic bath for 10 minutes at room temperature. TEM micrographs of a drop casted aliquot taken from the micelle solution after sonication showed a significant decrease in micelle contour length (See Scheme S2).

The attempted cross-linking of PFS₆₀-*b*-PDMS₆₆₀ micelles was repeated with 5, 10, and 15 μ L of Karstedt's Catalyst. In each case there was no evidence of micelle cross-linking.



Scheme S2. TEM micrographs of aliquots of cylindrical PFS₆₀-*b*-PDMS₆₆₀ micelles before, after addition of Karstedt's Catalyst, and after subsequent sonication.

Preparation of M(PFS-*b*-PDMS)-*b*-M(PI-*b*-PFS)-*b*-M(PFS-*b*-PDMS)-*b*-M(PI-*b*-PFS)-*b*-M(PFS-*b*-PDMS) Pentablock Micelles

PFS₆₀-*b*-PDMS₆₆₀ cylindrical micelles with a contour length of approximately 150 nm were formed by adding 1.2 mL of a PFS₆₀-*b*-PDMS₆₆₀ THF solution (10 mg/mL) to a stirring 122 mL hexane solution containing 3 mg of short, stub-like PFS₂₈-*b*-PDMS₅₆₀ cylindrical micelles.⁵ This solution was allowed to age for 2 days.

30 μ L of a PI₆₃₇-*b*-PFS₅₃ THF solution (50 mg/mL) was added to 10 mL of the hexane suspension of PFS₆₀-*b*-PDMS₆₆₀ cylindrical micelles. After aging for 2 days, 100 μ L of a PFS₆₀-*b*-PDMS₆₆₀ THF solution (10 mg/mL) was then added and the micelle suspension was aged for a further 2 days. After the completion of these procedures, the micelles were expected to have a

corona block composition of PDMS-PI-PDMS-PI-PDMS. Analysis by TEM was unable to differentiate between the corona blocks (Figure 4A).

The PI corona domains of the cylindrical pentablock comicelles were cross-linked with Karstedt's Catalyst as described above. After cross-linking, the PI corona appeared much darker in TEM micrographs and was now distinguishable from the PDMS domains (Figure 4B). EDX line analysis showed the localization of Pt on the PI corona regions (Figure S10).

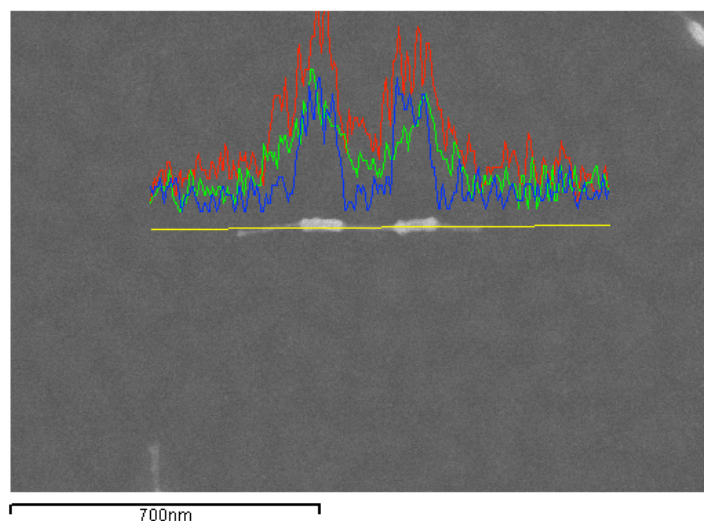


Figure S10. Dark field TEM micrograph and EDX line analysis of a $M_{(PFS-b-PDMS)}-b-M_{(PI-b-PFS)}-b-M_{(PFS-b-PDMS)}-b-M_{(PI-b-PFS)}-b-M_{(PFS-b-PDMS)}$ pentablock cylindrical micelle after addition of Karstedt's Catalyst. For the EDX trace, silicon is red, iron is green, and platinum is blue.

Preparation of $PI_{514}-b-PEO_{250}$ Spherical Micelles and Cross-Linking with Karstedt's Catalyst

2.0 mg of $PI_{514}-b-PEO_{250}$ was dissolved in 5 mL of THF in a 20 mL capped vial. 2 mL of decane was added to the $PI_{514}-b-PEO_{250}$ solution. The cap was removed from the vial and the THF was

allowed to evaporate over 3 days leaving behind approximately 2 mL of decane. DLS measurements of the solution were consistent with the formation of small spherical micelles with a $R_{H, app}$ of 25 nm and a PDI of 0.39 (Figure S11).

A 0.5 mL aliquot of the $PI_{514}-b-PEO_{250}$ micelles in decane was placed in a 7 mL vial. 5 μ L of Karstedt's Catalyst solution was added to the mixture and the solution was allowed to age for 1 day. TEM micrographs of a drop casted aliquot showed the presence of dark spheres, consistent with Pt stained $PI_{514}-b-PEO_{250}$ spherical micelles (Figure S12A). 4.5 mL of THF was then added to the mixture to form a solution with a 1:9 decane/THF ratio. TEM micrographs of a drop casted aliquot showed that the dark spheres persist in the 1:9 decane/THF solution, which is consistent with cross-linking of the $PI_{514}-b-PEO_{250}$ spherical micelles (Figure S12B). As THF is a good solvent for both PI and PEO, in the absence of cross-linking, $PI_{514}-b-PEO_{250}$ micelles should dissolve into unimers in a 1:9 decane/THF solution. DLS measurements of a 1:9 decane/THF solution of non-cross-linked $PI_{514}-b-PEO_{250}$ (5.0 mg/mL) gave a $R_{H, app}$ value of 8.3 nm and a PDI of 0.28 and is consistent with non-aggregated polymer chains in solution.

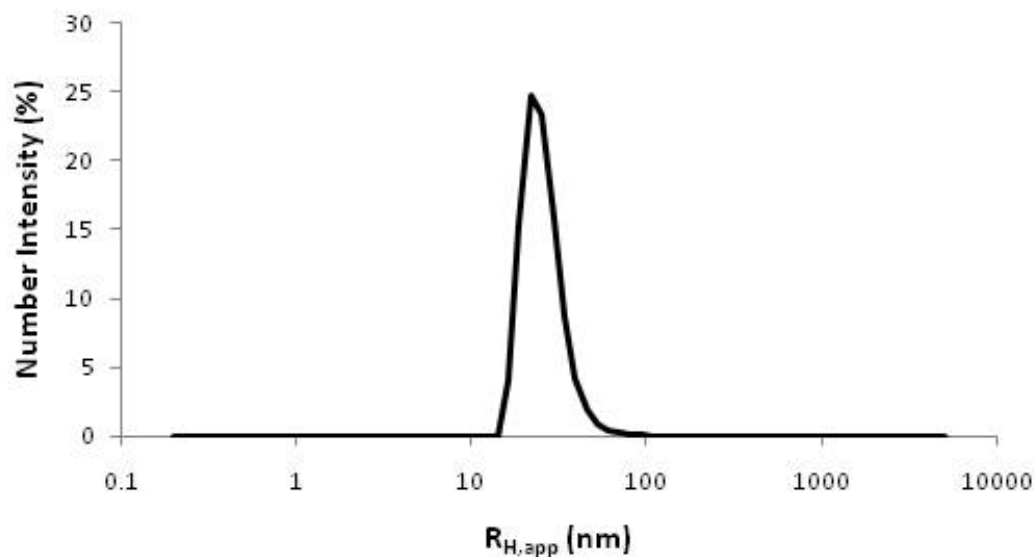


Figure S11. CONTIN plot of the DLS data for spherical PI₅₁₄-*b*-PEO₂₅₀ micelles in decane after removal of THF by slow evaporation.

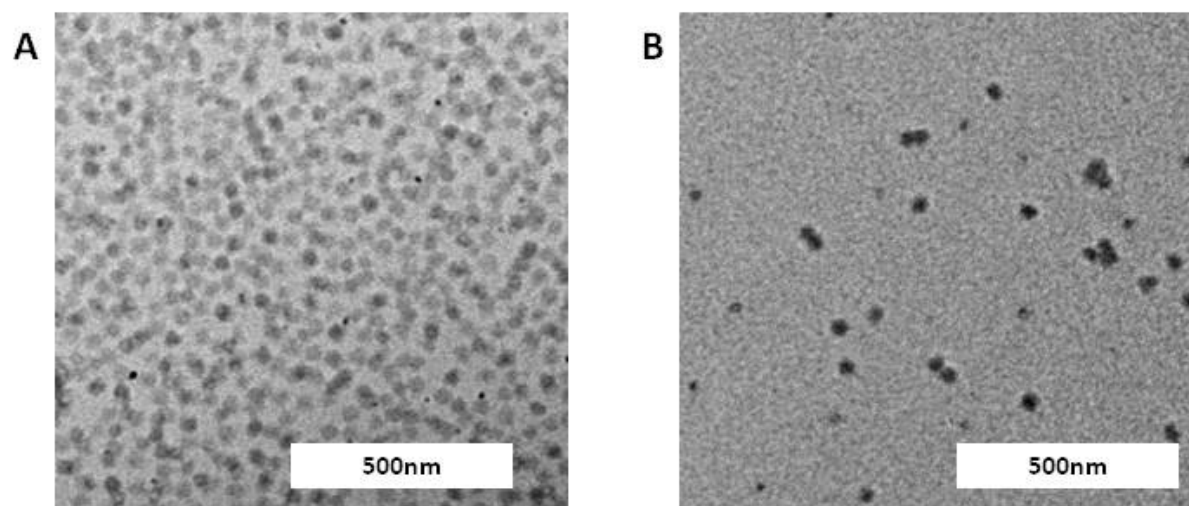


Figure S12. (A) TEM micrograph of PI₅₁₄-*b*-PEO₂₅₀ spherical micelles drop casted from a decane solution after addition of Karstedt's Catalyst (10 mol % Pt/olefin). (B) TEM micrograph of cross-linked PI₅₁₄-*b*-PEO₂₅₀ spherical micelles drop casted from a decane/THF (1:9) solution.

As THF is a good solvent for both PI and PEO, in the absence of cross-linking, PI₅₁₄-*b*-PEO₂₅₀ micelles should dissolve into unimers in a 1:9 decane/THF solution

Preparation of PFS₁₁₄-*b*-PDMS₈₁ Platelets

1.0 mg of PFS₁₁₄-*b*-PDMS₈₁ was placed in a solution composed of 18 mL decane and 2 mL xylenes. The solution was heated to 110 °C for 2 hours while stirring. After this time the stirring was stopped. The solution was cooled to 70 °C and kept at this temperature for 18 hours. Finally, the solution was cooled to room temperature and placed in a ultrasonication bath for 2 minutes to break up some of the larger platelet formations.⁶ TEM analysis showed the formation of platelet structures (Figure 5A).

Preparation of Scarf-Like Micelles

10 µL of a PI₆₃₇-*b*-PFS₅₃ THF solution (10 mg/mL) was added to 1 mL of the PFS₁₁₄-*b*-PDMS₈₁ platelet solution described above. The solution was allow to age for 2 days at room temperature. Analysis of an aliquot of the solution by TEM showed the formation of scarf-like micelles (Figure 5B).

Pt(0) cross-linking of the scarf-like micelles was performed in the same manner described in the cross-linking of the PI₆₃₇-*b*-PFS₅₃ cylindrical micelles above. After cross-linking, the PI corona domains were visible in the TEM (Figure 5C).

100 μ L of the scarf-like micelles solution was added to 1 mL of THF. TEM micrographs of an aliquot from the THF solution showed that the PDMS regions of the scarf-like micelles selectively dissolved away leaving the cross-linked PI_{637-*b*}-PFS₅₃ domains intact (Figure 5D).

Preparation of a PI₂₂₀₀ Polymer Gel Cross-Linked with Pt(0)

50 mg of PI₂₂₀₀ was added to 670 μ L of toluene. The solution was heated to 50 °C to help dissolution of the PI₂₂₀₀. At room temperature, 330 μ L of Karstedt's Catalyst (5 mol % relative to olefin groups) in xylenes was added to the PI₂₂₀₀ toluene solution. The final concentration of PI₂₂₀₀ in the toluene/xylenes solution is 50 mg/mL. The solution was allowed to age undisturbed for 18 hours. After 18 hours, the mixture solidified to form a gel.

Attempts to form polymer gels with 1,2-PB₁₉₂₀ and 1,4-PB₁₈₄₀ were performed using identical experimental procedures.

Addition of dppe to a Pt(0) Cross-Linked PI₂₂₀₀ Polymer Gel

To the surface of a 50 mg/mL PI₂₂₀₀ polymer gel in toluene/xylenes was added dppe (30 mg, 0.075 mmol). Where the dppe contacted the gel, de-gelation occurred and a bright yellow solution formed. The dppe/gel mixture was allowed to age for 2 hours. After 2 hours, de-gelation was complete and the resulting solution was a bright yellow color. A small aliquot of the yellow solution was dried and then redissolved in C₆D₆. ³¹P NMR spectroscopy showed dppe and dppe₂Pt as the only phosphorus containing compounds.

The toluene/xylenes solution was evaporated to leave a yellow residue. The residue was suspended in hexane and passed through a short neutral alumina column. The hexane was then

removed by evaporation, leaving a colorless residue. The colorless residue was dissolved in 1 mL THF and added to a stirring 20 mL MeOH solution. A white precipitate formed, was collected, and then dried under vacuum at 40 °C for 18 hours. The residue was identified by ^1H NMR spectroscopy and GPC as PI₂₂₀₀. By ^1H NMR spectroscopy and GPC, PI₂₂₀₀ appeared unchanged after cross-linking removal (Figures S13 – S15). A total of 41.5 mg of PI₂₂₀₀ was collected. Yield was 83% based on 50 mg of PI₂₂₀₀.

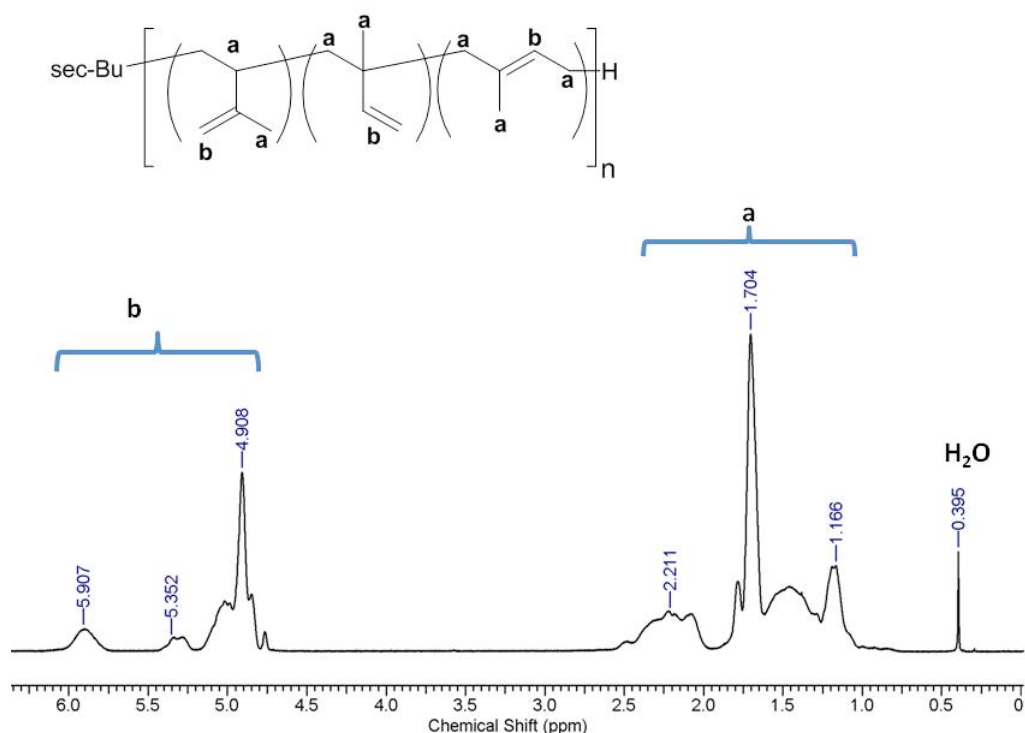


Figure S13. ^1H NMR spectrum (400 MHz, C_6D_6) of PI₂₂₀₀ homopolymer before cross-linking manipulations.

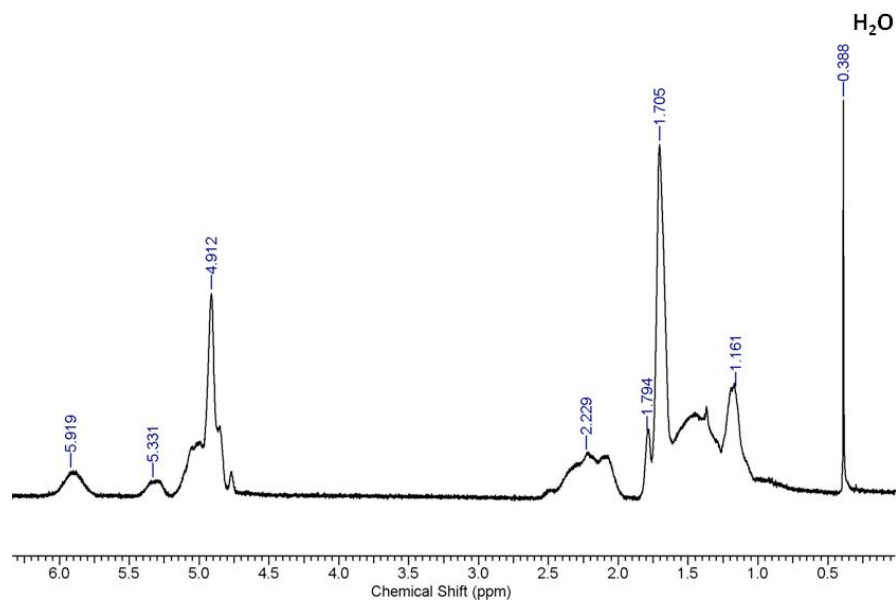


Figure S14. ^1H NMR spectrum (400 MHz, C_6D_6) of PI₂₂₀₀ homopolymer after removal of cross-linking.

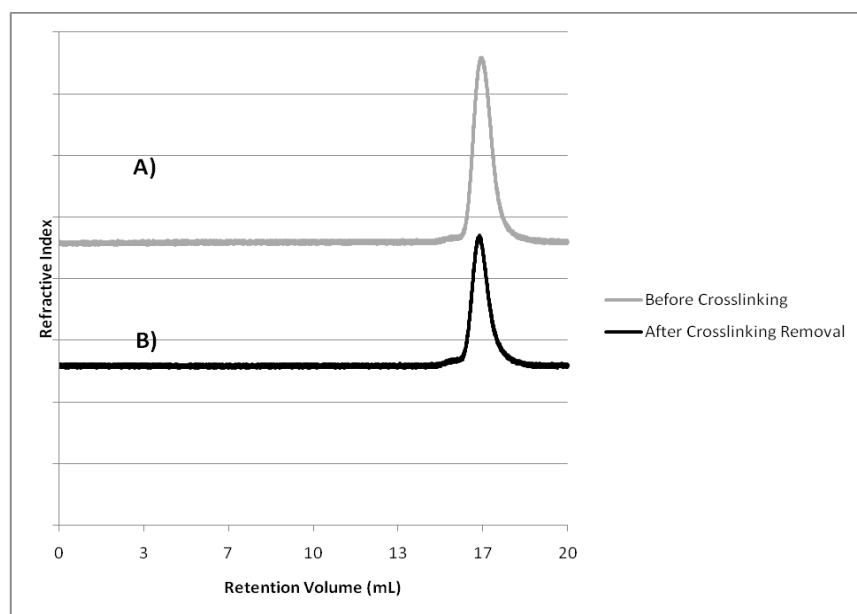


Figure S15. GPC traces of PI₂₂₀₀ homopolymer in THF (A) before cross-linking and (B) after cross-linking removal.

Preparation of a PI₂₂₀₀ Polymer Gel Cross-linked with TMDS

50 mg of PI₂₂₀₀ was dissolved in 1.0 mL of toluene. 6 μ L of Karstedt's Catalyst (0.1 mol % relative to olefin groups) in xylenes was added to the PI₂₂₀₀ toluene solution. 13 μ L of TMDS (20 mol % Si-H relative to olefin groups) was added to the solution. The solution was allowed to age undisturbed for 18 hours. After 18 hours, the mixture solidified to form a gel. After gel formation, dppe (30 mg, 0.075 mmol) was added to the surface. The surface of the gel turned yellow but did not de-gel.

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