Experimental Section

Materials and Methods. All chemicals were purchased from Aldrich Chemical Company and were used directly without further purification unless otherwise indicated. All solvents were aspirated with nitrogen gas before use. \(^1\)H NMR spectra were recorded on a JEOL ECS 500 spectrometer (500MHz). GPC was carried out on a Viscotek 270 instrument with a triple detector array (RALS, IV, RI, or UV) equipped with 2 GMHHR-M and 1 GMHHR-L mixed bed ViscoGel columns (eluent: THF; flow rate: 1 mL min\(^{-1}\)). All atomic force microscopy (AFM) images were recorded in air under ambient conditions on PicoScan 2500 (Agilent Technologies formerly Molecular Imaging, Corp.) equipped with an 8 \(\times\) 8 \(\mu\)m scanner. Intermittent contact mode was used for all imaging. The AFM tip used was a silicon-nitride AFM probe from Ted Pella Inc. UV-vis measurements were taken on an Agilent technologies 8453 spectrometer.

2,9-di(p-anisyl)-1,10-phenanthroline was prepared by adapting the procedure reported by Becher et al. \(^1\) p-bromoanisole 4.23 mL (34 mmol) was dissolved in 100 mL degassed ether. After cooling the solution to -30 \(^\circ\)C, tert-BuLi 50 mL (1.7 mol/L, 85 mmol) was added by
cannula. After stirring this mixture for 1.5 h, it was transferred to the solution of pre-dried 1, 10-
N, N phenanthroline (1.76 g, 9.78 mmol) in 20 mL degassed toluene. The reaction mixture then
stirred under nitrogen for 40 h. After hydrolysis at 0 °C with water, the bright yellow toluene
layer was decanted and aqueous layer extracted three times with dichloromethane. The combined
organic layer was rearomatized by addition of MnO₂ (35 g), with efficient stirring. The yellow
color partially disappeared. After MnO₂ was filtered and solvent removed, the crude product was
recrystallized from toluene. Final purification was achieved by silica column chromatography
using dichloromethane/methanol (100:1) as eluent to yield 1.6 g (3.9 mmol, 40%) of an
amorphous white solid. ¹H NMR (CDCl₃): 8.42 (m, 4H, Ho), 8.30 (d, 2H, H₄, 7), 8.11 (d, 2H, H₃,
8), 7.78 (s, 2H, H₅, 6), 7.14 (m, 4H, H₅), 3.92 (s, 6H, -OCH₃).

Scheme S1. Synthetic scheme for the ATRP initiator (1)
2, 9-di(p-phenol)-1, 10-phenanthroline was prepared by the procedure reported by Sauvage et al. Technical grade pyridine (16 mL) was placed in a 100 mL three-necked round-bottomed flask fitted with a thermometer and a magnetic stirrer. With rapid stirring concentrated hydrochloric acid (17.6 mL) was added. The flask was equipped for distillation, and water was distilled from the mixture until its internal temperature rose to 210 °C. After cooling to 140 °C, 2, 9-di(p-anisyl)-1, 10-phenanthroline (6.27 g, 16 mmol) was added as a solid and the reaction flask was fitted with a reflux condenser connected to a source of argon. The yellow mixture was stirred and refluxed for three hours (190 °C-220 °C). The hot reaction mixture was then diluted with 10 mL warm water and slowly poured into 60 mL hot water. The resulting bright yellow suspension was refrigerated overnight. After cooling, the precipitated solid was filtered by suction and washed with cold water. Crude acidic 2, 9-di (p-phenol)-1, 10-phenanthroline was suspended (it dissolves partially) in an ethanol-water mixture (250/8.5 mL) and neutralized with a dilute NaOH solution. After this pH-meter monitored neutralization (end-point: pH = 7.321, solution was diluted with hot water (300 mL). Neutral 2, 9-di (p-phenol)-1, 10-phenanthroline precipitated as beige solid during cooling down. Filtrated by suction, it was air dried to yield 5.85 g of an ochre solid. Upon further drying (high vacuum in presence of P2O5) the latter turned bright red (5.31 g, 92% yield) and could be utilized without further purification. 1H NMR (Deuterated DMSO): 9.88 (s, 2H, -OH); 8.33 (d, 2H, H4, 7); 8.31 (d, 4H, Ho); 8.25 (d, 2H, H3, 8); 7.88 (s, 2H, H5, 6); 6.97(d, 4H, Hm).

Bromo ethyl, 2-bromo propionic acid ester was prepared by mixing 2-bromo propionic acid 1.22 g (4 mmol), 2-bromoethanol 0.5 g (4 mmol) and DMAP 146.4 mg (0.6 mmol) in dry CH2Cl2 and followed by slow addition of DCC 2.3 g (4.4 mmol) to reaction mixture. The solution was stirred overnight under argon atmosphere. After that solution was filtered to remove
DCU solid and evaporation of solvent yields colorless liquid. The product was further purified by column chromatography using dichloromethane as an eluent to yield colorless liquid (1.5 g, 78.9% yield). $^{1}$H NMR (CDCl$_3$): 4.41 (t, 2H, -CH$_2$-O(CO)), 4.39 (q, 1H, -CH(Me)Br), 3.49 (t, 2H, -CH$_2$Br), 1.77 (d, 3H, -CH$_3$).

**ATRP initiator (1)** was prepared by mixing 2, 9-di(p-phenol)-1,10-phenanthroline 0.364 g (1 mmol), bromo ethyl, 2-bromo priopionic acid ester 0.138 g (2 mmol), anhydrous K$_2$CO$_3$ 0.264 g (10 mmol), 18-c-6 74 mg (0.1 mmol) in acetone and stirred overnight at room temperature under argon atmosphere. The solvent was evaporated under vacuum and the residue was extracted by CH$_2$Cl$_2$. The organic layer was washed twice with 1M HCl and one time with water. The organic layer was then dried by anhydrous sodium sulfate and the solvent was evaporated to yield a crude product, which was further purified by recrystalization using toluene as solvent to yield a yellow solid (0.5 g, 68.8% yield). $^{1}$H NMR (CDCl$_3$): 8.41 (m, 4H, H o), 8.25 (d, 2H, H 4, 7), 8.08 (d, 2H, H 5, 6), 7.74 (s, 2H, H 3, 8), 7.10 (m, 4H, H m), 4.95 (q, 2H, -CH(Me)Br), 4.51 (t, 4H, -CH$_2$-O(CO)), 3.52 (t, 4H, -PhOCH$_2$), 1.71 (d, 6H, -CH$_3$). Anal. calc. for C$_{36}$H$_{30}$N$_2$O$_6$Br$_2$: C, 56.53; H, 4.19; N, 3.88; Br, 22.12 Found: C, 56.47; H, 4.43; N, 4.04; Br, 20.84.

**PS complex (3)** was synthesized by using a reported procedure$^3$ of polymerization of styrene in nitrogen-filled tubes. The general synthetic procedure is as follows: 430 mg (4.1 mmol) styrene, 12.7 mg (0.0278 mmol) HMTETA, 10 mg (0.0138 mmol) initiator 1, 3.1 mg (0.0278 mmol) Cu(CH$_3$CN)$_4$BF$_4$ and 3.97 mg (0.0278 mmol) Cu(I)Br were mixed in 5 mL anisole. After the mixture was degassed by three freeze-evacuate-thaw cycles, the tube was sealed under vacuum and then subjected to polymerization in oil bath at 110 °C under nitrogen atmosphere for 5 h. The reaction was terminated by exposing to atmosphere oxygen and the copper residue was removed by passing through neutral alumina. After concentrating the polymer solution, the polymer was
precipitated from cold methanol and was characterized by GPC (Mn 6,405 g/mol, PDI 1.22, \( R_h \) 4.92 nm) and \(^1\)H NMR (CDCl3): 8.41 (m, 2H, \( H_o \)), 8.26 (d, 1H, \( H_4 \), \( \gamma \)), 8.08 (d, 1H, \( H_3 \), s), 7.75 (s, 1H, \( H_5 \), \( \delta \)), 7.11 (m, 2H, \( H_m \)), 7.2-6.4 (broad, \( H_{\text{PS aromatic}} \)), 4.97 (d, 1H, -CH(Ph)Br), 4.53 (t, 2H, -\((\text{CO})\text{OCH}_2\)), 3.53 (t, 2H, -PhOCH\(_2\)), 2.0-1.3 (broad, \( H_{\text{PS aliphatic}} \)), 1.72 (d, 3H, -CH\(_3\)) as shown in Fig. 2 and S1 respectively.

The intramolecular ATRC of PS complex (3) was performed as reported in literature.\(^4\) A 500 mL Schlenk flask containing a 100 mL THF solution of CuBr (574 mg, 4.0 mmol, 40 mM) and nanosized copper (254 mg, 4.0 mmol, 40 mM) was sealed with a rubber septum, evacuated with 4 freeze-pump-thaw cycles, backfilled with N\(_2\), and sealed from the Schlenk line. The flask was then placed in an oil bath and was stirred at 75 °C. After allowing the metal solution to reach the temperature of the bath, Me\(_6\)TREN (1.07 mL, 4.0 mmol, 40 mM) was introduced via a nitrogen-flushed syringe. A syringe pump held a 50 mL syringe containing an 18 mL THF solution of PS complex (3) (Mn = 6,405 g/mol, 5.5 mg; 1.383 µmol; 76.3 µM solution), which had separately been subjected to three freeze-pump-thaw cycles and backfilled with N\(_2\). The solution of PS complex (3) was slowly dripped through a needle piercing the rubber septum into the stirring THF solution of the metal ligand, over approximately 24 h (approximate rate = 0.75 mL/h, 2 µmol/h). After the contents of the syringe had been added to the reaction mixture, the reaction mixture was stirred for an additional 1 h. The resulting polymer was passed through an alumina column and precipitated into cold methanol prior to characterization by GPC (Mn 4,188 g/mol, PDI 1.56, \( R_h \) 4.58 nm) and AFM analysis as shown in Fig.2 and S2, respectively.

Demetallation of PS catenanes (4) was performed as per following procedure.\(^1\) KCN (0.1 g, 1.53 mmol) dissolved in water (10 mL) were added to PS catenanes (4) (3.5 mg, 0.88 µmol) in 40 mL mixture of THF: methanol (3:1) and stirred for 24 h at room temperature. After stirring
THF was evaporated to under vacuum and resulting precipitates of polymers were isolated by centrifugation. After purifying by re-dissolving in THF and precipitating out from methanol, the resulting PS catenanes was characterized by GPC as shown in Figure S3.

**Fig. S1** $^1$H-NMR analysis of the PS complex (3).
**Fig. S2** (a) AFM topography image of the PS catenanes on mica, (b) 3-D representation of the representative PS catenanes from (a), (c) 3-D image of #3 in (a), and (d) AFM amplitude image of the PS catenanes.
Catenane is derived from the Latin catena meaning "chain". A catenane is a mechanically-interlocked molecular architecture consisting of two or more interlocked macrocycles. The interlocked rings cannot be separated without breaking the covalent bonds of the macrocycles. AFM imaging on mica reveal a majority of the structures as composed of catenanes of various conformations. Statistically, other structures could represent partial open arms or intermolecular coupling of the 4 arms of PS complex (3). But the formation of the catenanes from the AFM is clear.

Fig. S3 The GPC traces of the PS catenanes (5) after demetallation.

Again, the interlocked ring structure of PS catenanes was clearly evident by the GPC traces of the demetalleted PS catenanes (Fig. S3), which shows that MW of PS catenanes (5) same as MW of PS catenanes (4) because of its interlocked cyclic structure. However the
shoulder peak at 26.2 mL indicates presence of acyclic PS complex (3) as an impurity in the ATRC product, which upon demetallation yields acyclic PS with approximately half the MW of PS complex (3).

To investigate the stability of initiator complex (2) during polymerization and to support the UV analysis of PS complex (3), demetallation of the PS complex (3) (Mn 4,341 g/mol, PDI 1.25) was performed and analyzed by GPC as shown below.

![GPC traces of the demetallation study of PS complex (3).](image)

**Fig. S4** The GPC traces of the demetallation study of PS complex (3).

The demetallation of PS complex (3) was performed using the same procedure as followed for PS catenanes (4). The GPC traces show the appearance of peak at a higher retention volume with a molecular weight (Mn 2,738 g/mol) that is approximately half of the molecular weight of the PS complex (3). This result clearly indicates that the initiator complex (2) is efficient enough to polymerize styrene and that the resulting polymers have a polymer-metal complex architecture.
References:


