Experimental Section

**General methods:** $^1$H-NMR, $^{13}$C-NMR and $^{31}$P-NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm and referenced to tetramethysilane and chloroform (proton and carbon) and external 85% phosphoric acid (phosphorus). Size Exclusion Chromatography (SEC) was performed on a Shimadzu LC10-AT, using Polymer Laboratories PL Gel 5 micrometer Mixed-D column, a Shimadzu SPD-10AV UV-Vis detector at 254 nm, and chloroform or tetrahydrofuran as eluent. Polystyrene standards were used for calibration. Sonication experiments were carried out with a Sonics VCX 500 Watt Ultrasound Processor purchased from Sonics & Materials Inc.

Syntheses of the ligands and the complexes were carried out under dry Argon atmosphere using standard Schlenk techniques. Toluene and tetrahydrofuran were distilled from sodium-potassium; dichloromethane and deutero-chloroform were distilled from P$_2$O$_5$. Potassium diphenylphosphide (0.5M in THF), methyltriflate, triflic anhydride and 2,6-di-tert-butylpyridine were purchased from Aldrich and used without further purification; palladium dichloride was purchased from STREM.
Synthesis of \( \alpha, \omega \)-bis(diphenylphosphino)poly-tetrahydrofuran, 1

In a typical polymerization, 100 µL (85.2 mg, 0.445 mmol) of 2,6 di-tert-butylpyridine was added to 200 ml (178.0 g, 2.47 mol) tetrahydrofuran. This mixture was stirred for 15 minutes, while cooling the mixture to 0°C. 800 µL (1.34 g, 4.76 mmol) Triflic anhydride was added to the mixture. After 20 minutes, 19.0 mL of a 0.5 M solution of potassium diphenylphosphate (9.51 mmol) in tetrahydrofuran was added to the reaction mixture. The mixture was left stirring for 15 minutes. Solvent was removed \textit{in vacuo} resulting in a dark yellow/black oil. This oil was dissolved in 200 mL of dichloromethane and stirred well. The suspension was filtered over a fritt in order to remove all potassium salts. Residual dissolved potassium salts were removed by filtration over a small layer of dried silica with dichloromethane as eluent. Dichloromethane was removed and the white solid was dissolved in 100 mL of diethyl ether. At -18°C, the poly-tetrahydrofuran crystallizes out and precipitates. This was repeated once, in order to remove all impurities. Finally, diethyl ether was evaporated \textit{in vacuo} yielding a white powder. (22.0 g, 67%)

\[ \text{THF, Argon} \]

\[ \text{KPPPh}_{2}, -78^\circ \text{C} \]

\[ \begin{align*}
\delta_{\text{H}} (400 \text{ MHz}): & \quad 7.45-7.30 (\text{m, } 20\text{H, Ph}), 3.23-3.62 (\text{m, } 4\ast\text{nH } \text{CH}_2\text{O}), 2.08 (\text{t, } 4\text{H, C}_\text{H}_2\text{P}) 1.73-1.48 (\text{m, } 4\ast\text{nH}, \text{CH}_2\text{CH}_2\text{O}) \\
\delta_{\text{C}} (121 \text{ MHz}): & \quad 139.0 (\text{s, } 4\ast\text{C, Ph}), 133.1 (\text{s, } 8\ast\text{C, Ph}), 128.7 (\text{s, } 12\ast\text{C, Ph}), 31.57 (\text{d, } 2\ast\text{C, CH}_2\text{P}), 70.9 (\text{m, } 2\ast\text{nC, CH}_2\text{O}), 26.8 (\text{m, } 2\ast\text{nC, CH}_2\text{CH}_2\text{O}) \\
\delta_{\text{P}} (162 \text{ MHz}): & \quad -16.2 (\text{s, } 2\text{P}), \text{M}_n = 7,300 \text{ g/mol} \\
\text{SEC: } \text{M}_n = 15,406 \text{ g/mol } \text{M}_w = 17,135 \text{ g/mol } \text{M}_n/\text{M}_w = 1.11, \text{ based on polystyrene standards.} \\
\text{MALDI-TOF: } 6,337 \text{ g/mol}
\end{align*} \]
Synthesis of Palladium dichloride (α,ω-bis(diphenylphosphino)poly-tetrahydrofuran), 2

A mixture of palladium(II)dichloride (51 mg, 0.287 mmol, 1.1 equivalents) and α,ω-bis(diphenylphosphino) polytetrahydrofuran 1 (1.88 g, 0.261 mmol) in dry toluene (188 mL) was stirred for 48 hours. The mixture was filtered in order to remove the excess palladium(II)dichloride and yielding a bright yellow solution. The solvent was not evaporated; the solution was immediately used in the sonication experiments.

δ_H (400 MHz): 7.80-7.10 (m, 20*mH, Ph), 3.23-3.62 (m, 4*m*nH CH2O), 2.46 (t, 4*mH, CH2P) 1.73-1.43 (m, 4*m*nH, CH2CH2O) δ_C (121 MHz): 139.44 (d, 2C, Ph) 132.73 (d, 4C, Ph), 128.42 (s, 4C, Ph), 128.33 (d, 2C, Ph), 131.57 (d, 2*nC, CH2P), 70.9 (m, 2*nC, CH2O), 26.8 (m, 2*nC, CH2CH2O) δ_P (162 MHz) toluene-d8: 16.4 (s, 2*mP)

(n is the degree of polymerization of polymer 1, m is the degree of supramolecular polymerization of coordination polymer 2.)

Synthesis of dodecyl(diphenyl)-phosphane

1-bromododecane (1.87 g, 7.5 mmol) was dissolved in dry THF (50 mL) and the stirred solution was cooled to -78°C with acetone/dry ice. A solution of potassium diphenylphosphane in THF (0.5 M, 15.0 mL, 7.5 mmol) was slowly added to the mixture. After complete addition, the mixture was stirred for an hour at -78°C and left to warm up to room temperature. The mixture was stirred overnight. Solvent was removed in vacuo and the solids were suspended in dry dichloromethane (40 mL) and filtered over a glass filter. In order to remove residual impurities the mixture was filtered over silica, that was dried from water and air before use. Solvent was removed in vacuo. The product, a clear liquid was obtained in 78% yield. The liquid crystallizes when cooled to 5°C.

δ_H (400 MHz): 7.35-7.49 (m, 10H, Ph), 2.08 (t, 4H, CH2P), 1.13-1.53 (m, 20H, CH2), 0.92 (t, 3H, CH3) δ_C (121 MHz): 139.44 (d, 2C, Ph) 132.73 (d, 4C, Ph), 128.42 (s, 4C, Ph), 128.33 (d, 2C, Ph), 31.94 (s, 1C, alkyl), 31.24 (d, 1C, alkyl), 29.68 (s, 1C, alkyl), 29.64 (s, 1C, alkyl), 29.37 (m, 3C, alkyl) 29.28 (s, 1C, alkyl), 28.06 (d, 1C, alkyl), 26.05 (d, 1C, alkyl), 22.72 (s, 1C, alkyl), 14.15 (s, 1C, alkyl) δ_P (162 MHz): -16.04 (s, 1P)
Synthesis of Palladium dichloride bis(dodecyl(diphenyl)-phosphane)

A mixture of palladium(II)dichloride (36.6 mg, 0.206 mmol, 0.55 equivalents) and dodecyl(diphenyl)-phosphane (133.0 mg, 0.375 mmol) in dry dichloromethane (7 mL) was stirred for 24 hours. The mixture was filtered in order to remove the excess palladium(II)dichloride and solvent was removed in vacuo, yielding a bright yellow solid in 92% yield.

δ_H (400 MHz): 7.70-7.22 (m, 20H, Ph), 2.41-2.27 (m, 4H CH2P), 1.28-0.98 (m, 40H, CH2), 0.91 (t, 6H, CH3), δ_P (162 MHz): 16.47(s, 2P)

Stopper experiment

A mixture of complex 2 in toluene (1.5 mM, 60 mL, 90 mmol) and palladium dichloride bis dodecyl(diphenyl)-phosphane (8.0 mg, 9 mmol) were stirred for 3 days. The solvent was not evaporated; the solution was immediately used in the sonication experiments.
Sonication experiments
In a typical sonication experiment, the reaction vessel was charged with 25 mL of the 1.5 mM toluene solution of polymeric complex 2. Argon was bubbled slowly through the stirred solution. The temperature of the mixture was kept constant at 20°C by cooling with water. The probe was put at approximately 1 cm distance off the bottom of the vessel. Sonication was performed with a Sonics VCX 500 Ultrasonic Processor with a 13 mm probe used at 30% of the maximum 125 µm amplitude. During the sonication experiment, SEC-samples were taken and frozen in liquid nitrogen. For analysis, the samples were swiftly heated up to room temperature and analyzed without further purification.

Sonication experiment 1: Reversible breakage
Coordination polymer 2, 1.5 mM in toluene, sonicated 1 h.

Experiment 2: Temperature effects
Coordination polymer 2, 1.5 mM in toluene, heated at 80°C for 3 h.
Sonication experiment 3: Sonication on non-equilibrium mixture
Coordination polymer 2, equilibrated 3 days at 0.35 mM, concentrated to 1.5 mM and immediately sonicated for 2 h.

Experiment 4: Equilibration of non-equilibrium mixture
Coordination polymer 2, equilibrated 3 days at 0.35 mM, concentrated to 1.5 mM, was left standing for 1 day.
$^1$H-NMR of free ligand 1

$^{13}$C-NMR of free ligand 1
$^{31}$P-NMR of free ligand 1

$^{31}$P-NMR of coordination polymer 2
$^{31}$P-NMR of coordination polymer 2 after 1 hour sonication