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Quantification of Ultrasound-Induced Chain Scission in Pd^{II}–Phosphine Coordination Polymers

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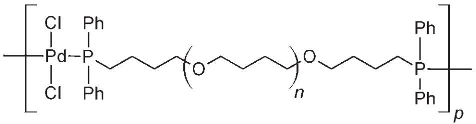
Abstract: A kinetically inert, reversible coordination polymer (**3**) was obtained through complexation of dicyclohexylphosphine telechelic poly(tetrahydrofuran) with palladium(II) dichloride. This coordination polymer is unreactive towards palladium(II) dichloride bis(1-diphenylphosphino)dodecane (**4**), because ligand dissociation in the coordination polymer is slow. However, upon ultrasonication of solutions of **3** in toluene in the presence of **4**, formation of palladium(II) heterocomplexes was observed with ^{31}P NMR spectroscopy. Heterocomplex formation, the consumption of **4**, and changes in molecular weight were used to quantify the scission process. In the presence of 60 equivalents of the alkyldiphenylphosphine stopper complex, the reduction in molecular weight was strongly enhanced; over a period of eight hours the weight-averaged molecular weight was reduced from 1.1×10^5 to 2.3×10^4 g mol^{-1} while 47 % of the palladium(II) complexes in the coordination polymer had been converted into heterocomplexes. These results show that the system of **3** in combination with scavenger **4** is a suitable system to study the efficiency of ultrasound-induced chain scission of coordination polymers.

Keywords: coordination polymers · heterocomplexes · phosphanes · supramolecular chemistry · ultrasound

Introduction

Reversible coordination polymers are dynamic supramolecular polymers[1,2] with coordinative bonds in their main chain. Much attention in this relatively new research area is directed towards the characterization of the dynamic properties of these polymers, such as exchange kinetics,[3] ring–chain equilibria,[4–6] solvent interactions,[6,7] and new metal–ligand combinations.[8] At the same time, coordination polymers are already beginning to find applications as smart materials, for instance, as stimuli-responsive[9] and photoactive polymers.[10,11] Our interest in this field concerns the direct manipulation of the coordination sphere of transition-metal complexes by mechanical forces. Ultrasound is known as one of the most efficient techniques to break polymers in solution,[12,13] but high molecular weights are required to transduce the mechanical forces.[14] Employing weaker bonds in the polymer chain allows for preferential scission at these bonds over other, stronger bonds.[15,16] Ultrasonication of reversible coordination polymers enables the specific rupture of a coordinative bond.[17] Our ultimate goal is to develop mechanochemical synthetic procedures in coordination chemistry and to enable the mechanical formation of highly active catalytic species.



1: $n \approx 100$, $p_{top} \approx 34$

Recently, we reported on the use of ultrasound to reversibly break coordination polymer **1**, which is based on diphenylphosphine telechelic poly(tetrahydrofuran) and palladium(II) dichloride.[17] The weight-averaged molecular weight (M_w) of the coordination polymer was reversibly reduced from 1.7×10^5 to 1.0×10^5 g mol^{-1} upon irradiation with ultrasound for one hour. Upon equilibration, the original molecular-weight distribution was fully restored within 24 h. The reversibility of the ultrasonic scission process indicated that only coordinative bonds and no covalent bonds were

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broken. Hence, the procedure constitutes a novel method to create coordinatively unsaturated metal ions.

For the application of this method in coordination chemistry and catalysis, the scission process needs to be highly efficient, and a method to quantify scission efficiency is desirable. However, quantification of scission in polymer **1** is complicated by relatively rapid equilibration and the formation of cyclic oligomers.

In this paper, we present the quantification of ultrasound-induced chain scission in kinetically stable coordination polymer **3**, which is composed of dicyclohexylphosphine telechelic poly(tetrahydrofuran) and palladium(II) dichloride. The use of an alkyldiphenylphosphine palladium(II) complex, which suppresses cyclization by scavenging reactive phosphine chain ends, is described, and the rate of ultrasonic chain scission is analyzed by using two independent methods: size-exclusion chromatography (SEC) and ^{31}P NMR spectroscopy.

Results

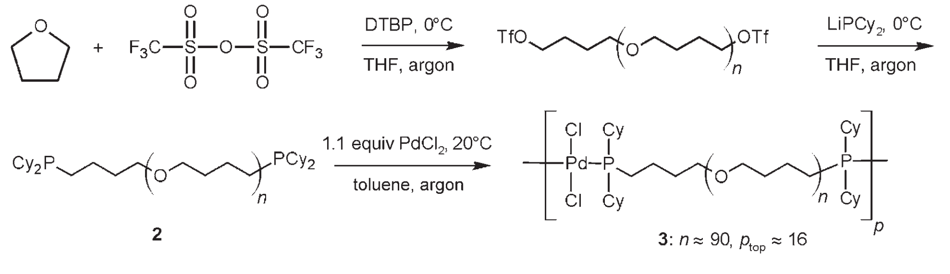
Synthesis of a kinetically stable coordination polymer: Recently we reported on the synthesis of several palladium(II) dichloride bis-phosphine complexes.[5] From studies concerning their ligand-exchange kinetics, it was concluded that alkyldicyclohexylphosphine ligands form extremely stable complexes with palladium(II) dichloride with equilibration times of several months. These ligands would be suitable for the synthesis of a coordination polymer that is kinetically more stable than polymer **1**.

Therefore, dicyclohexylphosphine telechelic poly(tetrahydrofuran) was synthesized by cationic polymerization of tetrahydrofuran, and was terminated with lithium dicyclohexylphosphine ($LiPCy_2$). This yielded polymeric ligand **2** with a number-average molecular weight (M_n) of 6.7×10^3 g mol^{-1}, obtained from ^{1}H NMR analyses, and a polydispersity index (PDI) of 1.11. Coordination polymer **3** was obtained by stirring a solution of ligand **2** in toluene (20.0 g L^{-1}, 2.91 mM) with an excess of palladium(II) dichloride for seven days (Scheme 1). SEC analysis of **3** showed the presence of high-molecular-weight material ($M_{top}=1.1\times10^5$ g mol^{-1} (M_{top}= peak molecular weight), $M_w=6.1\times10^4$ g mol^{-1}, based on polystyrene (PS) standards), accompanied by a peak at 1.0×10^4 g mol^{-1} that represents the cyclic monomer (see Figure 2a). The maximum degree of supramolecular polymerization (DP_{max}) is approximately 16 units, which corresponds to approximately 6% impurity in the material; most likely, monofunctionalized polymeric ligands or ligands with one oxidized phosphine end group act as a stopper.

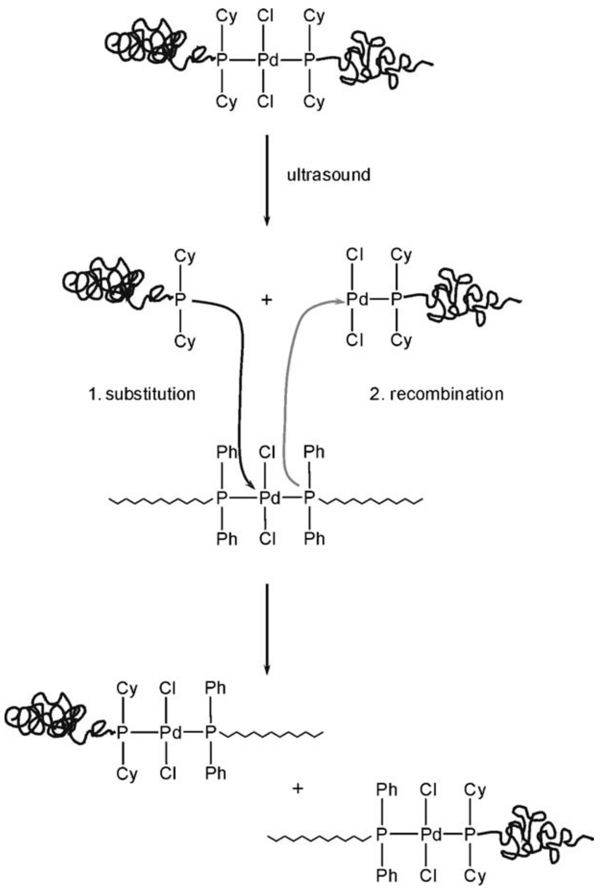
Design of the stopper complex: For the scavenging of reactive phosphine chain ends created by ultrasonic scission, a compound is required with high reactivity towards alkyldicyclohexylphosphine ligands and coordinatively unsaturated palladium, whereas the scavenger compound itself, and any of its reaction products, should not display reactivity towards the coordination polymer. These requirements suggested the use of palladium(II) dichloride with less-nucleophilic bis(alkyldiphenylphosphine) ligands, for example, complex **4**, as a candidate for scavenging chain ends. It was anticipated that the high nucleophilicity of the alkyldicyclohexylphosphine ligands would result in complete displacement of one alkyldiphenylphosphine ligand (Scheme 2), while the liberated alkyldiphenylphosphine ligand would be unreactive towards the coordination polymer, but would react with coordinatively unsaturated Pd chain ends.

The validity of this assumption was first studied by mixing 1-(dicyclohexylphosphino)dodecane **5** with four equivalents of complex **4** in [D$_8$]toluene (Figure 1). This immediately led to quantitative formation of heterocomplex **6**, as is evident from the ^{31}P NMR spectrum depicted in Figure 1. After mixing, the signal of free ligand **5** had disappeared and a new peak, originating from free 1-(diphenylphosphino)dodecane ligand **7**, was observed at $\delta=-16.0$ ppm. Formation of heterocomplex **6** was confirmed by the appearance of two doublets at $\delta=27.5$ and 13.0 ppm ($J_{P,P}=527$ Hz) in the ^{31}P NMR spectrum. The large coupling constant implies that the heterocomplex adopts a *trans* configuration in toluene.[18]

To evaluate the reactivity of stopper complex **4** towards the coordination polymer, a solution of **3** in toluene (1.5 mM) containing complex **4** (1.7 equiv) was stirred without sonication at 20°C. The reaction was followed by monitoring the reduction of the peak of **4** in the SEC trace (see the Supporting Information). Within the first hour approximately 1.2% heterocomplex formed, whereas after five hours only 2.2% heterocomplex was observed. This time course suggests that the initial exchange is due to the presence of impurities, such as bridged palladium(II) dichloride complexes and free dicyclohexylphosphine ligands, and that the true exchange rate between coordination polymer **3** and stopper complex **4** is very low. This hypothesis was verified by mixing a solution of the chloro-bridged coordination polymer **8** with stopper complex **4**. After 30 min, approximately 15% exchange had taken place, leading to the for-



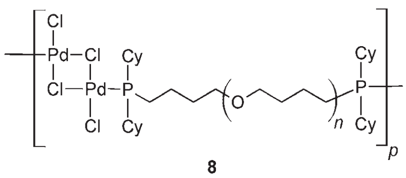
Scheme 1. Synthesis of α,ω-bis(dicyclohexylphosphino)poly(tetrahydrofuran) (**2**) and its palladium(II) chloride coordination polymer **3**. Tf = trifluoromethanesulfonyl.



Scheme 2. General scheme for the interception of dicyclohexylphosphine chain ends with a low-molecular-weight complex containing less-nucleophilic diphenylphosphine ligands.

mation of heterocomplexes (see the Supporting Information).

Quantification of scission by monitoring the reduction of molecular weight: Solutions of **3** in toluene (1.5 mM monomer) were sonicated for three hours by using a sonication



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probe in the presence of 0, 1.7, 10, and 60 equivalents of complex **4**. Samples for ^{31}P NMR and SEC analyses were taken at regular intervals (see Figure 2a). In the absence of

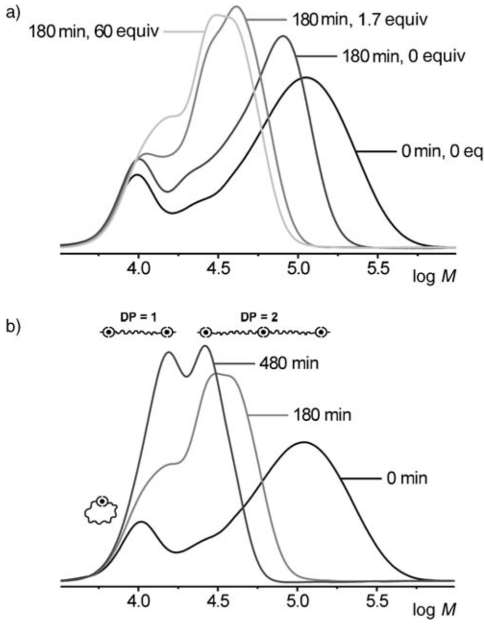
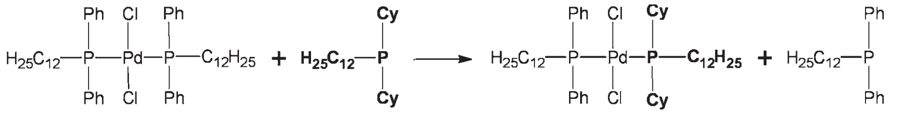


Figure 2. SEC traces measured before and after a) 3 h of sonication of **3** in the presence of 0, 1.7, and 60 equivalents of **4** and b) before and after 8 h of sonication of **3** in the presence of 60 equivalents of **4**, with assignment.

4, a decrease in the weight-averaged molecular weight from 1.3×10^5 to 7.6×10^4 g mol^{-1} was observed after three hours, while a greater decrease in M_w was observed in the presence of **4**, to 4.5×10^4 (1.7 equiv), 4.4×10^4 (10 equiv), and 4.1×10^4 g mol^{-1} (60 equiv). After eight hours of sonication, in the presence of 60 equivalents of **4**, M_w was further decreased to 2.3×10^4 g mol^{-1}.



$$H_{25}C_{12}-\underset{Ph}{\overset{Ph}{P}}-\underset{Cl}{\overset{Cl}{Pd}}-\underset{Ph}{\overset{Ph}{P}}-C_{12}H_{25} + H_{25}C_{12}-\underset{Cy}{\overset{Cy}{P}} \longrightarrow H_{25}C_{12}-\underset{Ph}{\overset{Ph}{P}}-\underset{Cl}{\overset{Cl}{Pd}}-\underset{Cy}{\overset{Cy}{P}}-C_{12}H_{25} + H_{25}C_{12}-\underset{Ph}{\overset{Ph}{P}}$$

4 **5** **6** **7**

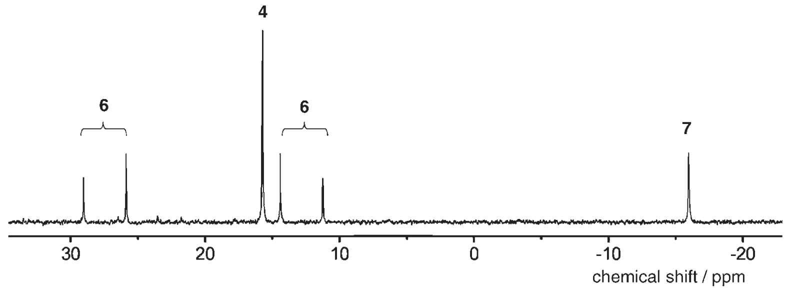


Figure 1. ^{31}P NMR spectrum of the product mixture obtained upon addition of **5** to a solution of **4** in [D$_8$]toluene.

In addition to giving rise to a faster decrease in molecular weight, the presence of **4** also led to the formation of different products. Upon extensive sonication for eight hours, the SEC trace of the solution containing 60 equivalents of **4** displayed two peaks corresponding to molecular weights of

1.5×10^4 and 2.6×10^4 g mol^{-1} (PS standards, see Figure 2b). These peaks are absent in the SEC trace of **3** sonicated in the absence of **4**, and are assigned to dodecyldiphenylphosphine-stoppered monomers and dimers, respectively. The molecular weights of these species were used to calibrate the number and weight-averaged degrees of polymerization (DP_n and DP_w, respectively) in the SEC traces of the sonication experiment in the presence of 60 equivalents of **4** (Figure 3a). These changes were used to calculate the amount of chain scission expressed as the fraction of broken complexes in the coordination polymer [Eq. (1)] by using the assumption that no recombination takes place. This analysis indicates that sonication results in 39 % scission of coordination complexes over the course of eight hours, with 25 % being broken after three hours (Figure 3b).

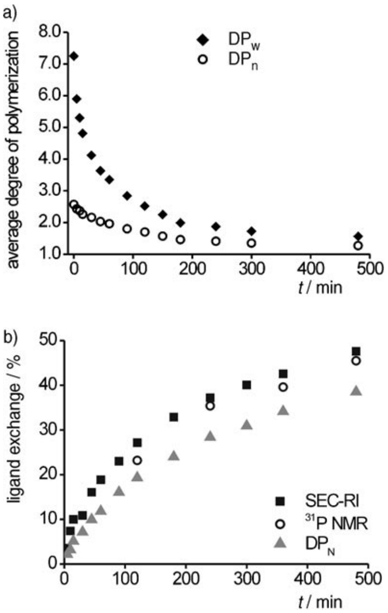


Figure 3. a) Weight- and number-averaged degree of polymerization and b) ligand exchange of **3** during sonication with 60 equivalents of **4**.

$$\text{Fraction of broken complexes in } \mathbf{3} = \frac{1}{DP_{N,t=x}} - \frac{1}{DP_{N,t=0}} \quad (1)$$

in which DP_N is the number averaged degree of polymerization. The SEC trace can only be used to evaluate chain scission when a high concentration of **4** is present. If scavenging is inefficient, an unknown fraction of cyclic species with lower hydrodynamic volumes[19] is formed, making calibration impossible.

Quantification of scission by monitoring ligand exchange with ^{31}P NMR and SEC analyses: The rate of ultrasound-induced chain scission of polymer **3** was further quantified by monitoring the formation of the palladium(II) heterocomplex with ^{31}P NMR spectroscopy. Upon sonicating the solutions of **3** (in toluene) containing alkyldiphenylphosphine complex **4**, two new doublets appeared in the ^{31}P NMR spectrum at $\delta = 27.5$ and 13.0 ppm ($J_{P,P} = 527$ Hz), which were assigned to the alkyldicyclohexylphosphine and the alkyldiphenylphosphine phosphorus atoms in the heterocomplex, respectively, in accordance with the earlier described ligand-exchange experiment. The fraction of broken complexes of **3** was calculated by determining the ratio of the peak intensities (integral, I) by using Equation (2):

$$\text{Fraction of broken complexes in } \mathbf{3} = \frac{I_{PCy_2\ \text{hetero}}}{I_{PCy_2\ \text{hetero}} + I_{PCy_2\ \text{homo}}} \quad (2)$$

The extent of ultrasonic scission was determined in an independent fashion by monitoring the decrease in intensity of the signal of **4** in SEC traces of the same solutions.[20] During sonication, **4** is consumed by ligand exchange and the intensity of the corresponding peak decreases. Taking the stoichiometry of the stopper complex into account, the amount of ultrasonic scission was calculated with Equation (3):

$$\text{Fraction of broken complexes in } \mathbf{3} = \frac{[\mathbf{4}]_{t=0} - [\mathbf{4}]_{t=x}}{[\mathbf{3}]_{t=0}} \quad (3)$$

In Figure 4, ultrasonic scission, as derived from NMR and SEC analyses, has been plotted against time. For sonication times below 30 min, NMR data are not available, because the signal to noise ratio of the peaks of the heterocomplex was insufficient. Nevertheless, a good agreement between the two quantification methods is observed. The plots of Figure 4 show that a higher concentration of stopper complex **4** led to increased heterocomplex formation. In the

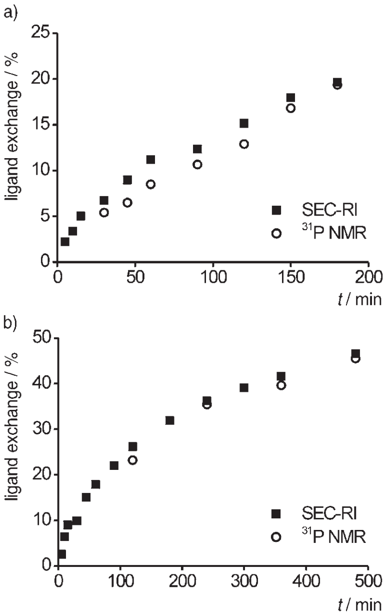
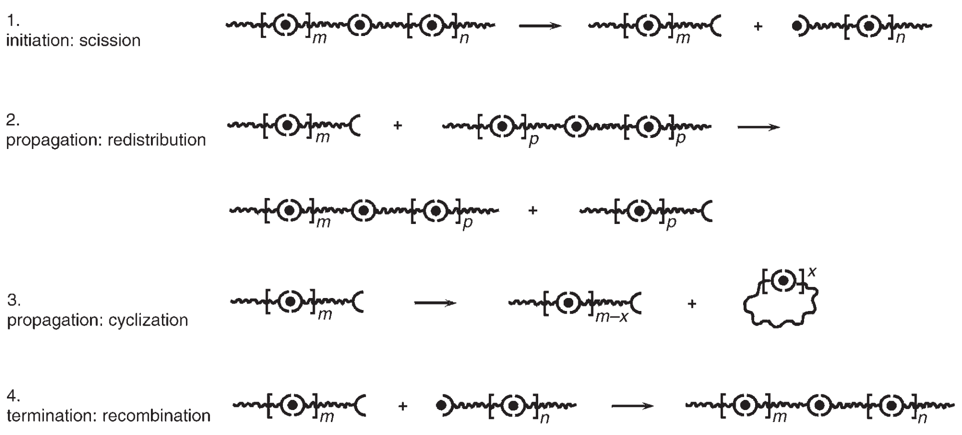


Figure 4. Ligand exchange in **3** in the presence of a) 1.7 and b) 60 equivalents of **4**.

presence of 1.7 equivalents of **4**, approximately 20 % of the complexes in the coordination polymer were converted into a heterocomplex after three hours, against 35 % when 60 equivalents of **4** were present; after eight hours of sonication, a total of 47 % of heterocomplex had formed. Because the presence of **4** is not expected to influence the rate of scission, the differences reflect the increased efficiency of scavenging. Even in the presence of 60 equivalents of **4**, scavenging is not guaranteed to be quantitative. The rate of heterocomplex formation in the presence of 60 equivalents of **4** is therefore a lower limit for the true rate of chain scission.

Discussion

In a previous publication on the reversible, ultrasound-induced chain scission of polymer **1**, we proposed that the phosphine-free chain ends initiate a series of ligand-exchange reactions, which is terminated by recombination of chain ends (Scheme 3). Because this process only leads to redistribution, and not to a reduction in molecular weight, the stable fragments observed with SEC analyses were proposed to be cyclic species formed by backbiting (step 3 in Scheme 3).



Scheme 3. Proposed mechanism for the reversible ultrasonic scission of coordination polymers in the absence of a chain-end scavenger.[17]

In the kinetically stable system of coordination polymer **3** in combination with efficient scavenging of chain ends by complex **4**, cyclization and redistribution are suppressed, and a higher efficiency of chain scission is predicted. Qualitative comparison of the SEC traces in Figure 2a shows that the addition of complex **4** indeed strongly enhances the efficiency of molecular-weight reduction. This confirms the hypothesis that without a stopper, only a fraction of the scission events results in a reduction of molecular weight.

The system of **3** in combination with scavenger **4** is a suitable system to study the efficiency of ultrasound-induced chain scission of coordination polymers. Three independent methods have been used to quantify the efficiency of the scission process. In principle, the method based on the reduction in DP observed with SEC analyses can be used to analyze the scission experiment either in the absence or the presence of an excess of **4**, because the coordination polymer is kinetically inert and does not re-equilibrate during the experiment. However, only in the presence of **4** can the method be used in a quantitative manner, because in the absence of stopper an unknown amount of cyclic material with smaller hydrodynamic volume is formed. Quantification of the scission efficiency in the presence of 60 equivalents of stopper shows that the DP_n is reduced from 2.7 to 1.3 over the course of eight hours, implying that during this time each chain, on average, is broken more than once. It is also evident that the efficiency of the process is much higher in the initial stages of sonication, when longer chains are still present, than during the last four hours. This is in line with the higher susceptibility of longer chains to scission.[12,21,22] The chain-length dependence of the scission rate means that in the present system of highly polydisperse polymers it is difficult to give a number for the overall rate of scission.

The other two methods to quantify scission described here directly probe the amount of ligand exchange by measuring either the intensity of the heterocomplex in the ^{31}P NMR spectrum, or the amount of stopper complex consumed according to SEC analyses. These data give scission rates that are in very good agreement with each other. Comparison of these data with the DP measurements also gives a fair agreement, although the amount of chain scission based on DP gives a lower estimate for the rate of scission (39 vs 47 % after 8 h, see Figure 3b). The difference may be ascribed to a reduction in the fraction of cyclic species upon sonication. Because linear products have a larger hydrodynamic volume than the corresponding rings, this results in an underestimatation of the change in DP.

Conclusion

In summary, all three methods used to quantify chain scission have limitations. Although the SEC traces give the most detailed information on the scission process, using these traces to extract changes in DP is restricted by the need for calibration and the presence of a changing fraction of cyclic species. The other two methods, using NMR or the signal of the stopper, are limited in the amount of information they give on changes in molecular-weight distribution, but these methods are convenient and their results are in excellent agreement with each other.

The heterocomplex formation reported here is an important step toward ultrasound-induced coordination mechanochemistry and mechanocatalysis. For application in catalysis, however, practical applications require an increased scission rate. In future work, addressing this issue by using coordination polymers with star and network architectures will be investigated. The use of ultrasound in the synthesis of new coordination compounds on the other hand, is within reach when monofunctionalized polymeric phosphine ligands are used. These ligands will lead to complexes with a single metal center in the middle of the chain, which will allow quantitative scission and enable ultrasound-controlled coordination chemistry.

Experimental Section

General procedures: ^{1}H NMR (400 MHz), ^{13}C NMR (100 MHz), and ^{31}P NMR (162 MHz) spectra were recorded on a Bruker 400 spectrometer. Chemical shifts are referenced to tetramethylsilane and chloroform (proton and carbon, respectively) and external 85 % phosphoric acid (phosphorus). Size-exclusion chromatography was performed on a Shimadzu LC10-AT instrument, using a Polymer Laboratories PL Gel 5 μm mixed-D column (linear range of $M_r = 200$–$400\,000$ g mol^{-1}), a Shimadzu SPD-10AV UV/Vis detector at 254 nm, and chloroform as the eluent at a flow rate of 1 mL min^{-1} (20 °C). Polystyrene standards were used for calibration. Sonication experiments were carried out with a Sonics VCX 500 Watt Ultrasonic Processor purchased from Sonics & Materials Inc. A 13 mm probe was used at a frequency of 20 kHz, at 30 % of the maximum amplitude of 125 μm. Syntheses of the ligands and the complexes were carried out under a dry argon atmosphere using standard Schlenk techniques. Tetrahydrofuran was distilled from a sodium–potassium alloy; diethyl ether was distilled from molecular sieves; dichloromethane and deuterated chloroform were distilled from P_2O_5. Diethyl ether, acetonitrile, and *n*-hexane were degassed before use. *n*-Butyllithium was titrated before use. *n*-Butyllithium (1.6 M) was purchased from Aldrich; palladium dichloride (99.9 %) and dicyclohexylphosphine (98 %) were purchased from STREM. The syntheses of 1-(diphenylphosphino)dodecane, 1-(dicyclohexylphosphino)dodecane, and their palladium(II) dichloride complexes have been reported earlier.[5]

α,ω-Bis(dicyclohexylphosphino)poly(tetrahydrofuran) (2): Dicyclohexylphosphine (1.04 g, 5.24 mmol, 2.2 equiv) was dissolved in tetrahydrofuran (30 mL) and the stirred solution was cooled to −90 °C. *n*-Butyllithium in hexane (1.6 M, 3.27 mL, 5.2 mmol, 2.2 equiv) was slowly added to the mixture. After complete addition, the yellow mixture was stirred and left to warm to room temperature.

A mixture of di-*tert*-butylpyridine (DTBP; 42.6 mg, 0.22 mmol, 0.09 equiv) and dry tetrahydrofuran (100 mL) was cooled to 0 °C with ice. Trifluoromethane sulfonic anhydride (0.67 g, 2.4 mmol) was added to the mixture. After stirring for 50 min at 0 °C, a solution of lithium dicyclohexylphosphine in tetrahydrofuran was added to the reaction mixture. This mixture was stirred for 30 min and left to warm to room temperature. The solvent was removed under vacuum, resulting in a yellow oil. In order to remove residual impurities, the oil was dissolved in 150 mL diethyl ether and this mixture was filtered over silica that had been dried from water and air. At −18 °C, **2** crystallized out and precipitated. This was repeated once to remove all impurities. Finally the solvent was removed under vacuum yielding a white solid (10.9 g, 68 %). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.55$–3.2 (m, $n \times 4$H, CH_2O), 1.74–1.17 ppm (m, $n \times 4$H, CH_2CH_2O; 44 H, alkyl); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 70.70$ (s, $n \times 2$C, CH_2O), 33.40 (d, 4 C, alkyl), 30.45 (d, 8 C, alkyl), 29.09 (d, 8 C, alkyl) 27.44–25.34 (m, $n \times 2$C, CH_2CH_2O; 4 C, alkyl), 21.27 ppm (d, 2 C, PCH_2); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = -3.25$ ppm (s, 2 P); molecular weight: by end-group determination (^{1}H NMR): $M_n = 6700$ g mol^{-1}; by SEC (PS standards): $M_n = 15200$ g mol^{-1}, $M_w = 16900$ g mol^{-1}, PDI $= M_w/M_n = 1.11$.

Palladium(II) dichlorido [α,ω-bis(dicyclohexylphosphino)poly(tetrahydrofuran)] (3): Due to the sensitivity of ligand **2** towards oxygen, a large amount of the ligand is rapidly complexed by using a soluble palladium source and the insoluble palladium dichloride was used to obtain perfect stoichiometry.[5] Dichloro(1,5-cyclooctadiene)palladium(II) (91 mg, 0.32 mmol, 0.75 equiv), palladium(II) dichloride (27 mg, 0.15 mmol, 0.35 equiv), and **2** (2.69 g, ≈0.27 mmol) were dissolved in dry toluene (135 mL) and this mixture was stirred for 7 d. The mixture was filtered to remove the excess palladium(II) dichloride yielding a clear, yellow solution. The solvent was not evaporated; the solution (20 g L^{-1}) was immediately used in sonication experiments. Only a small sample was dried for analysis purposes. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.58$–3.22 (m, $n \times 4$H, CH_2O), 1.90–1.19 ppm (m, $m \times n \times 4$H, CH_2CH_2O;$m \times 44$H, alkyl); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 70.74$ (s, $m \times n \times 2$C, CH_2O), 33.03 (s, $m \times 4$C, alkyl), 29.43 (s, $m \times 8$C, alkyl), 28.96 (d, $m \times 8$C, alkyl), 27.52–26.3 (m, $m \times n \times 2$C, CH_2CH_2O; 4 C, alkyl), 22.09 ppm (s, 2 C, PCH_2); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 23.24$ ppm (s, $m \times 2$P) (*n* is the degree of polymerization of polymer **2**, *m* is the degree of supramolecular polymerization of coordination polymer **3**).

Dipalladium(II) (di-μ-chlorido) dichlorido [α,ω-bis(dicyclohexylphosphino)poly(tetrahydrofuran)] (8): Coordination polymer **3** (1.23 g, 0.178 mmol) was dissolved in toluene (50 mL) and palladium(II) dichloride (51 mg, 0.178 mmol) was added. The mixture was heated to 80 °C for 24 h. The solvent was removed under vacuum yielding a dark yellow oil (1.18 g, 95 %).

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 3.60$–3.34 (m, $n \times 4$H, CH_2O), 2.00–1.25 ppm (m, $m \times n \times 4$H, CH_2CH_2O; $m \times 44$H, alkyl); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 70.54$ (s, $m \times n \times 2$C, CH_2O), 35.36 (s, $m \times 4$C, alkyl), 29.24 (s, $m \times 8$C, alkyl), 28.76 (d, $m \times 8$C, alkyl), 26.62 (m, $m \times n \times 2$C, CH_2CH_2O; 4 C, alkyl), 22.051 ppm (s, 2 C, PCH_2); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 55.29$ ppm (s, $m \times 2$P) (*n* is the degree of polymerization of polymer **2**, *m* is the degree of supramolecular polymerization of coordination polymer **8**).

Sonication experiments: Part of the 20.0 g L^{-1} solution of **3** in toluene (2.91 mM) was diluted with toluene to 10.0 g L^{-1} (1.45 mM) and a water-cooled glass vessel was filled with 30.0 mL of this diluted solution. The solution was sonicated while argon was slowly bubbled through it, and samples for SEC analysis were taken at regular intervals. These samples were immediately frozen in liquid nitrogen and left to warm to room temperature only just before SEC measurement. In the case of quantification experiments, a specific amount of complex **4** was added (1.7 equiv: 65.5 mg, 7.40×10^{-5} mol; 10 equiv: 385 mg, 4.35×10^{-4} mol; 60 equiv: 2.31 g, 2.61×10^{-3} mol).

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