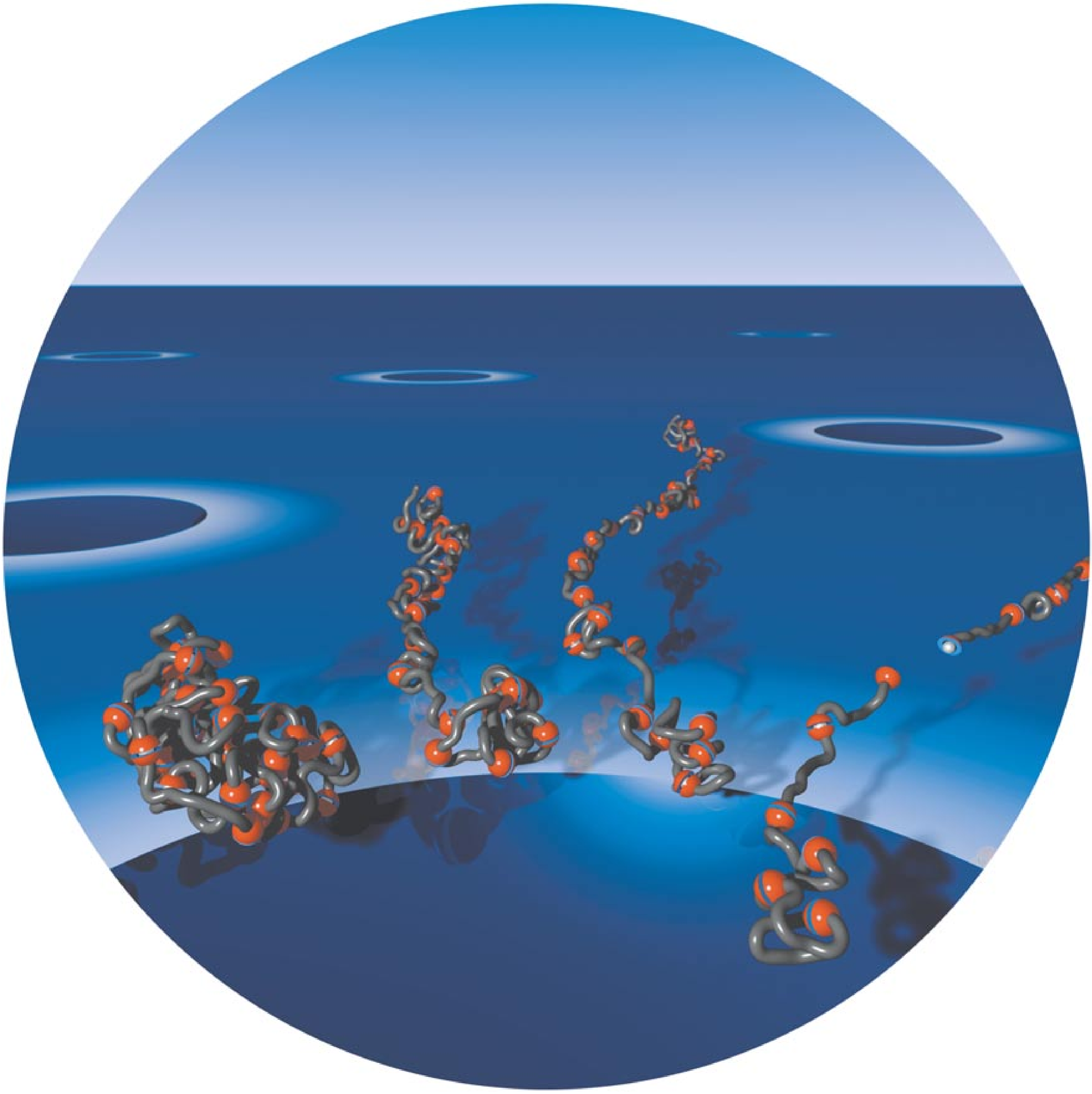
Zuschriften



Bei der Ultraschall-induzierten Kettenspaltung in gelösten Pd^{II}-Koordinationspolymeren dissoziieren nur die Phosphanliganden von den Palladiumatomen ab, weshalb die Spaltung reversibel ist. Das ursprüngliche Molekulargewicht des Polymers wird anschließend wieder erreicht. Einzelheiten hierzu finden Sie in der Zuschrift von J. M. J. Paulusse und R. P. Sijbesma auf den folgenden Seiten.

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Coordination Polymers

Reversible Mechanochemistry of a Pd^{II} Coordination Polymer**

*Jos M. J. Paulusse and Rint P. Sijbesma**

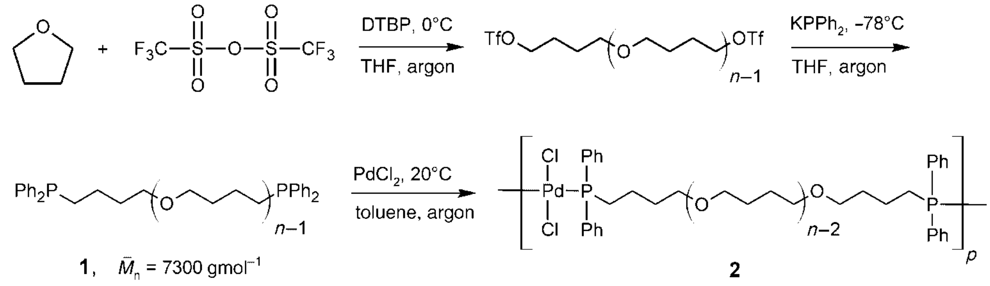
The design and synthesis of appropriate ligands is a well-established, but sometimes cumbersome method for controlling the coordination chemistry of transition-metal complexes. Manipulation of the coordination sphere by mechanical means is an exciting, yet barely explored alternative,[1] which may open up novel avenues in coordination chemistry and catalysis. Although mechanical forces act on even the smallest molecules, the effect of extensional forces is most pronounced in macromolecular species. If these forces act on a coordination polymer[2] of sufficient length, the noncovalent bonds may be broken.[3] Reversibility[4,5] of the coordinative interactions could then result in the continuous reformation of polymer chains until a steady-state degree of polymerization is reached. Irreversible disruption of covalent bonds is known to occur in polymers subject to strong shear forces;[6] it is the basis of some processing technologies, such as the mastication of natural rubber,[7] and even causes undesired degradation of macromolecules in chromatography.[8] Ultrasonication is one of the most efficient methods to induce breakage in polymer chains in homogeneous solution.[9] The shear forces required for chain scission are provided by the collapse of cavitation bubbles created by ultrasound.

Herein, we report on the reversible sonochemistry of high-molecular-weight coordination polymers in dilute solution. The polymeric diphosphane **1** was prepared by the cationic polymerization of tetrahydrofuran initiated by triflic anhydride[10] with subsequent termination by the diphenylphosphane anion ($\bar{M}_n = 7300\,\text{g mol}^{-1}$; $\bar{M}_w/\bar{M}_n = 1.11$). Linear coordination polymers **2** were obtained by stirring a solution in toluene of ligand **1** with a small excess of palladium dichloride for 2 days (Scheme 1).

Size-exclusion chromatographic (SEC) analysis of the equilibrated samples of **2** at different concentrations (Figure 1a) shows the presence of high-molecular-weight material[11] ($M_{top} = 2.50\times10^5\,\text{g mol}^{-1}$, $\bar{M}_w = 1.70\times10^5\,\text{g mol}^{-1}$, based on polystyrene standards), as well as peaks at 10500 and 23000 g mol^{-1}, which decrease in intensity relative to the peak for the high-molecular-weight material with increasing concentration. The low-molecular-weight peaks correspond well with the molecular weights of cyclic monomers and dimers (7500 and 15000 g mol^{-1}). The molecular-weight distributions in Figure 1a show that even at the lowest concentration high-molecular-weight material is present, and the data are in line with an equilibrium between cyclic and linear complexes with a critical polymerization concentration[12] of approximately 0.15 mM.[13]

In linear coordination polymers the degree of polymerization is strongly influenced by any stoichiometric imbalance between the bifunctional ligand and the metal, or by the presence of monofunctional ligands.[4c,5] Indeed, the addition of 1-dodecyl(diphenyl)phosphane (as a palladium dichloride complex to preserve the metal to ligand stoichiometry) to **2** led to a decrease in the molecular weight after equilibration, which confirms the linear nature of the polymer (Figure 1b).

The ultrasound-induced scission of coordination polymer **2** was studied by using a sonication probe in toluene under argon. A 1.5 mM solution, which had been equilibrated for 3 days, was sonicated for 1 h at a constant temperature of 20 °C. Samples were taken during the experiment and analyzed by SEC. The results of the sonication experiment are shown in Figure 2a. After sonication for 1 h, the $\bar{M}_w$ had decreased from $1.70\times10^5\,\text{g mol}^{-1}$ to $1.02\times10^5\,\text{g mol}^{-1}$.



Scheme 1. Synthesis of the polymeric diphosphane ligand **1** and coordination polymer **2**. DTBP = 2,6-di-*tert*-butylpyridine, Tf = trifluoromethanesulfonyl.

^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectroscopy showed that no chemical degradation of complex **2** had occurred. Furthermore, when the sample was left for 1 day, the original molecular-weight distribution was restored nearly quantitatively. To test the reversibility of the sonochemical degradation, a 1.5 mM solution was sonicated for 1 h and left to equilibrate for 23 h. This procedure was repeated five times. In Figure 2b, the weight-averaged molecular weight of the sample after each sonication and equilibration period is shown, and there is no sign of irreversible polymer degrada-

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[*] J. M. J. Paulusse, R. P. Sijbesma
Laboratory of Macromolecular and Organic Chemistry
Eindhoven University of Technology
P.O. Box 513, 5600 MB Eindhoven (The Netherlands)
Fax: (+31) 40-2472-655
E-mail: r.p.sijbesma@tue.nl

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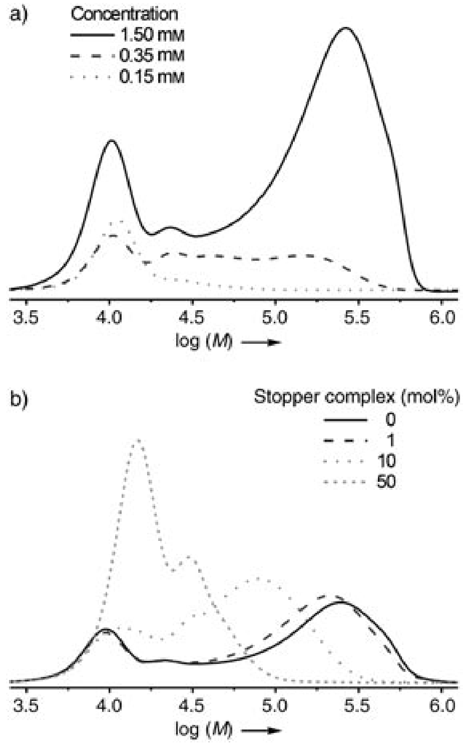


Figure 1. a) Molecular-weight distributions of **2** equilibrated in toluene at different concentrations; b) molecular-weight distributions of **2** (1.5 mM in toluene) equilibrated in the presence of different quantities of $[PdCl_2(dodecyl(diphenyl)phosphane)_2]$.

tion. The reversibility of the effects of sonication shows that no covalent bonds are broken in the process, and that the mechanical degradation is highly selective for the weaker palladium–phosphane coordination bonds.

Although the temperature was kept constant at 20 °C during all sonication experiments, we wanted to confirm that the decrease in molecular weight is indeed brought about by the mechanical action of ultrasound, and not by a trivial heating effect. Therefore, an equilibrated solution of **2** was heated at 80 °C for 3 h and then analyzed at room temperature by SEC. Heating resulted in a much smaller decrease in $\bar{M}_w$ than sonication, from 1.70×10^5 to $1.50\times10^5\,\mathrm{g\,mol^{-1}}$. Moreover, heating led to an increase in lower-molecular-weight material over the whole molecular-weight range, particularly in monomeric cyclic products, whereas sonication led to an increase in polymeric material of a more specific length (after 5 min of sonication the greatest increase was found at $M = 1.90\times10^5\,\mathrm{g\,mol^{-1}}$).

In a second control experiment, a solution of complex **2** was equilibrated for 3 days at 0.35 mM. This sample was subsequently concentrated swiftly by partially evaporating the solvent to give a 1.5 mM solution with a molecular-weight distribution corresponding to that of a less concentrated solution. Part of this sample was sonicated and showed a large decrease in molecular weight, whereas the molecular-weight distribution of the rest of the sample shifted towards higher molecular weight (Figure 3). This experiment shows that sonication moves the composition of the solution away from thermodynamic equilibrium.

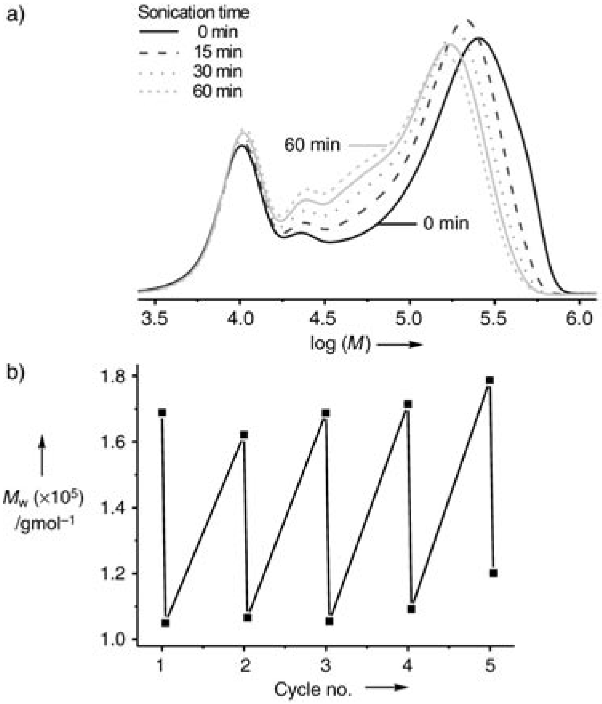


Figure 2. Ultrasound-induced decrease in the molecular weight of **2** (1.5 mM in toluene): a) molecular-weight distribution of samples taken during sonication; b) weight-averaged molecular weight ($\bar{M}_w$) during a reversibility test consisting of five cycles of sonication (1 h) followed by equilibration (23 h).

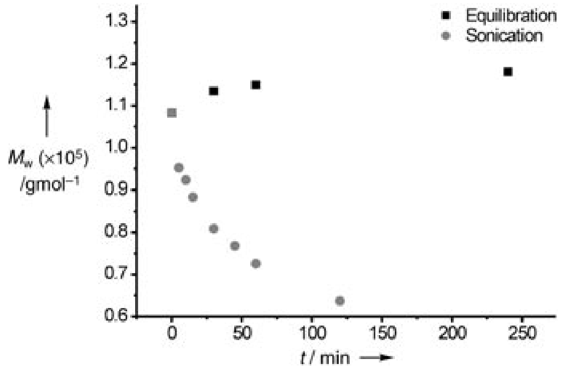
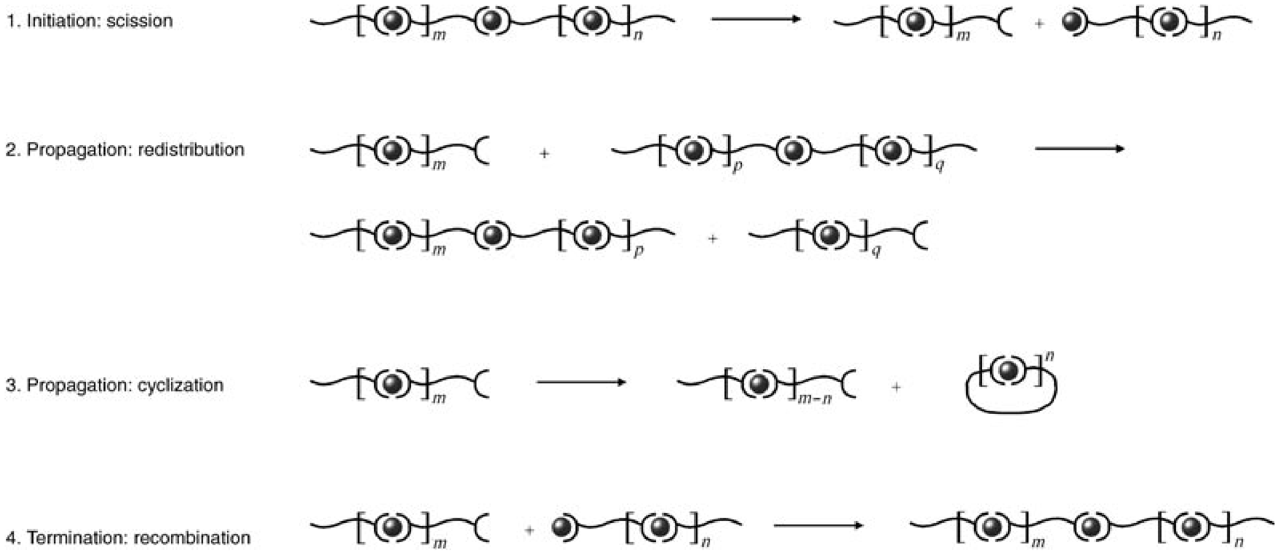


Figure 3. Molecular-weight evolution of equilibrating and sonicated samples of solutions 1.5 mM in **2** of non-equilibrium composition (see text for details).

Ultrasonic chain scission is a nonrandom process that acts preferentially on longer chains.[7,9] In solutions of **2**, this phenomenon is evidenced by the complete disappearance of the highest-molecular-weight polymers after short sonication times (Figure 2a). Several observations suggest a mechanism by which cyclic polymers are formed. For a decrease in molecular weight of any linear polymer, either additional chain ends or rings have to be formed (or a combination of both). Ligand exchange in palladium(II)–phosphane complexes is known to occur predominantly through an associative mechanism and is therefore strongly accelerated by trace



Scheme 2. Proposed elementary steps upon sonication of **2**.

amounts of free phosphane.[14] Because sonicated solutions of **2** equilibrate at the same rate as non-equilibrium solutions obtained by other means (e.g. by rapidly increasing the concentration), the presence of significant amounts of free phosphane end groups after sonication may be excluded, thus suggesting that the newly formed polymer is mainly cyclic. We propose that the phosphane chain ends formed by cleavage of the polymer react rapidly with a palladium complex either intramolecularly or intermolecularly (Scheme 2). In each case, upon substitution at the palladium center a new reactive phosphane end group is formed and a chain reaction is initiated which terminates when a free phosphane reacts with a coordinatively unsaturated palladium(II) chain end. However, an intermolecular reaction merely results in redistribution to give a statistical (most probable) chain-length distribution and does not change the average molecular weight of the polymer. On the other hand, intramolecular attack of a phosphane end group results in the splitting off of a cyclic compound and a net decrease in molecular weight, as observed for sonicated solutions of **2**.

The results presented herein demonstrate that ultrasound may be used to mechanically induce ligand dissociation from transition-metal complexes, thus making it a novel method for studying and controlling the chemistry of coordination complexes. The creation of vacant coordination sites in combination with the complete reversibility of the process point the way to the application of this principle in transition-metal catalysis. Present efforts are focused on identifying the polymer architecture and experimental conditions required for optimal effectiveness of the sonochemical process, and on studying the reactivity changes induced by ligand dissociation.

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