Selectivity of mechanochemical chain scission in mixed palladium(II) and platinum(II) coordination polymers†

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

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The selectivity of ultrasound induced chain scission was studied in reversible polymers with coordinative bonds (Pd–P and Pt–P) of different strengths in series.

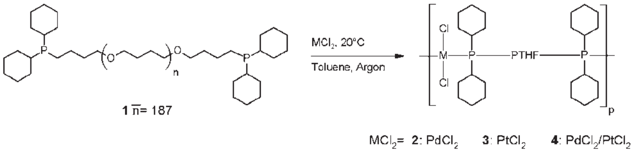
The mechanical activation of specific bonds in macromolecules offers interesting perspectives in chemical synthesis,[1–4] with ultrasound being one of the most efficient ways to produce mechanical forces on macromolecules in solution.[5] In sonicated solutions, the collapse of cavitation bubbles induces shear forces that readily break covalent polymers. The macroradicals that form in this way have, for example, been used in the preparation of block-copolymers.[6] Although effective, the raw power of ultrasound generally does not lead to well-defined products. Often, multiple scission events occur on a single chain and scission does not take place at predictable sites. However, Moore and coworkers recently showed that ultrasound can also be used to control chemical pathways by merely stretching polymer chains.[7,8]

In order to use ultrasonic chain scission in synthesis, the selectivity of the scission process should be increased. Several attempts have been made to this end, by preparing polymers containing weak linkages. Encina *et al.* showed that ultrasonic scission of polyvinylpyrrolidone polymers containing peroxide linkages proceeded preferentially at the oxygen–oxygen bonds.[9] The peroxide linkages broke approximately 5000 times faster than carbon–carbon bonds. This selectivity stems from the large difference in bond energies, *i.e.* 146 kJ mol^{-1} for peroxides *vs.* 351 kJ mol^{-1} for carbon–carbon bonds. Recently, Berkowski *et al.* reported on the site-specific cleavage of polyethylene glycol polymers containing a single diazo-linkage, either in the center or placed off-center.[10] Scission was shown to take place exclusively at the weak link, owing to the low bond energy of the diazo-group (100–125 kJ mol^{-1}).

Reversible linear coordination polymers[11–20] are equilibrium mixtures of cyclic oligomers and linear polymers.[21,22] The dynamic nature of such systems is determined by the rate of ligand exchange,[18,23,24] which also depends on the strength of the coordinative bonds.[18,25] Ultrasonic scission of coordination polymers based on palladium(II) dichloride and diphenylphosphine telechelic polytetrahydrofuran occurs selectively at the relatively weak palladium–phosphorus coordinative bond ($E_b < 150$ kJ mol^{-1}) and is therefore a fully reversible process.[26] Cleavage is specific in these polymers, because the difference in dissociation energies of the weak and strong bonds is very large. In the present report we explore the limits of site-specific cleavage by using polymers with two types of coordinative bonds with slightly different strengths. To this end, coordination polymers were prepared from bifunctional ligands and a mixture of two metal salts. In previous work we demonstrated that $PdCl_2$ and α,ω-bis(dicyclohexyl–phosphine)–polytetrahydrofuran are excellent building blocks, because they form soluble, kinetically stable coordination polymers.[25] Determination of changes in the degree of polymerization *via* size exclusion chromatography (SEC) is straightforward and allows for quantification of chain scission.[27]

Palladium and platinum dihalides were identified with DFT calculations as suitable combinations of metal salts to form breakable bonds with similar strengths in coordination polymers with bis(dicyclohexylphosphine) ligands. Total energies of palladium and platinum complexes of pentyldicyclohexyl phosphine were calculated, as well as those of the dissociated complexes. In this way, bond energy differences of 27, 21, and 19 kJ mol^{-1} were calculated for the chlorides, bromides and iodides, respectively. (See ESI†) The chlorides, with respective dissociation energies of 141 and 169 kJ mol^{-1} for the $PdCl_2$ and $PtCl_2$ complexes were selected for the experimental evaluation of scission selectivity in coordination polymers with dicyclohexylphosphine telechelic polytetrahydrofuran **1**.

Ligand **1** was synthesized *via* a cationic ring opening polymerization of tetrahydrofuran[28] and subsequent termination with lithium dicyclohexylphosphine.[27] SEC was used to determine the number average molecular weight ($M_n \sim 1.2 \times 10^4$ g mol^{-1} and polydispersity index (PDI ~ 1.14). Homonuclear coordination polymers **2** and **3** were prepared from this macromolecular ligand with $PdCl_2$ and $PtCl_2$, respectively (Scheme 1). Heteronuclear coordination polymer **4** was prepared using an equimolar mixture of palladium(II) and platinum(II) dichloride. ^{31}P NMR measurements indicated full complexation of the phosphine ligands in all polymers. Furthermore, the final palladium and



Scheme 1 Synthesis of palladium(II) and platinum(II) dichloride based homo- and heteronuclear coordination polymers **2–4**.

Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands. E-mail: R.P.Sijbesma@tue.nl; Fax: +31 40 247 2655; Tel: +31 40 247 3111

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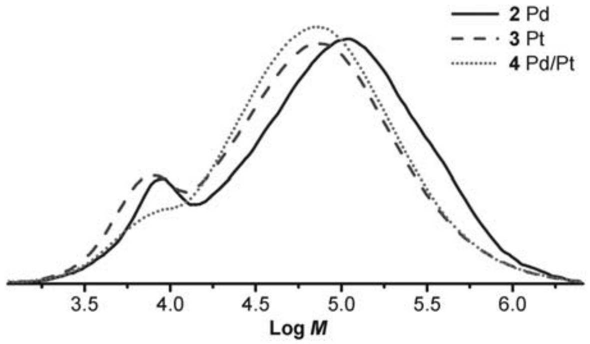


Fig. 1 Size exclusion chromatography traces of homo- and heteronuclear coordination polymers **2–4**.

platinum ratio in heteronuclear coordination polymer **4** was determined to be 53 : 47. Size exclusion chromatography showed similar molecular weights ($M_n \sim 2.2$ to 2.8×10^4 g mol^{-1}). Due to the presence of cyclic oligomers, relatively high polydispersities were observed for all three polymers ($M_w/M_n \sim 4.8$) (Fig. 1).

Scission rates and selectivities upon sonication of toluene solutions (10 g L^{-1}) of the individual coordination polymers were determined in the presence of palladium(II) dichloride bis(1-dodecyl)diphenylphosphine (**5**). Complex **5** acts as a scavenger, which selectively intercepts free phosphine groups created by scission, but does not interact with coordinated phosphines in the polymer.[27] Control experiments showed that 1.6 and 0.4% scission of polymers **2** and **3**, respectively had taken place without sonication for 2 h. By reacting with free chain ends exclusively, **5** serves as a tag, which enables identification of scission products with NMR (Scheme 2).

After sonication in the presence of 10 equivalents of **5** for 4 h, the molecular weight of coordination polymer **2** had decreased from $M_n \sim 2.8 \times 10^4$ to 1.2×10^4 g mol^{-1} (Fig. 2, top). Determination of the fraction of broken coordination sites was performed by measuring the decrease in intensity of the signal of scavenger **5** in SEC and showed that approximately 54% of the coordinative bonds had been broken after 4 h. (see ESI†) The molecular weight of platinum(II) coordination polymer **3** was reduced from $M_n \sim 2.7 \times 10^4$ to 1.3×10^4 g mol^{-1} through sonication for 5 h (Fig. 2, center). During this time, approximately 47% of the coordinative bonds in the polymer had broken as determined from the SEC signal of **5**. The extent of scission was also calculated using ^{31}P NMR spectroscopy, which contained peaks of unreacted complexes, as well as heterocomplexes that were formed by the reaction of free chain ends with **5** (see Fig. 3). Integration of the characteristic ^{31}P NMR signals showed that 49% of the coordinative bonds in the polymer had recombined with **5**, in excellent agreement with the extent of scission determined from SEC.

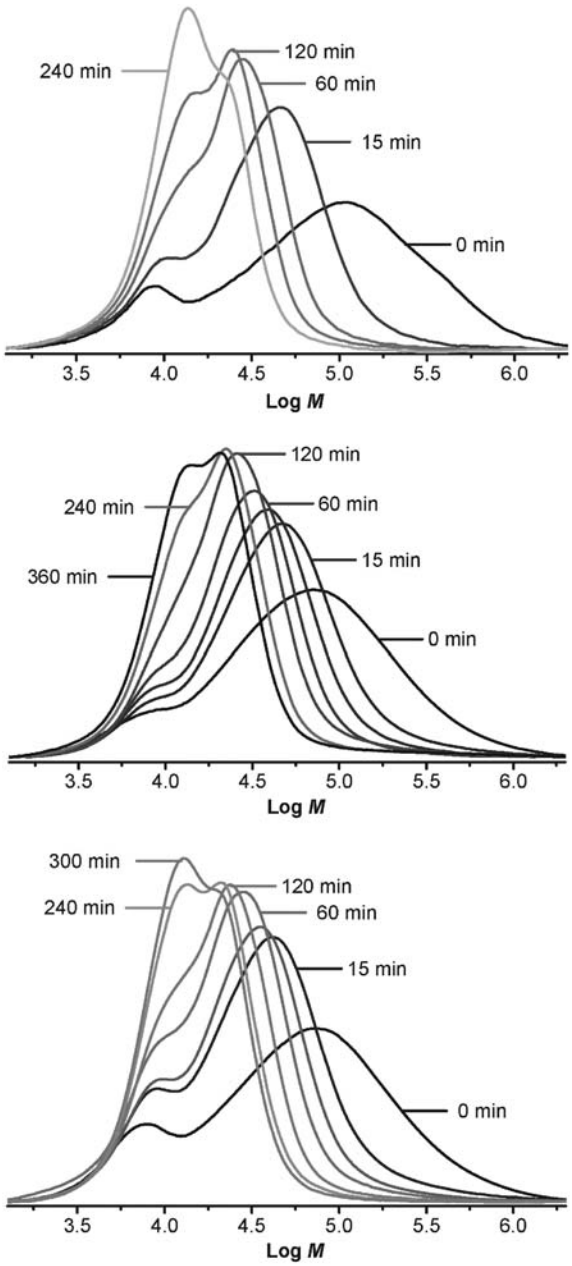
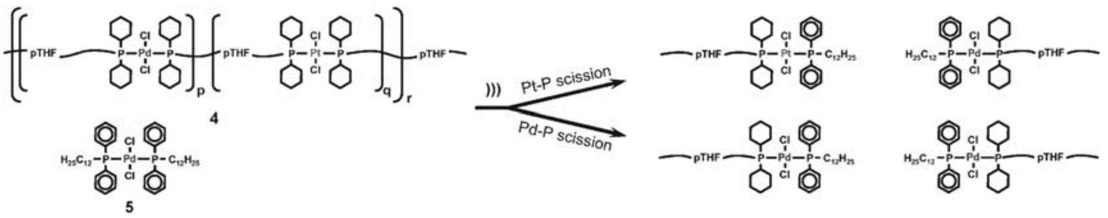


Fig. 2 SEC-traces measured at regular intervals during the sonication of palladium(II) based coordination polymer **2** (top), platinum(II) based coordination polymer **3** (center), and heteronuclear coordination polymer **4** (bottom), in the presence of 10 equivalents of complex **5**.



Scheme 2 Reaction of scavenger complex **5** (bottom left) with sonicated heteronuclear coordination polymer **4** (top left) resulting in the formation of palladium and platinum heterocomplexes.

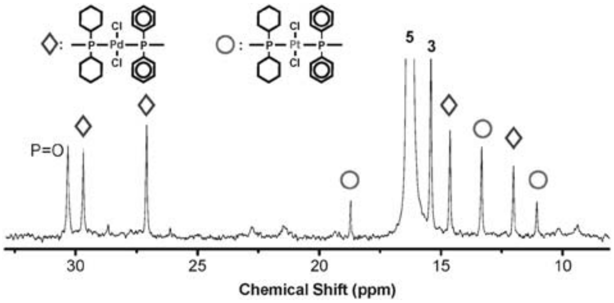


Fig. 3 ^{31}P NMR spectrum of platinum coordination polymer **3** after sonication in the presence of scavenger **5** for 5 h.

For mixed coordination polymer **4** a very similar overall scission rate was observed. The molecular weight of this polymer decreased from $M_n \sim 2.2 \times 10^4$ to 1.2×10^4 g mol^{-1} over the course of 5 h (Fig. 2, bottom). ^{31}P-NMR analysis of the sonicated solutions of polymer **4** revealed that the palladium and platinum centers did not break at the same rate (see Fig. 4). After 5 h, 63% of the Pd centers had been ruptured, compared to 53% of the Pt centers. However, during the first hour, the palladium centers ruptured approximately 3 times faster than the platinum centers.

With these results, limits on selectivity of ultrasound induced chain scission of polymers have been observed for the first time. It was previously demonstrated that stresses in ultrasound induced shear fields, which are strong enough to break covalent bonds, give absolute selectivity in breaking bonds with a difference in bond strength of approximately 200–225 kJ mol^{-1}.[10] The present experiments show that with a difference in bond strength of 27 kJ mol^{-1}, selectivity is still observed, but is limited. Although significant, the differences in breaking rate are much smaller than observed for thermal ligand exchange of palladium(II) and platinum(II) complexes,[29] which differ in rate by a factor of approximately 10^5.

An important factor that is expected to limit selectivity in the current system is the high molecular weight polymer chain between coordination sites ($M_n \sim 1.2 \times 10^4$ g mol^{-1}). As a result of this, neighboring coordinated metals in a chain are separated by approximately 120 nm, and the distance from the center of the chain, where the accumulation of shear force is at its maximum, may be very different. In the present system, rupture probabilities are therefore largely determined by the position of a given metal site on the chain, rather than by the strength of its bonds relative to the coordinative bonds on the neighboring metal. We are presently investigating the effect of decreasing the distance between metal sites, since at the high loading rates in ultrasonic experiments, selectivities may even *exceed* those of thermal ligand exchange processes,[30] and thereby enable controlling chemical reactions mechanically.

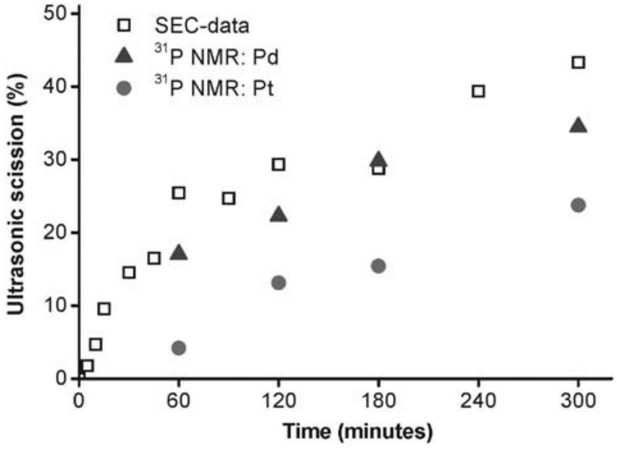


Fig. 4 Ultrasonic scission of heteronuclear coordination polymer **4** as determined from SEC, and partial contributions of palladium and platinum centers as determined from ^{31}P NMR.

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