Controlled Radical Polymerization (ATRP and CMRP) of Vinyl Monomer Mediated by Cobalt(II/III) Complexes

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The aim of the present dissertation was to study the role of: (a) cobalt(II) complexes containing 2-formiminopyrolyl chelating ligands combined with the tert-butyl α-bromoisobutyrate radical initiator; (b) cobalt(II) complexes containing 2-formylpyrrolyl chelating ligands and pyridine combined with tert-butyl α-bromoisobutyrate or AIBN radical initiators; and (c) cationic cobalt(III) complexes containing 2-formylpyrrolyl chelating ligands, trimethylphosphine and a bromide anion, in the molecular weight control of the radical polymerizations of methyl methacrylate (MMA) and styrene. For the cationic complex (c), we attempted to ascertain the initiation mechanism, since this complex was active even in the absence of initiator. For systems involving (c) alone or (a) together with tert-butyl α-bromoisobutyrate, syndiotactic-rich poly(methyl methacrylate) (PMMA) was obtained. The polymerization of styrene was only achieved with the system (c), resulting in atactic poly(styrene). The polymerization of MMA followed a free radical polymerization mechanism for both systems (c) and (a)+initiator. The polymerization of styrene in the presence of system (c) exhibited molecular weight control, with $M_n$ value eight times higher than those predicted for living polymerization. The influence of AIBN in system (c), as radical initiator, was tested in the $M_n$ control and in the polymerization kinetics. For MMA polymerization, the AIBN addition did not show any influence in the polymerization control at 50 °C and 70 °C, except an increase in the system activity. For styrene polymerization, the AIBN addition improved the molecular weight control, pointing to a reverse ATRP mechanism.

Keywords: Controlled/Living Radical Polymerization, vinyl monomers, ATRP, reverse ATRP, CMRP, cobalt complexes.

Introduction

Controlled radical polymerization is defined by Szwarc11 as “living” radical polymerization. It consists in a chain growth process exempt of any reaction that can interrupt the normal growth of the chain, like termination or chain transfer reactions. Therefore, it is possible to functionalize the terminal group of the polymer, as well as synthesize co-polymers by sequential addition of different monomers. However there is a key difference between “living” and “controlled” polymerization. In “living” radical polymerization there is a total absence of termination and chain transfer reactions, while in “controlled” radical polymerization those reactions are minimized.

To ensure molecular weight control and narrow dispersivities, rapid initiator decomposition at the beginning of the polymerization reaction is necessary and a dynamic equilibrium between the propagating and dormant species is required. Figure 1 explains the mechanism of controlled radical polymerization in a concise way.

The homolytic cleavage of the initiator generates two radicals, one stable and the other one reactive. The reactive radical initiates the polymerization reaction rapidly and the stable radical protects the propagating chain from termination reactions. The rapid decomposition of the initiator assures that all propagating radicals grow at the same time, but to ensure a radical polymerization with a controlled fashion, it is essential that the equilibrium constant between the dormant species and the propagating...
radical \((K_a/K_d)\) is greater than the polymerization equilibrium constant \(K_e\).\(^2\) Otherwise, the active species, or propagating radical, will be formed at different times of the polymerization and the dispersivity will be broader.\(^3\)

The propagating radical is in equilibrium with the dormant species, which implies that new monomer molecules are added to the propagating radical until the reaction with the stable radical occurs, forming the dormant species which does not participate in any chain termination reaction. This species can react with the monomer again after suffering a reverse activation, repeating the activation/deactivation cycle. If this cycle occurs frequently during the time of the polymerization, all the chains have approximately the same probability to grow, leading to narrow dispersivities.

At the beginning of the polymerization, the concentration of stable and reactive radicals is the same, but during the course of the reaction, the concentration of stable radicals, or dormant species, increases, due to the equilibrium shift towards the dormant species. The shift occurs because of the initiation termination, the reversible deactivation of propagating radicals at the beginning of the polymerization, as well as the irreversible addition of the reactive radical to the monomer. For this reason the stable radical is also called persistent radical. It works as controlling or mediating agent, since it is reactive enough to quickly react with the propagating chains and convert them reversibly into the dormant species, hence avoiding the termination of chains. This effect is known as Persistent Radical Effect (PRE).

Controlled radical polymerization is a vast subject, characterised by the activation/deactivation cycle mechanism, such as Atom Transfer Radical Polymerization (ATRP) and its particular case of Reverse ATRP, as well as Organometallic Mediated Radical Polymerization (OMRP), the latter undergoing two different types of mechanisms: reversible deactivation or Degenerative Transfer radical polymerization (DT). There are more types of controlled radical polymerizations which will not be addressed, since they are out of the scope of this work.

A typical system in ATRP is composed of a metal “catalyst”, an organometallic/coordination complex in its lowest oxidation state, and an initiator, usually an alkyl halide \((R-X)\), where the halogen is usually a bromine atom.\(^4\) In this type of polymerization, the activation/deactivation cycle mechanism is assured by the halogen exchange from the complex to the active species (deactivation) and from the dormant species to the complex (activation).\(^5\) In Reverse ATRP the complex possesses a halide or alkyl bond, meaning that the complex is in its higher oxidation state. Therefore, the initiator is a typical free radical initiator, such as AIBN, which will extract the halide from the complex and initiate the monomer, following at this point the same mechanism as the normal ATRP.\(^6\) Both, ATRP and reverse ATRP equilibriums are shown in Figure 2.

![Figure 2: Simplified mechanisms of control for: (a) ATRP, and (b) for reverse ATRP.](image)

As mentioned, OMRP can undergo two different control or activation/deactivation cycle mechanisms. In the reversible deactivation mechanism, the metal complex acts as a stable free radical, with its two consecutive oxidation states. In the lowest oxidation state, the metal complex reacts reversibly and caps the active species, forming the dormant species (deactivation) that can be reactivated by homolytic cleavage of the carbon-metal bond (activation).\(^7\) When the mechanism follows a DT mechanism, the control is not assured by the PRE, but instead by the exchange of the metallic complex, in its higher oxidation state, between the dormant species and a propagating radical, or active species. In this case the complex acts as a transfer agent. Both reversible deactivation and DT mechanisms can be observed in Figure 3.

![Figure 3: Simplified mechanisms of control for: (a) reversible deactivation and (b) for DT.](image)

In some cases it is possible to influence the system to undergo the desired mechanism by
changing the concentration of initiator. In fact, the reversible termination mechanism is favoured by a concentration of initiator lower than the metal and the DT is favoured by a concentration of initiator higher than the metal.

Since the discovery by Wayland of the controlled radical polymerization of acrylate monomers with a cobalt(III) complex containing a porphyrin and an alkyl group as ligands, the most successful metal used in OMRP being cobalt. This type of CRP is also known as Cobalt Mediated Radical Polymerization (CMRP). This discovery was only possible due to studies performed with the vitamin B12 molecule, which showed the homolytic cleavage’s reversibility of the cobalt-carbon bond and consequently PRE. Despite this success, CMRP seemed restricted to the polymerization of acrylate monomers. Only after 10 years Jérôme et al. reported the first successful CMRP of a non-acrylate monomer, the vinyl acetate CRP in the presence of bis(acetylacetonate) cobalt(II) complex. This success was a strong incentive for the development of OMRP and in particular the development of CMRP.

The objective of this work was the study of controlled radical polymerization of vinyl monomers, such as MMA and styrene, using cationic cobalt(III) complex 1 as mediator in CRP via ATRP, reverse ATRP or CMRP mechanisms. Complex 1 had already been characterized but not published, and is a cationic 18 electron cobalt(III) complex with a bromide anion and phosphines coordinated to the metal. In a previous work of our group, it had already been isolated from the reaction of Co(II) complex 2 with a stoichiometric amount of initiator tert-butyl α-bromoisobutyrate (3), this mixture being itself an effective mediator in the CRP of styrene and MMA. Both complexes 1 and 2 can be represented in Figure 4.

![Figure 4: Complex 1 tested in controlled radical polymerization of MMA and styrene. Complex 2 is its synthetic precursor being itself an efficient CRP mediator.](image)

The work developed previously with the Co(II) complex 2 along with initiator 3 evidenced the controlled polymerization of MMA, via CMRP mechanism, and styrene, via ATRP mechanism. Consequently, it was possible to prepare a diblock copolymer, by sequential addition of styrene and MMA. Initially, the polymerization of the styrene block formed a macro-initiator containing a bromine atom in one of the end groups of polystyrene. The employment of this macroinitiator in the presence of MMA and complex 2 as mediator, resulted in the formation of the diblock copolymer shown in Figure 5.

![Figure 5: Polymerization mechanisms of MMA, styrene and block copolymerization of polystyrene-b-MMA, initiated by tert-butyl α-bromoisobutyrate (3) and mediated by complex 2.](image)

A first idea to explore would be whether complex 1 is a good candidate for reverse ATRP mediation. Figure 6 shows the AIBN (4) initiator used in reverse ATRP conditions.

![Figure 6: Structure of AIBN (4), the initiator used in reverse ATRP conditions.](image)

Three more complexes shown in Figure 7 were tested in the present work. Their study will not be mentioned in this article since they were basically inactive in CRP (via ATRP or CMRP).

![Figure 7: Further complexes tested as CRP (ATRP/CMRP) mediators in the present work, although leading to unsuccessful results.](image)
Results and Discussion:

Synthesis and characterization of Co(III) complex 1: the synthesis of the Co(III) complex started with the in situ preparation of \([\text{CoCl}_2\text{L}_2]\), where \(L\) represents trimethylphosphine (PMe₃). The Co(II) precursor of the particular type \([\text{Co}^\text{II}\{\kappa^2\text{N},\text{O}-\text{NC}_3\text{H}_2\text{C}(\text{H})=\text{O}\}_2\text{L}_2]\) was prepared by a method published in the literature, reacting the cobalt adduct with the sodium salt of 2-formylpyrrole. Brownish crystals were obtained after crystallization at -20 °C in n-hexane. The Co(III) complex 1, was prepared by the oxidation of the Co(II) complex 2 with tert-butyl α-bromo-isobutyrate (3), in toluene, at 30 °C for 24 hours. The synthesis of complex 1 is shown in Figure 8.

![Figure 8: Synthesis of the Co(III) complex 1.](image)

Polymerization behaviour of complex 1: The Co(III) system was active per se, without the use of an initiator, in the polymerization of MMA and styrene. Different molar ratios monomer:complex 1 were tested in the polymerization of MMA at 50 °C (500:1, 1000:1 and 2000:1) and styrene at 70 °C (250:1, 500:1, 1000:1). The rates of polymerization of MMA were higher than for styrene. The polymerization of both monomers showed a first order kinetics for the monomer consumption and the apparent propagation rate constant increased with a decrease in the monomer:complex 1 molar ratio.

For the polymerization of MMA, none of the molar ratios tested showed control of the polymer molecular weight. The molecular weight evolution with the conversion of the MMA was typical of free radical polymerization.

The polymerization of styrene presents some degree of control over the molecular weight, since the \(M_n\) varies linearly with the conversion. However, the \(M_n\) is four to eight times higher than that predicted for living polymerization.

The dispersivities of the PMMAs and poly(styrenes) obtained in this study were always higher than 1.5 (\(M_w/M_n>1.5\)).

Figures 9 and 10 compile the kinetics and molecular weight results of the polymerizations of MMA and styrene.
Influence of AIBN as initiator: To test whether the system could control the molecular weight via a reverse ATRP mechanism, AIBN was added as a radical initiator. Figure 11 represents the decomposition and initiation mechanisms of AIBN.

The addition of the AIBN had no effect on the kinetics of the system for the polymerization of MMA. Since the system does not require any radical initiator, it is possible that the AIBN homolytic cleavage was not fast enough to have influenced the system. In this way, the complex may have generated the propagating radical much faster than the homolytic cleavage of AIBN.

The study of the PMMA molecular weight versus conversion reveals that the AIBN had no effect on the control of the molecular weight, since the M_n's are similar in both systems, with and without AIBN, as shown in Figure 12a.

For the styrene polymerization, the presence of AIBN as radical initiator improves the polymerization rate. The molecular weight control of the poly(styrene) was also improved, since the addition of the radical initiator lowered the molecular weight to just two times higher than predicted for living polymerization, instead of the previous eight times higher obtained without AIBN, as shown in Figure 12b.

The results led to the conclusion that adding AIBN induces polymerization control via a reverse ATRP mechanism for the polymerization of styrene.

Microstructure of the polymers obtained: _1^H and _13^C NMR spectra of the PMMA obtained, showed a syndiotactic-rich structure (Pr>0.7), calculated by relative integration of the triad’s resonance found in the α-methyl protons’ region. Two resonances can also be distinguished in the spectra: one at 5.3 ppm and another at 6.2 ppm. These resonances correspond to terminal double bonds of the vinyl group (-C(COOMe)=CH_2).
The $^{13}$C{H} NMR revealed an atactic poly(styrene) ($P_s=0.41$), calculated by relative integration of the triads resonances found in the ipso carbon region.$^{(12)}$

**Mechanistic discussion:** Based on the literature$^{(9)}$ and on the performed experiments, it is possible to propose a mechanism for the initiation of the polymerization of MMA and styrene, as shown in the Figure 13.

![Figure 13: Possible initiation mechanism for the studied system.](image)

This mechanism is based on the possible equilibrium existing between the coordination of the bromide anion and the release of one of the PMe$_3$. The homolytic cleavage of the Co-Br bond, with re-coordination of PMe$_3$ to the metal-center, leads to the formation of complex 2 and the nucleophilic attack of the bromide radical on the less substituted carbon of the vinyl monomer. This may be supported by the inactivity the polymerization of MMA and styrene mediated by cationic complexes, such as [Co($\kappa^3$N,O-NC$_6$H$_5$C(H)=O)$_2$(PMe$_3$)$_2$]BF$_4$ and [Co($\kappa^3$N,O-NC$_6$H$_5$C(H)=O)$_2$(PMe$_3$)$_2$]B(C$_6$H$_5$)$_2$, which are both isostructural with complex 1, but contain non-coordinating anions, such as [BF$_4$]$^-$ and the [B(C$_6$H$_5$)$_2$]$.^2$ This indicates clearly that the Br ion is responsible for the initiation of these polymerizations and not the [Co($\kappa^3$N,O-NC$_6$H$_5$C(H)=O)$_2$(PMe$_3$)$_2$]$^+$ cation.

The studies show that the polymerization of the MMA follows a free radical polymerization (Figure 14). This observation enables the assumption that the chain transfer is much faster than the activation/deactivation equilibrium, leading to the complex 2 ineffectiveness in the mediation and molecular weight control, therefore excluding an ATRP or CMRP mechanism. Since the addition of AIBN, as radical initiator, did not improve the control of the molecular weight, the possibility of a reverse ATRP mechanism is also excluded.

![Figure 14: Possible chain propagation mechanism.](image)

In the polymerization of styrene, molecular weight control occurred to some extent, being possible that the initiation follows the mechanism of Figure 13. Nonetheless, since the dispersivities and molecular weight are much higher than the values predicted for living polymerization, the control mechanism would be in accordance with Figure 15, in which the activation/deactivation equilibrium shifts toward the chain propagation reaction.

![Figure 15: Possible activation/deactivation equilibrium.](image)

The addition of AIBN in the polymerization of styrene, results in an improvement of the molecular weight control. Since complex 1 is a cobalt(III) species, it is possible that the addition of AIBN, as a radical initiator, promotes the control of the molecular weight via reverse ATRP, as shown in Figure 16.

![Figure 16: Possible mechanism of reverse ATRP mechanism for the polymerization of styrene in the presence of radical initiator AIBN.](image)

**Conclusions**

The complex [Co($\kappa^3$N,O-NC$_6$H$_5$C(H)=O)$_2$(PMe$_3$)$_2$]$^+$Br (1) was very active in the polymerization of MMA up to a ratio of monomer:complex of 2000:1, at 70 °C, and styrene up to a ratio of monomer:complex of 1000:1, at 70 °C.

The PMMA and the poly(styrene) obtained had typical microstructures of radical polymerization, the PMMA being mainly syndiotactic and the poly(styrene) atactic.

The complex exhibited some degree of molecular weight control, with $M_s$ eight times above the values predicted for living polymerization. This complex polymerized the MMA, presumably via a free radical mechanism.

To test the possibility of whether the complex [Co($\kappa^3$N,O-NC$_6$H$_5$C(H)=O)$_2$(PMe$_3$)$_2$]$^+$Br (1) could mediate the polymerization via reverse ATRP, AIBN
was added, as radical initiator. The poly(styrene) formed showed an improvement in the molecular weight control, indicating a reverse ATRP mechanism could be operating in the tested conditions. For the polymerization of MMA, the addition of AIBN had no effect in the molecular weight of the polymer.

The studies performed suggest the initiation of the monomers could be performed by the bromide radical, itself originated from the homolytic cleavage of the Co-Br bond. The PMMA formation followed a free radical polymerization and the poly(styrene) growth followed a relatively controlled polymerization mechanism via a ATRP.

Experimental

Materials: For manipulations containing compounds sensitive to oxygen and/or moisture, a vacuum/nitrogen dual line and Schlenk techniques were employed. The collected solvents were dried with molecular sieves and were distilled with the appropriate drying agent (CaH₂ for dichloromethane, 1,2-dichloroethane and n-hexane; sodium for toluene, THF and diethyl ether). A procedure from the literature was followed for purification and drying of solvents. For the drying process, the monomers were stirred under nitrogen with the recommended drying agent (CaH₂ for MMA, styrene, and vinyl acetate) and then distilled trap-to-trap. In case of solid reactants, they were dried and deoxygenated under a minimum vacuum of 10⁻¹ mbar, for at least 30 min.

Synthesis of 2-formylpyrrole: A solution containing 11.2 ml (120 mmol) of POCl₃ in toluene was prepared and added slowly under nitrogen to a prepared solution of 10.8 ml (140 mmol) of DMF in toluene in an ice bath. The mixture was allowed to warm to room temperature, obtaining a biphasic mixture. A 13.4 ml (200 mmol) solution of pyrrole in toluene was prepared and added slowly to the previous mixture. A change in colour from bright yellow to dark yellow was noted. The mixture was stirred under slow flow of nitrogen overnight. A mixture of water and ice was added to the mixture, already in an ice bath. NaHCO₃ was added until a pH of 7 was achieved, and afterwards a NaOH in water solution (40% m/V) was added until a pH 12 was obtained. The mixture color became reddish-orange. The mixture was stirred for 60 min and filtered to obtain a brown solid. The aqueous phase was extracted with chloroform and dried with MgSO₄. The suspension was filtered and the volatiles were evaporated in a rotary evaporator giving rise to a brownish oil. The product was extracted from the oil with hot n-hexane and stored at -20 °C. A yellowish orange solid precipitated overnight, which was filtered from the supernatant and dried under vacuum.

Synthesis of 2-formiminopyrrole: The procedure from the literature was followed. 1.426 g (15 mmol) of 2-formilpyrrole, 15 mmol of the correspondent aniline (aniline, 2,6-dimethylaniline, 2,6-disopropylaniline), a catalytic amount of p-toluensulfonic acid and MgSO₄ in 7.5-8 ml of ethanol were suspended in a 100 ml flask. The suspension was heated to reflux, with a condenser and a guard tube of CaH₂, and was left stirring over the weekend. NaHCO₃ was added while hot to neutralise the acid. The mixture was allowed to cool to room temperature and CH₂Cl₂ was added. The suspension was filtered with Celite® and further washed with CH₂Cl₂. The volatiles were evaporated in the rotary evaporator and the resulting product was extracted with refluxing n-hexane, and stored at -20 °C. A brown powder precipitated, which was filtered and dried. Yields, aniline=63%, di-Me-aniline=n.d., di-Pr-aniline=67%.

Synthesis of [Co(κ²N,N-NC₆H₄C(H)=2,6-R₂NC₆H₄H)₂] (R=H, Me or Pr): 85 mg (3.54 mmol) of NaH in THF were suspended in a Schlenk tube and the neutral ligand was added slowly under a nitrogen countercurrent. An immediate evolution of hydrogen occurred. The suspension was stirred for 90 minutes under a slow flow of nitrogen. In another Schlenk tube 146 mg (1.13 mmol) of CoCl₂ in THF were suspended. The ligand precursor’s sodium salt was added dropwise to the suspension of CoCl₂ in a cold bath at -80 °C. The suspension was stirred for 1 h. The cold bath was removed and the suspension further stirred for 2 h. Afterwards the volatiles were evaporated under dynamic vacuum and the complex was extracted with n-hexane. The solution was then concentrated and stored at -20 °C. Brown crystals precipitated, which were filtered from the supernatant and dried. Yield, 19.6% (R=H).

Synthesis of [Co(κ²N,O-NC₆H₄C(H)=O)₂(PMe₃)₂]: To prepare the cobalt adduct, a 4 ml (4 mmol) solution of PMe₃ (1 M in toluene) in THF was prepared in a pipette. In a Schlenk tube 260 mg (2 mmol) of CoCl₂ in THF were suspended. The PMe₃ was added dropwise to the previous suspension while in a cold bath at -20 °C. After the addition, the cold bath was removed. The mixture was allowed to warm to room temperature and was further stirred for 2 h.

In another Schlenk tube 105.6 mg (4.4 mmol) of NaH in THF were suspended and 380 mg (4 mmol) of
2-formilpyrrole were added slowly under a nitrogen counter flow, with immediate hydrogen formation. The solution was stirred for 2 h under nitrogen flow. The ligand’s sodium salt was added dropwise to the cobalt adduct previously prepared in a cold bath at -20 °C. The cold bath was removed and the suspension was stirred overnight. The volatiles were evaporated under dynamic vacuum and the complex was extracted with n-hexane. The solution was concentrated and stored at -20 °C. Brown crystals precipitated and were filtered from the supernatant and dried. Yield, 62%.

**Synthesis of [Co(x^2N,O-NC=C(C)=O)_{2}(PMe$_3$)$_2$]**

**Br:** A solution of 0.3 ml (1.61 mmol) tert-butyl-α-bromoisobutyrate in toluene was prepared in a pipette.

The complex [Co(x^2N,O-NC=C(C)=O)_{2}(PMe$_3$)$_2$] was dissolved in a minimum amount of toluene and the previous solution was added dropwise. The solution was heated to 30 °C and stirred for 24 h. An orange suspension was obtained, which was filtered and washed with toluene until the extracts became colourless and the powder was dried. The powder was dissolved in dichloromethane, concentrated and double-layered with n-hexane in a 1:4 ratio. Reddish orange crystals were obtained. Yield, 100%.

**Synthesis of [Cu(NC$_3$H$_7$C(H)=N-2,6-Pr$_2$)$_2$]**

In a Schlenk tube 54.7 mg (2.28 mmol) of NaH in THF were suspended and 509.8 mg (2 mmol) of the ligand (N(H)C$_3$H$_7$C(H)=N-2,6-Pr$_2$C$_6$H$_3$) were added slowly under counter flow of nitrogen. The suspension was stirred for 90 min under nitrogen. In another Schlenk tube 54.7 mg (2.01 mmol) of CuBr were suspended. The suspension of the ligand precursor’s sodium salt was slowly added dropwise while in a cold bath at -80 °C. The resulting suspension was stirred overnight. The volatiles were evaporated under dynamic vacuum and the resulting powder was washed with n-hexane and diethyl ether and extracted with toluene until the extracts became colourless. The solution was then concentrated, double-layered with n-hexane in a 1:4 ratio and stored at -20 °C. A pale yellow solid precipitated, which was filtered from the supernatant and dried. Yield, 70%.

**Synthesis of [Co(x^2N,O-NC=C(C)=O)_{2}(py)$_2$]**: In a Schlenk tube 157 mg (6.5 mmol) of NaH were suspended, and 389.9 mg (4.1 mmol) of 2-formylpyrrrole were slowly added in counter-flow, and immediate release of hydrogen was observed. The suspension was stirred for 2 h.

A solution with 2 ml (24.8 mmol) of pyridine and THF was prepared in a pipette. The cobalt adduct was prepared by suspending CoCl$_2$ (260 mg; 2 mmol) in THF in another Schlenk tube, by adding the solution of pyridine dropwise. The suspension was stirred for 30 min.

The suspension of the ligand precursor’s sodium salt was added to the adduct, in a cold bath, at -80 °C. After the addition, the bath was removed and the suspension stirred overnight. The volatiles were evaporated under dynamic vacuum and the resulting powder was washed with n-hexane and extracted with toluene until colourless extracts were obtained. The solution was concentrated and stored at -20 °C. Browns crystals were obtained. Yield, 70%.

**General polymerization procedure:** The necessary amount of complex was weighed to a Schlenk tube under nitrogen flow. The appropriate solvent (toluene or 1,2-dichloroethane) was added to the complex with a degassed syringe. The solution was thermostated to the required temperature by an oil bath. The required amount of degassed and purified monomer was added quickly via a degassed syringe. Periodically, aliquots were taken from the reaction mixture. Aliquots of the reaction mixture were treated in methanol, resulting in precipitated polymer, which was further washed in methanol. Subsequently, the polymer was filtered, dried under vacuum, weighed and stored in vials. All samples were analysed by GPC/SEC and some were chosen for NMR spectroscopy analysis.

**Characterizations:**

**GPC/SEC:** The GPC/SEC analyses were performed by eluting THF solutions of the samples in THF through two PolyPore columns protected by a PolyPore guard column (Polymer Labs), thermostated at 30 °C in a Warter oven, which were mounted on a Waters 1515 isocratic HPLC pump. The samples were detected by a Waters 2414 differential refractometer. The THF used was filtered through PTFE Pall 0.45 µm membrane filters and degassed in an ultrasound bath, while the samples were filtered through 0.20 µm PTFE GVS filters.

**NMR Spectroscopy:** Diamagnetic compounds were analysed by NMR spectroscopy acquired in Bruker “AVANCE III” 300 and 400 spectrometers. The solutions were prepared in deuterated solvents, stored at 4 °C with molecular sieves (CDCl$_3$), or under
nitrogen with molecular sieves (CD₂Cl₂, CDCl₂CDCl₂, toluene-δ₈) at room temperature.

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