

# Controlled Radical Polymerization of methyl methacrylate and styrene mediated by a cobalt(II)-based initiator system

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*The role of cobalt(II) complexes containing 2-formylpyrrolyl chelating ligands and phosphine ligands combined with a bromo-alkyl ester, an alkyl bromide or an azo compound in the formation of suitable initiator systems for vinyl monomer controlled radical polymerization was studied. The formation of syndiotactic-rich ( $P_r > 0.7$ ) poly(methyl methacrylate) (PMMA) and atactic ( $P_r = 0.49$ ) poly(styrene) was achieved, in high yields, with higher reaction rates in the first case. Polymerization of styrene was successfully controlled by the initiator system  $[\text{Co}\{\kappa^2\text{N}, \text{O}-\text{NC}_4\text{H}_3-\text{C}(\text{H})=\text{O}\}_2(\text{PMe}_3)_2]$  (**1**)/tert-butyl- $\alpha$ -bromoisobutyrate (**2**), at 50 and 70 °C, whereas for methyl methacrylate (MMA) control was only possible below 50 °C. Other sources of cobalt(II) were used, such as  $\text{CoCl}_2(\text{PMe}_3)_2$  and  $\text{CoCl}_2(\text{PPh}_3)_2$ , the first being very active in the initiation of MMA, similar to the one observed in the previous case and able to control its polymerization below 50 °C. The use of a coordinating solvent (THF) reduces the polymerization rate mediated by  $\text{CoCl}_2(\text{PMe}_3)_2$ , but does not affect the polymerization rate in the case of complex **1**. MALDI-TOF mass spectrometry pointed to a chain-end bromination of the poly(styrene) obtained in a controlled way, as opposed to poly(methyl methacrylate). The controlled polymerization of MMA in the presence of a poly(styrene) macroinitiator and complex **1**, prepared in molecular weight control conditions, was successful, resulting in the formation of the block-copolymer poly(styrene)-b-poly(MMA).*

**Keywords** ATRP, CMRP, cobalt(II) complexes, controlled/living radical polymerization, OMRP, vinyl monomers,

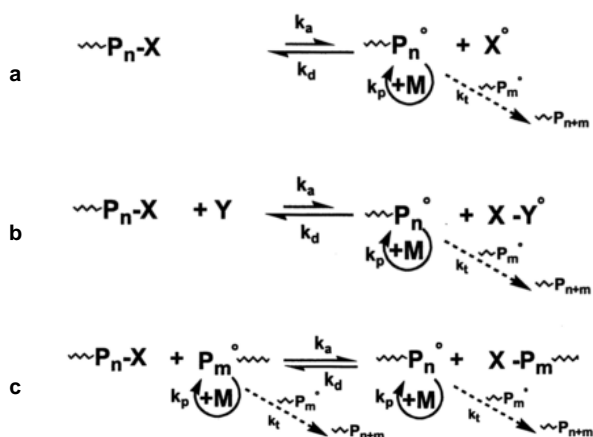
## Introduction

The discovery of living anionic polymerization, by Szwarc *et al.*,<sup>1</sup> played a pioneering role in the field of controlled chain polymerization, paving the ground for the later development of controlled radical polymerization (CRP).<sup>2,3</sup> This type of polymerization consists in the minimization (or elimination) of chain-breaking reactions, such as chain transfer or termination, by establishing an equilibrium between propagating radicals and a dormant species. Deactivation of the dormant species involves the protection of the propagating chain. Conversely, the activation of the dormant species turns the propagating chain into a living status and susceptible to the addition of further monomer units. Chain growth is attained by successive activation/deactivation steps of the dormant species. A controlled process should exhibit first order kinetics relative to monomer addition, molecular weight should be proportional to monomer conversion, polydispersity should statistically decrease with monomer conversion in a Poisson-like distribution and every chain should be

end-functionalized. The activation/deactivation equilibrium is determined by the persistent radical effect: when a slow termination reaction takes place, the concentration of living radicals increases, shifting the equilibrium to the formation of termination products and avoiding chain transfer. This effect is known as the Ingold-Fisher effect,<sup>4</sup> causing a dormant species accumulation, as persistent radicals cannot terminate with itself, but only with the propagating species, which creates a self-regulating effect.

From a mechanistic point of view, the equilibrium between propagating radicals and dormant species, resulting in controlled polymerization, is achieved in three different ways (Fig. 1).<sup>5</sup> In controlled radical polymerization by SFRP (*Stable Free Radical Polymerization*), a radical species,  $X^\cdot$ , is involved in the activation/deactivation equilibrium of the propagating polymeric chain. Species  $X^\cdot$  is usually a nitroxide or an organometallic/coordination compound (Fig. 1a). In ATRP (*Atom Transfer Radical Polymerization*), the species Y, an organometallic/coordination compound, is involved in an equilibrium with a halogen atom, X, by

means of a redox process. The halogen is responsible for the quick protection/deprotection sequence of the polymeric propagating chain (Fig. 1b). In degenerative transfer radical polymerization (DT), the initiation is conventional (analogous to free radical initiation), and the control is possible due to a transfer agent, by means of a transfer group, X, which does not exhibit a persistent radical effect (Fig. 1c).



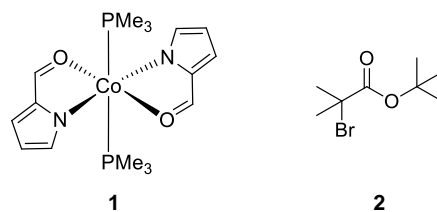
**Figure 1** Simplified controlled radical polymerization mechanisms: (a) SFRP; (b) ATRP; (c) DT.

OMRP (*Organometallic Mediated Radical Polymerization*) is of particular interest for the present study and, generally, is a type of CRP that allows control over polymerizations based on the reversible homolytic cleavage of a weak bond between an alkyl group and a transition metal species. OMRP can occur via SFRP or DT mechanisms. In OMRP it is the organometallic compound itself which acts as a reversible capping agent of the growing chains in the activation/deactivation equilibrium (breaking/formation of a metal-chain bond). The adopted mechanism usually cannot be classified exclusively as radical, but as a combination of radical and coordination. This statement has been the source of much discussion.<sup>6</sup>

CMRP (*Cobalt Mediated Radical Polymerization*) is a particular case of OMRP occurring with cobalt complexes, having its origin in the use of organocobalt(III) complexes to generate carbon-centered radicals, owing to the facile Co-C homolysis, and to their propensity to exhibit the persistent radical effect. By analogy with vitamin B12,<sup>7</sup> the first organocobalt complex used as initiator was a five-

coordinate cobalt(III) porphirin, the fifth ligand being an alkyl group R. These complexes give rise, by Co-R homolytic cleavage, to a carbon-centered radical R• that initiates polymerization, whilst the radical cobalt(III) complex – a persistent radical – coordinates itself reversibly to the growing polymeric chain, protecting it. This mechanism, dominated by the persistent radical effect, is typical of  $\alpha$ -monosubstituted vinyl monomers containing electron-withdrawing vinyl monomers. Alternatively, a CCT (Catalytic Chain Transfer)<sup>8</sup> process may occur, especially for  $\alpha$ -methylsubstituted vinyl monomers. In this case, the stereochemical hindrance induced by the coordination sphere of the porphirin renders the  $\alpha$ -methyl protons susceptible to  $\beta$ -elimination to the electron-rich metal center.

In this work, we study the controlled radical polymerization of methyl methacrylate (MMA) and styrene using as initiator system a 1:1 mixture of a Co(II) complex and a radical initiator. Among the complexes synthesized and studied by our group,<sup>9–11</sup> the Co(II) complex containing 2-formylpyrrolyl ligands stabilized by trimethylphosphine (**1**) (Fig. 2) was selected, since it was a 19-electron species with oxidation state +2, which could be efficient in one-electron transfer processes by oxidation to the state +3, with great tendency to attain electronic saturation (18 e<sup>-</sup>). The initiator, *tert*-butyl- $\alpha$ -bromoisobutyrate (**2**), was selected from a collection of typical commercial initiators used in ATRP processes, allowing the formation of very stable tertiary radicals.



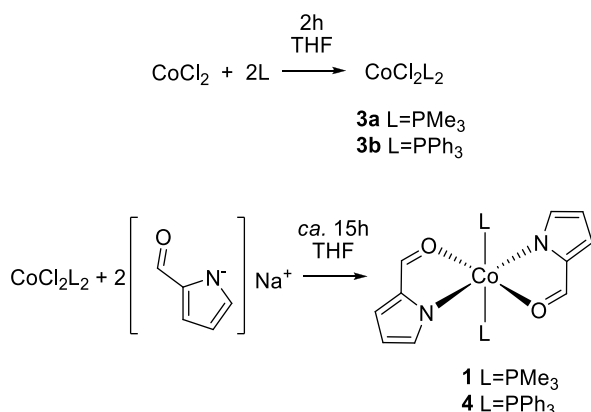
**Figure 2** Cobalt(II)-based initiator system tested in the controlled radical polymerization of methyl methacrylate and styrene.

## Results and Discussion

### Synthesis and characterization of Co(II) complexes:

The synthesis of the Co(II) complexes started by the preparation of the respective cobalt dichloride adducts, in the form  $\text{CoCl}_2\text{L}_2$ , where L represents

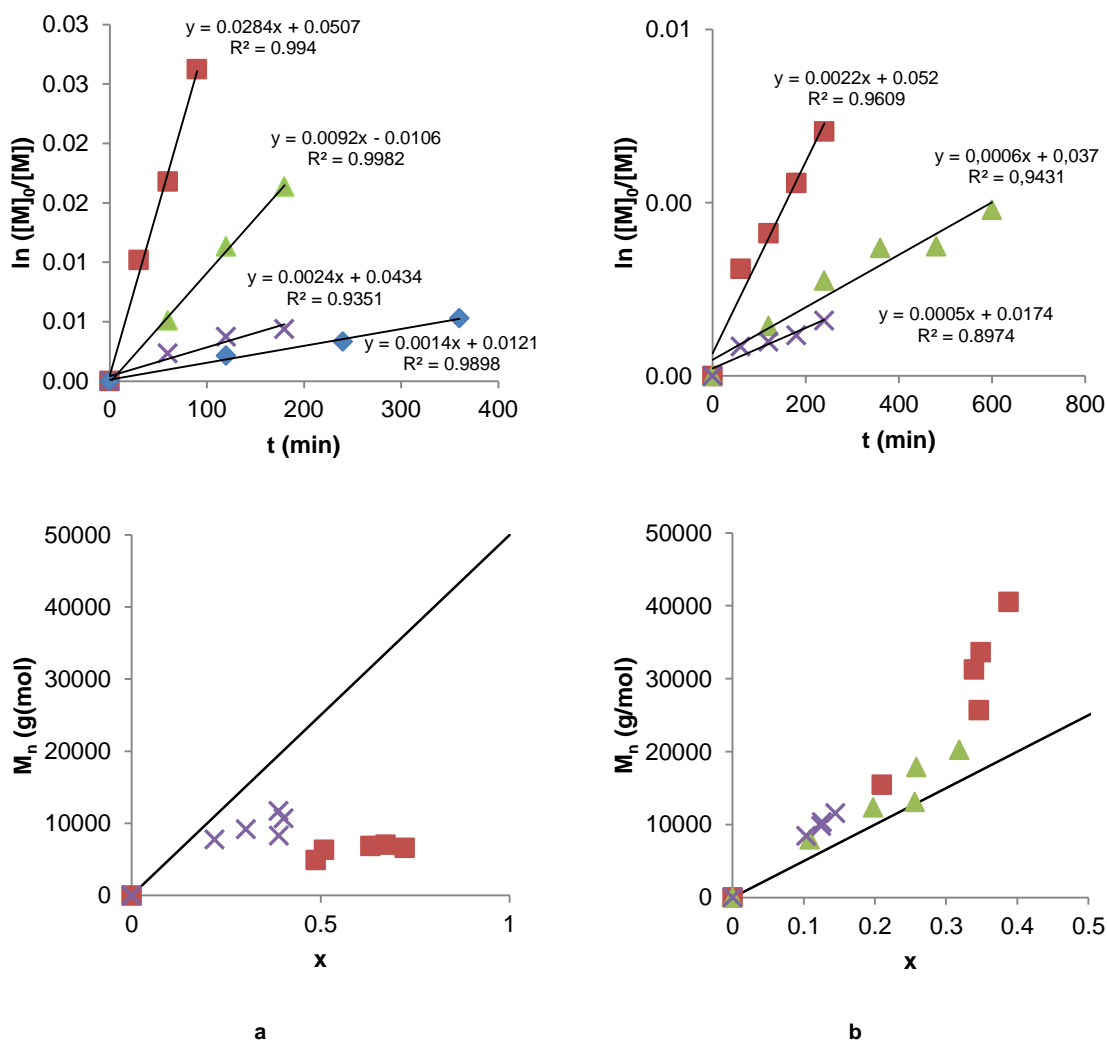
trimethylphosphine (**3a**), triphenylphosphine (**3b**) and triphenylarsine (Fig. 3). For L= PMe<sub>3</sub> and PPh<sub>3</sub>, bottle-green and turkish-blue powders were obtained, respectively. For L=AsPh<sub>3</sub>, unknown in the literature, isolation was not successful. The synthesis of 2-formylpyrrole was carried out by formylation of pyrrole, performed in Vielsmeier-Haack conditions.<sup>12</sup> The 2-formylpyrrolyl Co(II) complexes of the type [Co{κ<sup>2</sup>N,O-NC<sub>4</sub>H<sub>3</sub>-C(H)=O)<sub>2</sub>L<sub>2</sub>] (**1** and **4**) were prepared by the method published in the literature,<sup>9</sup> reacting cobalt dichloride adducts with the sodium salt of 2-formylpyrrole (Fig. 3). For the complex with L=PMe<sub>3</sub> (**1**), a microcrystalline red-brown solid was obtained from crystallization at -20 °C, in n-hexane, the structure of which was confirmed by EPR and X-ray diffraction.<sup>9</sup> The compound with L=PPh<sub>3</sub> (**4**), not reported in the literature, had an elemental analysis that proved to be inconclusive.



**Figure 3** Preparation of the Co(II) complexes used in this study.

**General behavior of the initiator system:** In preliminary polymerization tests, the initiator system **1/2** afforded, after two and three hours, 70% of styrene conversion and full conversion of MMA, respectively, at 90 °C and monomer:metal:initiator molar ratio of 100:1:1.

Following these results, several molar ratios (500:1:1 and 1000:1:1, at 90 °C) and temperatures (70, 50, 25, 0 °C, at a monomer:metal:initiator molar ratio equal to 500:1:1), were tested. The rate of polymerization of MMA was consistently superior to that of styrene. Generally, the initiator system **1/2** showed first order kinetics for monomer consumption and the corresponding apparent propagation constant increases with temperature and with decreasing monomer:metal:initiator molar ratios (top plots of Fig. 4). The activation energies for the polymerization of MMA and styrene were 31 and 55 kJ.mol<sup>-1</sup>, respectively. As observed for the polymerization of MMA, molecular weight control improves as temperature decreases, because the corresponding experimental results lie closer to the ideal living polymerization straight line (bottom of Fig. 4a). Improvement in molecular weight control of the PMMA formed is related to the decrease in chain transfer reactions, since molecular weight increases, getting closer to the living polymerization line. Therefore, the polymerization of MMA is controlled by chain transfer at higher temperatures. The molecular weight control is more easily achieved in the polymerization of styrene than in the case of MMA, also improving as the temperature decreases. In the latter case, the polymerization is not controlled at higher temperatures, resulting in higher molecular weights than those predicted by a living system. Some degree of thermal polymerization of styrene was observed at 90 °C, the termination of which occurs by recombination, giving rise to high molecular weight polystyrenes in uncontrolled conditions (bottom of Fig. 4b). Polydispersities were always smaller than 1.80 (and as low as 1.28), but only in the polymerization of styrene at 70 °C was observed a clear decrease of M<sub>w</sub>/M<sub>n</sub> with the conversion.

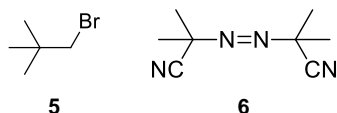


**Figure 4** Plot of  $\ln([M]_0/[M])$  and  $M_n$  (a – MMA; b – styrene) versus time and conversion, respectively, in the corresponding reactions at variable temperatures, with a monomer:metal:initiator molar ratio of 500:1:1 (■ - 90 °C; ▲ - 70 °C; × - 50 °C; ◆ - 25 °C; --- - line for ideal "living" system).

**Microstructure of the homopolymers obtained:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the PMMA obtained correspond, for all reaction conditions used, to a syndiotactic-rich structure, with a content of syndiotactic diads ( $P_r$ ) higher than 70%, calculated by relative integration of the triad resonances found in the  $\alpha$ -methyl protons region.  $P_r$  decreased with reaction temperature, which is related to the repulsion between the  $\alpha$ -methyl group and the ester group of successive repeating units: *racemo* addition is favored as temperature decreases.<sup>13</sup> We also observed two resonances at 5.3 and 6.1 ppm that correspond to the geminal protons of the terminal vinyl  $-\text{C}=\text{CH}_2$  double bonds. As expected, the  $^1\text{H}$  NMR of the polystyrene obtained is not very sensitive to tacticity,<sup>14</sup> and showed two minor doublet resonances,

which correspond to terminal vinyl  $-\text{CH}=\text{CH}-$  double bonds. The corresponding coupling constant ( $^3J_{\text{HH}}$ ) of 18 Hz (whose molar fraction is lower than 3%) is typical of a *trans*- $\text{CH}(\text{Ph})=\text{CH}-\text{CH}(\text{Ph})-\text{CH}_2-$  group, probably originated from chain transfer reactions occurring by  $\beta$ -hydrogen elimination. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra of polystyrene revealed  $P_r$  equal to 0.49, by relative integration of the triad resonances observed in the *ipso* carbon region, which is a clear indicator of an atactic microstructure.

**Radical initiator influence:** The influence of the type of radical initiator used was tested by varying the substitution level of the carbon where the radical is centered (using neopentyl bromide (5)), as well as the type of initiation (using AIBN (6)).



**Figure 5** Neopentyl bromide (**5**) and AIBN (**6**).

When using **5** as initiator, MMA conversion is nine times lower than the one observed with initiator **2**, due to the high instability of the primary radical involved. Such system does not follow a first order kinetics, which suggests a great lack of molecular weight control. Molecular weights are substantially higher than those expected in a living polymerization, at low conversions, which is typical of a conventional radical process, where initiation is slow (low half-life of radicals), giving a low concentration of radical originated from **5** and a low propagation rate (Fig. 1a). In this way, the effective monomer:initiator molar ratio is much higher than the one initially defined, leading to higher molecular weights. In the case of the initiator system complex **1**/AIBN (**6**), contrary to the system with initiator *tert*-butyl- $\alpha$ -bromoisobutyrate (**2**), the activation/deactivation equilibrium is definitely CMRP-based. The first system is less active than the latter one for both monomers, but propagation kinetics is still a first order process. In both cases, the molecular weights are consistently above the living polymerization line. This observation can be attributed either to the irrelevance of the Co(II) complex in mediating the process of molecular weight control, or to the fact that a fraction of radicals generated by homolytic decomposition of **6** are irreversibly recombined. In both cases, the concentration of the radical generated by decomposition of **6** is lower than expected, making that the effective monomer:initiator molar ratio is higher than that initially defined. This hypothesis could be confirmed by performing a blank reaction only with the monomer and **6**. However, polydispersities were never higher than 1.70.

**Cobalt(II) source influence:** The effect of the cobalt source was evaluated by using the adducts  $[\text{CoCl}_2(\text{PMe}_3)_2]$  (**3a**) and  $[\text{CoCl}_2(\text{PPh}_3)_2]$  (**3b**). In the polymerization of MMA mediated by **3a**, conversion was higher than that observed with complex **1** (about 1.4 higher), while conversion of MMA with **3b** is negligible. The first observation indicates that the organic

coordination sphere of **1** has a negative impact on the MMA polymerization kinetics and on the molecular weight control in relation to the  $\text{CoCl}_2(\text{PMe}_3)_2$  parent precursor. This observation is probably related to the electronic nature of the complexes: while **3a** is coordinatively unsaturated (15 electrons), **1** is oversaturated (19 electrons), leading, upon an electron transfer process, to a 14 and an 18 (saturated configuration) electron count, respectively.

**Solvent effects:** The influence of the solvent in the reactivity of the system was tested by using THF, a polar and coordinating entity. The kinetics using THF as a solvent is similar to the one observed with toluene, for both monomers. However, in terms of molecular weight control, the system is more efficient in the case of MMA polymerization and less efficient in the case of styrene polymerization, when compared with the corresponding results for reactions performed in toluene. The decrease in control observed for styrene polymerization in THF is a case where this solvent exerts a coordinative pressure on the metal center, making it less effective, not favoring the activation/deactivation equilibrium. In addition, THF is a worse solvent than toluene for styrene and polystyrene.<sup>15</sup>

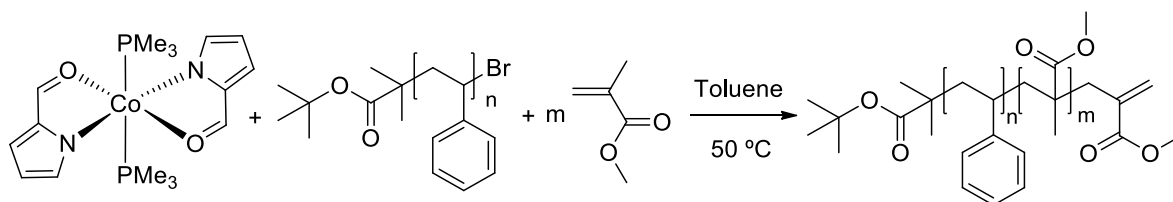
**MALDI-TOF spectrometry:** MALDI-TOF mass spectrometry was specifically used to establish whether or not the polymers obtained were chain-end brominated, as it was supposed to happen in the case of an operating ATRP mechanism. Two samples of each polymer type were analyzed. Both PMMA samples were successfully ionized, at least in a sufficient extent to record the respective spectra. Several signals separated by 100 mass units appeared in the PMMA spectrum. Lack of an isotopic distribution characteristic of a bromine atom in the ionized fraction led to the conclusion that, at least, the ionized PMMA chains were not end-brominated.

In the polystyrene case, none of the samples were ionized by the MALDI technique. In fact, bromine-terminated polystyrene is usually impossible to ionize via MALDI.<sup>16</sup> The lack of ionization of the polystyrene sample may indicate that the great majority of these polymer chains are chain-end brominated.

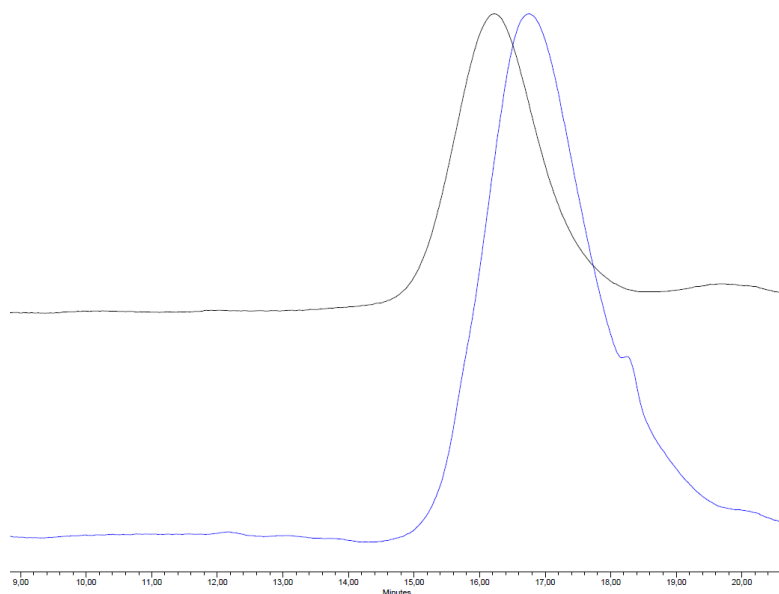
**Block copolymerization tests:** Block copolymerization is the more direct application of controlled radical

polymerization. A successful test was achieved by starting the growth of a polystyrene block through the polymerization of styrene in molecular weight control conditions (initiator system **1/2**, 50 °C and monomer:metal:initiator equal to 500:1:1), for about 24 h, under nitrogen atmosphere, followed by evaporation of the volatiles to dryness. The resulting solid had a molecular weight of 5500 g/mol. With this information and assuming a chain-end bromination (as suggested by MALDI-TOF analysis), it was possible to calculate MMA and complex **1** quantities, in order to maintain molecular weight control conditions. The growth of a second block used the previous solid as a macroinitiator to polymerize MMA to a maximum conversion of 17% (Fig. 6). In fact, MMA polymerization with this polystyrene macroinitiator occurred in a controlled way, with appreciable activity. After work-up, the new solid had a molecular weight of 12100 g/mol. It is clear that the GPC/SEC chromatogram

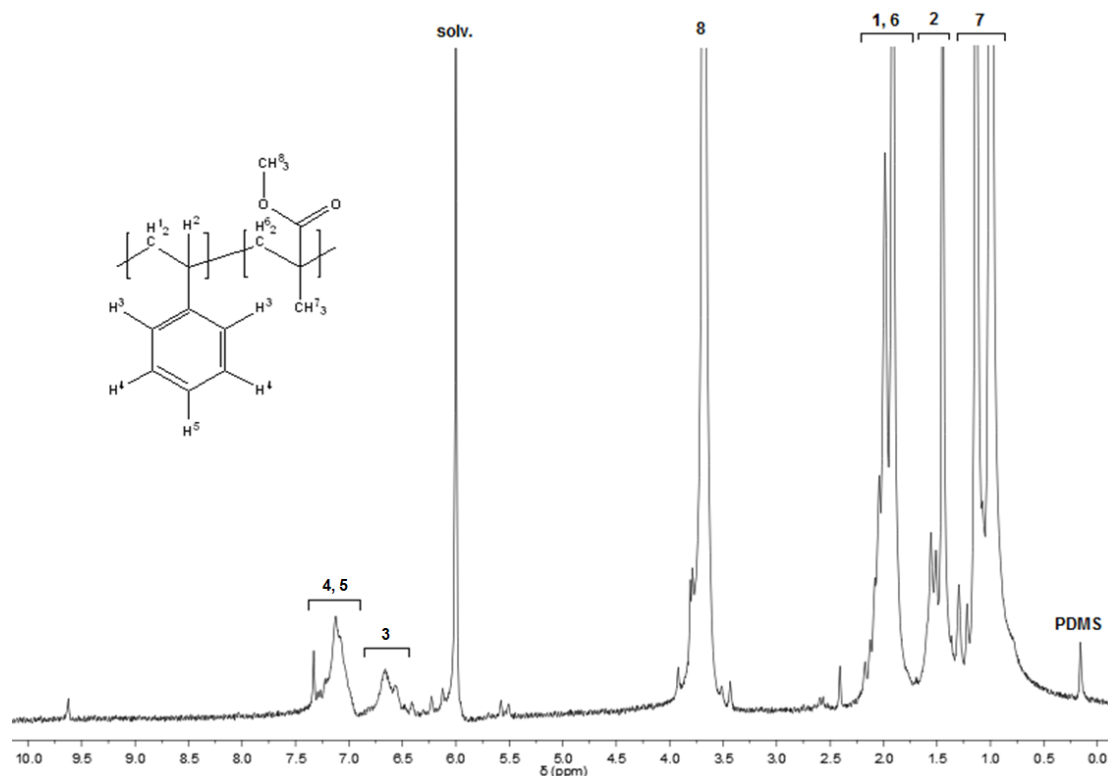
of this new solid (Fig. 7), resulting from the block-copolymerization of MMA with the polystyrene macroinitiator, has a smaller retention time than that of the polystyryl bromide precursor and, as expected, the respective polydispersity decreased (1.76 vs. 1.43, respectively). This fact is a strong indicator of the formation of the block copolymer poly(styrene)-*b*-poly(MMA). The <sup>1</sup>H NMR spectrum of the final block-copolymer (Fig. 8) reveals resonances between 6.25 and 7.5 ppm, indicating the presence of a styrenic fraction in the solid sample. So far, the formation of a block-copolymer cannot be confirmed exclusively by <sup>1</sup>H NMR, because the chemical shifts of the merging repeating units are not yet assigned in the spectra. These assignments would require <sup>13</sup>C NMR and 2D correlation experiments and, therefore, a more detailed and prolonged study.



**Figure 6** Reaction of formation of a poly(styrene)-*b*-poly(MMA) block-copolymer from a brominated polystyrene macroinitiator.



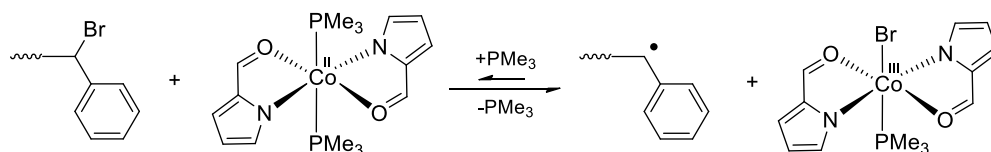
**Figure 7** Superimposition of the GPC/SEC chromatograms of the brominated polystyrene macroinitiator (blue line;  $M_n=5500$  g/mol;  $M_w/M_n=1.76$ ) and of the poly(styrene)-*b*-poly(MMA) block-copolymer (black line;  $M_n=12100$  g/mol;  $M_w/M_n=1.43$ ).



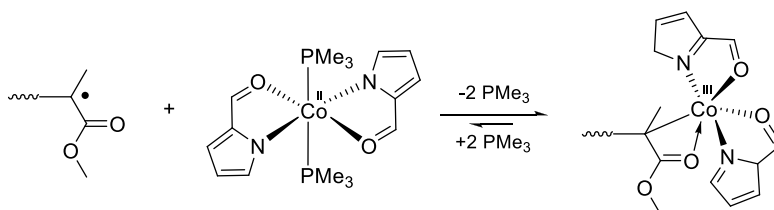
**Figure 8** <sup>1</sup>H NMR spectrum of the poly(styrene)-*b*-poly(MMA) block copolymer ( $M_n=12100$  g/mol), obtained from the polymerization of MMA using the initiator system composed by complex **1** and an end-brominated polystyrene macroinitiator ( $M_n=5500$ ) (300 MHz, 120 °C,  $C_2D_2Cl_4$ ).

**Mechanistic discussion:** The molecular weight control was achieved for both monomers MMA and styrene, but somewhat different mechanisms were observed. In fact, the system exhibited a radical nature, with its activity being only due to the simultaneous presence of both the metal complex and the radical initiator. In the polymerization of styrene one can assume that the mechanism is ATRP-based, because the MALDI-TOF analysis and the growth of the block-copolymer proved by GPC/SEC pointed to a brominated end-functionalized polystyrene. The brominated polystyrene chains along with complex **1** successfully mediated the controlled polymerization of styrene, through the activation/deactivation equilibrium established by the  $Br^\bullet$  radical, which is in permanent exchange with the propagating chain and the Co complex (Fig. 9). On the other hand, the MALDI-TOF analysis and the presence of vinyl end groups in the homo- and copolymer proves that the polymerization of MMA, at least to a certain extent, is controlled by chain transfer. This fact suggests a CMRP-type mechanism, where the

activation/deactivation mechanism may involve a reversible  $Co-C_{chain}$  homolytic bond cleavage with additional terminal chelation of the carboxylic oxygen to the metal that, upon homolytic bond cleavage, gives rise to the PMMA propagating radical (Fig. 10). The chelation hypothesis results in the formation of a strained four-membered coordination ring. Stereochemical proximity of the  $\alpha$ -methyl group favors chain transfer reactions through  $\beta$ -hydrogen elimination from the chain to the metal, with formation of a Co(III) hydride species. This hydride species can reinitiate polymerization through homolytic cleavage of the Co-H bond, followed by addition of  $H^\bullet$  to the monomer, giving rise to methyl isopropylformate and vinyl double bond chain end-groups, with regeneration of complex **1**. Therefore, the PMMA obtained will be a mixture of methyl isopropylformate and *tert*-butyl isobutyrate terminated polymers in one end and vinyl double bonds in the other end (also with some probability for the occurrence of chain-end bromination).



**Figure 9** Presumed activation/deactivation equilibrium occurring in the polymerization of styrene.



**Figure 10** Presumed activation/deactivation equilibrium occurring in the polymerization of MMA.

## Conclusions

The complex  $[\text{Co}\{\kappa^2\text{N},\text{O}-\text{NC}_4\text{H}_3-\text{C}(\text{H})=\text{O}\}_2(\text{PMe}_3)_2]$  (**1**) combined with the initiator *tert*-butyl  $\alpha$ -bromoisobutyrate (**2**) is an effective initiator system for the controlled radical polymerization of methyl methacrylate and styrene. The initiator system proved to be very efficient for both MMA and styrene monomers (but more active for the first), even at monomer:metal:initiator molar ratios as high as 1000:1:1 and at room temperature. The PMMA obtained revealed a syndiotactic-rich content whereas the polystyrene was atactic. The initiator system successfully controlled the polymerization of MMA below 50 °C, and of styrene at 50 and 70 °C. Only MMA polymerized in the presence of  $[\text{CoCl}_2(\text{PMe}_3)_2]$ , with similar results to those observed for  $[\text{Co}\{\kappa^2\text{N},\text{O}-\text{NC}_4\text{H}_3-\text{C}=\text{O}\}_2(\text{PMe}_3)_2]$ . In reactions performed in THF, better results were observed for MMA in terms of molecular weight control, but worse for styrene. Considering several arguments, one can conclude that polymerization of styrene occurred via an ATRP mechanism, whereas MMA polymerization followed a catalytic chain transfer mechanism, with an activation/deactivation equilibrium typical of CMRP. Chain-end bromination of the polystyrene enabled its use as macroinitiator, together with complex **1**, in the controlled radical polymerization of MMA, leading to the formation of the block-copolymer poly(styrene)-*b*-poly(methyl methacrylate), opening up possibilities of preparation of other interesting polymer architectures.

## Experimental

**Materials:** Operations involving organometallic compounds were conducted under nitrogen atmosphere (*Air Liquide*) using suitable glovebox and dual vacuum-nitrogen line techniques. Solvents were dried with molecular sieves and distilled under nitrogen and suitable drying agents (sodium for toluene, diethyl ether and THF;  $\text{CaH}_2$  for *n*-hexane and dichloromethane). Liquid reagent purification used a general procedure,<sup>17</sup> where drying used a suitable agent ( $\text{NaH}$  for MMA;  $\text{CaH}_2$  styrene;  $\text{NaSO}_4$  for MA, isopropyl bromide and neopentyl bromide;  $\text{CaCl}_2$  for acrylonitrile), with stirring under nitrogen atmosphere, followed by *trap-to-trap* distillation. AIBN (*Fluka*) was used as received having been evacuated to a minimum vacuum of  $10^{-4}$  bar, for at least 30 min.

**Synthesis of 2-formylpyrrole:** A solution of 10.8 mL (140 mmol) of dimethylformamide in toluene was prepared, in an ice bath. A solution of 11.2 mL (120 mmol) of phosphorus oxychloride in toluene was slowly added to the first, under nitrogen. The reaction mixture was allowed to warm to room temperature, after which a two-phase separation is observed. A solution of 13.4 mL (200 mmol) of pyrrole in toluene was slowly added to the previous mixture, the color changing from light to strong yellow. The reaction mixture was left stirring overnight, under nitrogen. A water and ice mixture was added to the previous mixture and, in an ice bath, sodium hydrogen carbonate was added until pH 7. Sodium hydroxide was subsequently added until pH 12. The



reaction mixture gradually turned orange-red and was stirred for about 1 h, and filtered, to give a brownish solid. The aqueous phase was extracted with chloroform and dried with anhydrous magnesium sulfate. The dried solution was filtered and evaporated to dryness under vacuum until a brown red oil was obtained. The oil was dissolved in boiling n-hexane and stored at -20 °C. The precipitate was filtered and dried under vacuum.

**Synthesis of [CoCl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>] (3a):** 0.894 g (6.93 mmol) of anhydrous cobalt dichloride were suspended in THF in a Schlenk tube. A solution of 13.9 mL (13.9 mmol) of trimethylphosphine (1 M in toluene) in THF was prepared in a Schlenk tube. The trimethylphosphine solution was added dropwise to the cobalt dichloride suspension, at -20 °C. The resulting suspension was dark green. After addition, the mixture was allowed to warm to room temperature, being further stirred for 2 h. The mixture was evaporated to dryness. The dark green solid was washed with n-hexane until extracts were colorless. The washed solid was dried under vacuum, giving a bottle-green powder. Yield, 100%.

**Synthesis of [CoCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (3b):** 1.29 g (10 mmol) of anhydrous cobalt dichloride were suspended in THF in a Schlenk tube. A solution of 5.26 g (20 mmol) of triphenylphosphine in THF was prepared in a Schlenk tube. The triphenylphosphine solution was added dropwise to the cobalt dichloride suspension, at -20 °C. The resulting suspension was turkish-blue. After the addition, the mixture was allowed to warm to room temperature, being further stirred for 2 h. The mixture was evaporated to dryness. The blue solid was washed with n-hexane until extracts were colorless. The washed solid was dried under vacuum, giving a turkish-blue powder. Yield, 100%.

**Synthesis of [Co{κ<sup>2</sup>N,O-NC<sub>4</sub>H<sub>3</sub>-C(H)=O}<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>] (1):** 0.102 g (4.25 mmol) of sodium hydride were suspended in THF, in a Schlenk tube. 0.387 g (4.07 mmol) of 2-formylpyrrole was added to the suspension. The mixture was stirred for 2 h, under a slow stream of nitrogen, in order to purge the H<sub>2</sub> formed in the reaction. 0.568 g (2.02 mmol) of [CoCl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>] was suspended in THF. The solution of the 2-formylpyrrolyl sodium salt was filtered dropwise into the [CoCl<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub>] suspension, at -20 °C. After the addition, the mixture was allowed to warm to room temperature and was left stirring overnight

for ca. 15 h. The suspension changed from dark green to brown-green. The mixture was evaporated to dryness and further extracted with n-hexane until extracts were colorless. The resulting solution was concentrated until saturation and stored at -20 °C. Brown microcrystals were obtained and analyzed by EPR and X-ray diffraction, confirming its structure. Yield, 80%.

**General polymerization procedure:** The appropriate mass of metal complex was weighed under nitrogen in a degassed Schlenk tube. The metal complex was dissolved in toluene (or THF) and the appropriate amount of monomer was added to the previous solution and the temperature set the desired value. A solution (in toluene or THF) of the appropriate radical initiator was quickly injected into the reaction mixture. Aliquots of the reaction mixture were periodically withdrawn from the reaction mixture. The aliquots content was dissolved in chloroform (or THF) and evaporated to dryness. The resulting solids were dried under vacuum, weighed, stored in vials. All the samples were analyzed by GPC/SEC and some selected samples were analyzed by NMR.

**Synthesis of poly(styrene)-*b*-poly(methyl methacrylate):** Using the same procedure described above, the polymerization of styrene was carried out at 50 °C and a monomer:metal:initiator molar ratio 500:1:1. After 24 h of reaction, the reaction mixture was dissolved in THF and passed through a dried silica column (*Aldrich*), under nitrogen, in order to try to retain the residual metal complex. The resulting solution was evaporated to dryness, stored in a degassed Schlenk tube and dried under vacuum. 0.821 g of a brownish solid were obtained. The molecular weight of the solid was determined by GPC/SEC (M<sub>n</sub>=5500 g/mol). 0.041 g of cobalt complex **1** and 0.57 g of the polytyrlyl bromide solid were transferred to a degassed Schlenk tube. The solid mixture was dissolved in 5.5 mL of toluene. 5.5 mL of methyl methacrylate were added to the previous solution and the mixture was thermostated at 50 °C (monomer:metal:initiator molar ratio of 500:1:1). Aliquots were withdrawn periodically and, after workup, analyzed by GPC/SEC, and some of them by NMR.

**Characterizations:** NMR spectra were acquired in a *Bruker "AVANCE III"* spectrometer, at 300 or 400 MHz. Solution samples were prepared in deuterated solvents

(Aldrich), stored at 4 °C (CDCl<sub>3</sub>) or under nitrogen atmosphere (CDCl<sub>3</sub>, 1,1,2,2-tetrachloroethane-*d*<sub>2</sub>, toluene-*d*<sub>6</sub>), at room temperature. Chemical shifts for <sup>1</sup>H and <sup>13</sup>C nuclei were referenced to the residual proton-resonances of the corresponding solvents, which were in turn referenced to TMS.

GPC/SEC was performed by eluting THF solutions of the polymeric samples at 35 °C or 40 °C (*Waters oven*) in two PolyPore columns (protected by a PolyPore guard column) (*Polymer Labs*) mounted on a *Waters 1515* isocratic HPLC pump. Detection was performed by a *Waters 2414* differential refractive index detector. THF was filtered through 0.45 μm PTFE *Pall* membrane filters and degassed in an ultrasound bath. Solution samples were filtered through 0.20 μm PTFE *GVS* filters. The system was calibrated with *TSK Tosoh Co.* polystyrene standards.

MALDI-TOF analyses were conducted at the Laboratório de Análises Requisite, Universidade Nova de Lisboa, Monte da Caparica, in a Voyager-DE™ PRO Workstation time-of-flight spectrometer, using the MALDI technique, with positive reflector. For poly(methyl methacrylate) and poly(styrene), the matrices DHB+Na and dytranol+Ag were used, respectively.

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