

Dual Function of β -Hydroxy Dithiocinnamic Esters: RAFT Agent and Ligand for Metal Complexation

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The reversible addition-fragmentation chain-transfer (RAFT) process has become a versatile tool for the preparation of defined polymers tolerating a large variety of functional groups. Several dithioesters, trithiocarbonates, xanthates, or dithiocarbamates have been developed as effective chain transfer agents (CTAs), but only a few examples have been reported, where the resulting end groups are directly considered for a secondary use besides controlling the polymerization. Herein, it is demonstrated that β -hydroxy dithiocinnamic esters represent a hitherto overlooked class of materials, which are originally designed for the complexation of transition metals but may as well act as reversible CTAs. Modified with a suitable leaving group (R-group), these vinyl conjugated dithioesters indeed provide reasonable control over the polymerization of acrylates, acrylamides, or styrene via the RAFT process. Kinetic studies reveal linear evolutions of molar mass with conversion, while different substituents on the aromatic unit has only a minor influence. Block extensions prove the livingness of the polymer chains, although extended polymerization times may lead to side reactions. The resulting dithiocinnamic ester end groups are still able to form complexes with platinum, which verifies that the structural integrity of the end group is maintained. These findings open a versatile new route to tailor-made polymer-bound metal complexes.

with defined length.^[1–5] Among them, the reversible addition-fragmentation chain-transfer (RAFT) process enables a plethora of possibilities for polymeric architectures, meanwhile being suitable for a broad variety of monomers.^[6–13] Generally, trithiocarbonates and aromatic dithioesters are used to polymerize more activated monomers, such as styrenes, (meth)acrylates or (meth)acrylamides, while less activated monomers such as vinyl esters or *N*-vinyl amides require xanthates or dithiocarbamates to maintain control.^[14,15] This versatility makes the RAFT process highly attractive for the preparation of various functional polymers.^[16,17] Furthermore, the process tolerates the incorporation of several reactive end groups as an attractive opportunity to create α,ω -heterotelechelic polymers for site-specific modifications or conjugations.^[18–22] In fact, the literature is rich with numerous examples of chain transfer agents (CTA) that contain reactive moieties either attached to the functional leaving group R or the stabilizing unit Z.^[23–36] Another alternative is the


cleavage of the dithioesters, xanthates, or trithiocarbonates to release the thiol end group, which however requires additional synthetic steps post polymerization.^[37–41]

1. Introduction

Reversible deactivation radical polymerization methods are considered as a versatile tool to create narrowly distributed polymers

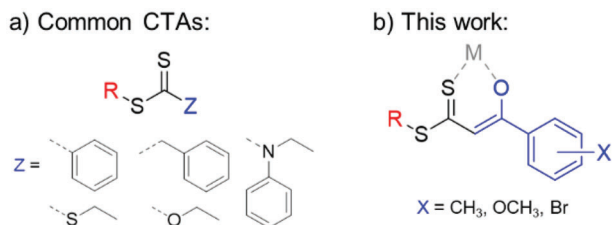
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DOI: 10.1002/marc.202200428



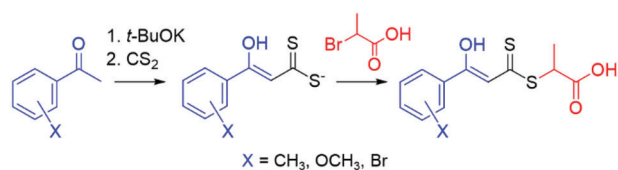
Scheme 1. a) Chemical structure of most common CTAs^[11]; b) chemical structure of β -hydroxydithiocinnamic acid derivatives and their metal (M) coordinating site.

A far more elegant attempt relies on a direct utilization of the functional CTA end group as frequently reported for anchoring of trithiocarbonate or dithiobenzoates end groups onto gold surfaces or nanoparticles.^[42–46] The group of Barner-Kowollik further successfully established efficient hetero-Diels–Alder reactions using either specifically designed CTAs or light-induced reactions on conventional dithioester benzoates.^[47–53] Nevertheless, the bivalent uses of the inherent RAFT motif as a reactive moiety remain scarce in the literature, which is partly related to the limited option in the structural design of the CTA without sacrificing its ability to control the polymerization.^[14,54] Interesting, but so far overlooked compounds are β -hydroxydithiocinnamic esters, which are well known for their ability to form complexes with a variety of metals including Pt, Pd, Ni, Cu, or Ru.^[55–65] The structure differs from common CTAs based on trithiocarbonates or dithiobenzoates (**Scheme 1**), but the conjugation of the vinyl benzene moiety (Z-group) might still be sufficient to stabilize the intermediate radical in the RAFT process.

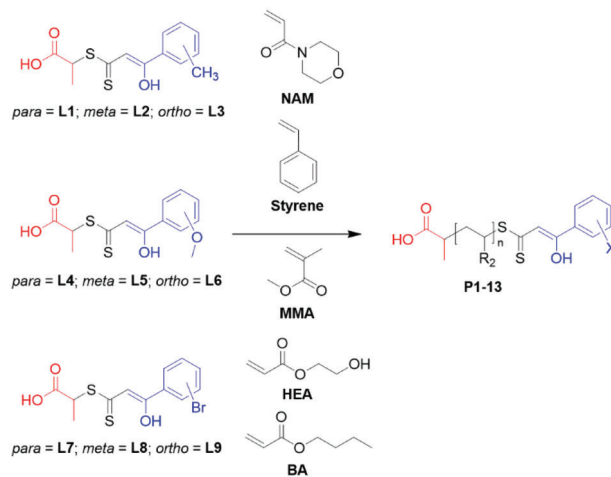
The group of Destarac and co-workers have previously examined dithiocinnamic acid derivatives as CTAs in RAFT, but the vinylogous character of their RAFT agents caused a severe retardation during polymerization.^[66] The β -hydroxy modified ligands presented in this work might circumvent the observed degeneration by a Diels–Alder reaction, as the additional hydroxy group increases the steric hindrance and electron density at the vinyl group. The present work focuses on testing the suitability of these modified ligands (**Scheme 1**) as CTAs in the RAFT process. Moreover, we have investigated the reaction of the resulting polymers with Pt(II) metal, which were subsequently characterized by spectroscopic and elemental analysis techniques.

2. Results and Discussion

The described β -hydroxydithiocinnamic acid derivatives (**L1–L9**) can be prepared in one step from the corresponding acetophenone derivatives in accordance with previously reported routes (**Scheme 2**).^[55,56] Interestingly, the free acid group simplifies the purification procedure and pure compounds are conveniently obtained after washing and recrystallization without the need for column chromatography. The specific experimental conditions as well as the synthetic pathways are described in the ESI, which further contains detailed characterization data including crystallographic data (molecular structure given in Figure S1, Supporting Information) and UV-vis spectra in solution (Figure S2, Supporting Information).



Scheme 2. General procedure for the synthesis of the β -hydroxydithiocinnamic acid derivatives.



Scheme 3. Chemical structures of the ligands, monomers, and the resulting polymers.

Scheme 3 depicts an overview of the examined β -hydroxydithiocinnamic acid derivatives and the set of monomers tested during the RAFT polymerization. The polymerization procedure and the corresponding characterization by NMR and size exclusion chromatography (SEC) are described in the ESI. The tested monomers include the acrylates *n*-butyl acrylate (BA) and 2-hydroxyethyl acrylate (HEA), the acrylamide *N*-acryloyl morpholine (NAM), and styrene which are all known to be polymerizable with common trithiocarbonate and aromatic dithioester based RAFT-agents. Methyl methacrylate (MMA) was further included as a representative for methacrylates, but the *R*-group of our β -hydroxydithiocinnamic acid derivatives might not be suitable for efficient chain transfer. In all cases, azobisisobutyronitrile (AIBN) was used as the initiator (CTA/initiator ratio: 20/1). Given a temperature of 70 °C and a polymerization time of 24 h, around 95% of the initiator should be decomposed resulting in a theoretical livingness of all polymers of >95%, if an initiator efficiency of 0.5 is assumed.

L1 was chosen to first evaluate the general potential of these compounds for controlling the polymerization of the different monomer types. The impact of different substituents on the benzene ring was investigated using the monomer *N*-acryloyl morpholine (NAM).

An overview of all combinations and the resulting polymers (after 24 h of polymerization) is given in **Table 1** (SEC traces for polymers **P1–P5** are given in the ESI, Figure S3, Supporting Information). Narrowly distributed polymers were obtained for the acrylates and styrene ($\bar{D} < 1.2$), while the dispersity is slightly increased for NAM. MMA, however, could not be controlled by

Table 1. Summary of all prepared polymers.

Polymer	Monomer	CTA (X)	Conversion, ^{a)} 24 h [%]	$M_{n,theos}$ ^{b)} [kg mol ⁻¹]	$M_{n,NMR}$ ^{c)} [kg mol ⁻¹]	$M_{n,SEC}$ ^{d)} [kg mol ⁻¹]	\bar{D} ^{d)}
P1	NAM	L1 (Me)	79	5.9	7.8	7.1	1.24
P2	BA	L1 (Me)	92	6.2	8.2	8.4	1.18
P3	Styrene	L1 (Me)	18	1.2	2.4	2.9	1.11
P4	HEA	L1 (Me)	96	5.9	6.3	10.4	1.18
P5	MMA	L1 (Me)	60	–	–	213.0	1.88
P6	NAM	L2 (Me)	68	5.1	6.6	5.8	1.23
P7	NAM	L3 (Me)	67	5.0	5.6	5.3	1.23
P8	NAM	L6 (OMe)	83	6.2	8.3	6.4	1.29
P9	NAM	L5 (OMe)	78	5.8	6.4	5.5	1.31
P10	NAM	L4 (OMe)	82	6.1	6.8	5.8	1.31
P11	NAM	L9 (Br)	71	5.4	6.6	5.9	1.26
P12	NAM	L8 (Br)	40	3.2	4.0	2.6	1.40
P13	NAM	L7 (Br)	55	4.2	5.0	4.4	1.32

^{a)} Determined from ¹H-NMR; ^{b)} Calculated from conversion and the targeted DP of 50; ^{c)} Precipitated polymers, determined from ratio of aromatic signals to signals of repeating units in ¹H NMR (precipitated polymers); ^{d)} Precipitated polymers, determined by SEC (Eluent: DMAc + 0.21 wt% LiCl, PMMA-calibration).

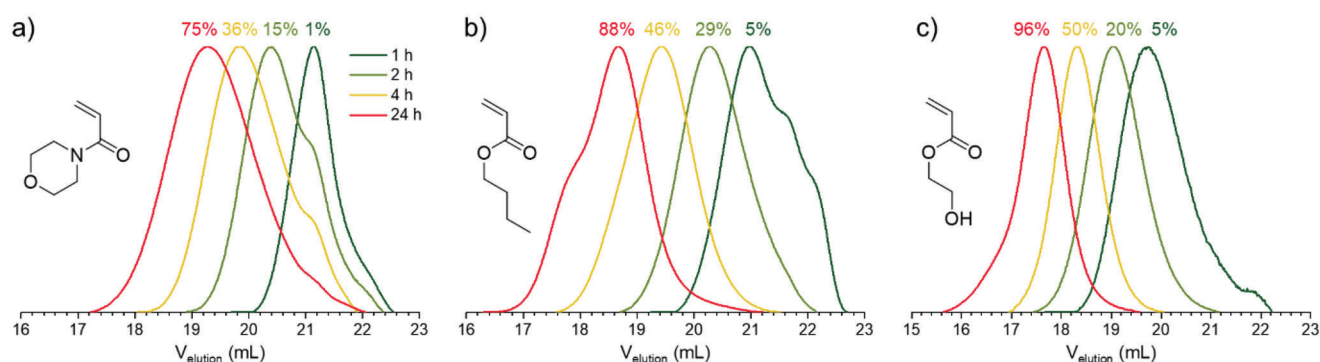


Figure 1. Normalized SEC traces of samples (1, 2, 4, and 24 h) taken during the polymerization of a) NAM (P1), b) BA (P2), and c) HEA (P4) (DMAc/LiCl, RI-detection).

these compounds, which corresponds to observations for established CTAs with similar poor leaving groups R.

Analyzing the progress of the reaction, SEC samples were taken at different time points of the polymerizations. Exemplarily chosen SEC traces for the polymerizations of NAM (P1), BA (P2), and HEA (P4) are depicted in Figure 1 (corresponding graphs normalized to conversion are given in Figure S4, Supporting Information, while an overview of all taken samples is given in Figure S6, Supporting Information).

A closer look at the corresponding conversions revealed pseudo-linear kinetics in the first hours after a short induction period for all polymerizations (Figure 2). The apparent reaction rates k_p^{app} are in the range of 0.17–0.23 for both acrylates, but one order of magnitude lower for styrene, which is expected due to the low propagation rate of the latter.

Interestingly and against our expectations, the polymerization rate for NAM is lower than for the acrylates, which coincides with the broader dispersity observed for the acrylamide. Nevertheless, a linear evolution of molar mass is observed for all polymers, but a closer look at the SEC traces of polymerizations of NAM (Figure 1 and Figure S6, Supporting Information) reveals a gradually

disappearing shoulder at high elution volume. As this signal is most prominent in the first samples, where the conversion was still close to zero, we initially assumed it corresponds to the CTA. However, the elution times did not match with the corresponding SEC measurements of the pure CTA (Figure S5a, Supporting Information). A closer look at the ¹H NMR spectra of the kinetic samples taken at the beginning of the polymerization (0 h) and after 1 h revealed that indeed the characteristic signal for tertiary CH group (on the R-group) next to the dithioester disappeared (Figure S5b, Supporting Information). Unfortunately, the signal of the newly formed CH group could not be identified, but we nevertheless consider that the species formed in the first hour of the polymerization corresponds to the single monomer insertion of NAM during the preequilibrium of the RAFT polymerization. This species is then continuously consumed during the main equilibrium. More detailed studies were, however, not considered. More interesting were the courses of the polymerization of the acrylates. In the case of BA, a shoulder at higher molar masses appears at late stages and high conversions (>80%) of the polymerization (Figure 1 and Figure S6, Supporting Information). Even in the case of HEA a similar trend becomes apparent

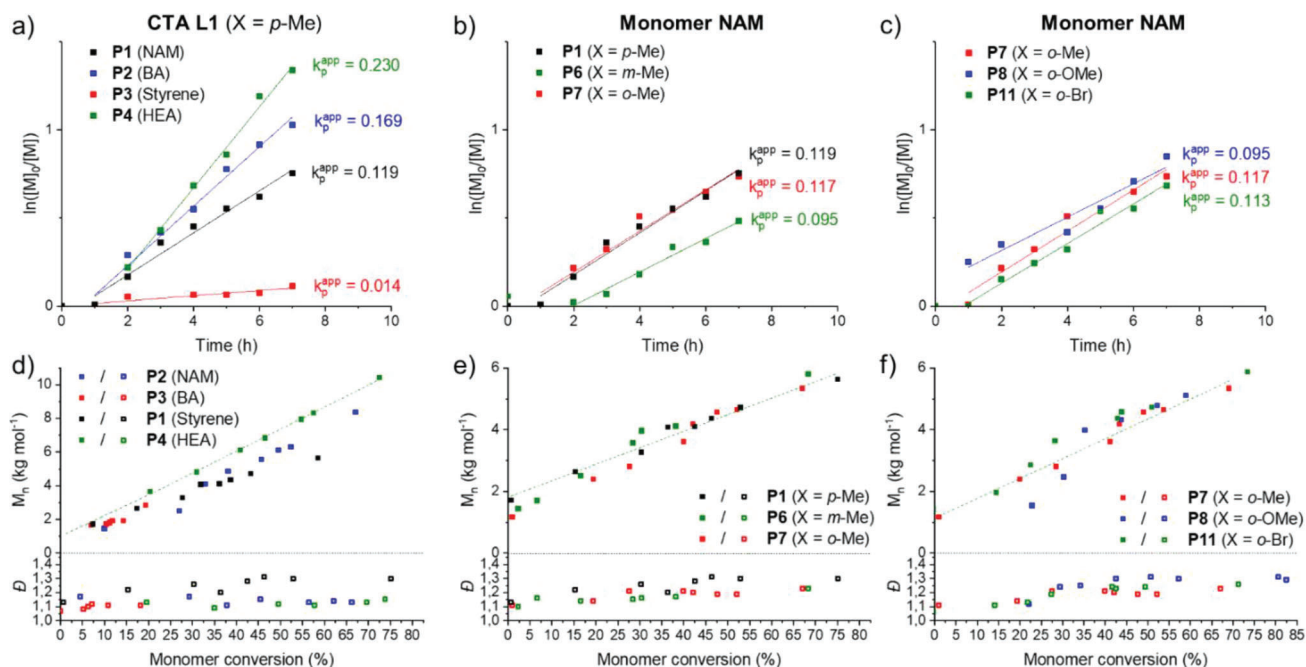


Figure 2. Polymerization kinetics (including apparent rate constants k_p^{app}) in dependence of a) the type of monomer using L1 as CTA, b) the position of the methyl substitution at the aromatic ring (X), and c) the type of substituent on the aromatic ring (both b) and c) using NAM as monomer); d)–f) evolution of molar mass (M_n) and dispersity \bar{D} with monomer conversion of the corresponding polymerizations shown above.

at very long polymerization times (24 h). Shoulders at higher molar masses have previously been reported for acrylates and particularly for BA as a result of a formation of a PBA macromonomer by backbiting β -scission.^[67] In our case, however, the shoulder was quite prominent compared to the previous reports, which is why we consider that additional side reactions might contribute to this formation of a high molar mass shoulder. Common termination by combination seems not to play a major role, since the β -hydroxydithiocinnamic ester end group is still present as indicated by a similar intense UV-vis signal (detection at 350 nm) in the SEC trace (Figure S7, Supporting Information). However, a chain-chain coupling by radical reaction of a propagating chain end with the double bond of the cinnamic acid end group cannot be excluded as well, as if high conversions are reached even less reactive vinyl groups might react.^[68]

Comparing the different substitution patterns on the benzene ring of the CTAs, no significant influence of the position of the methyl group on the reactivity becomes apparent as similar kinetics for all compounds are observed (Figure 2). Apart from varying the position, the substituent was exchanged for either a methoxy group (L4–L6) or the halogen bromine (L7–L9). While the first should induce a strong electron-donating effect on the aromatic system, the latter should cause the opposite. However, comparing the results of the polymerization of NAM, no significant differences in the reaction rate were found for L3, L6, and L9 (Figure 2C). Interestingly, changing the *ortho*-substitution (L9) of the bromo-ligands to a *meta* (L8) or *para* (L7) position, increases the dispersities of the polymers and reduces the reaction rate (Figure S8, Supporting Information). We assume that the more accessible meta and particular the para position of the bromine group might favor side reactions, or the latter positions induce an unfa-

vorable inductive effect. In the case of the methoxy substituent, only a slight decrease in the reaction rate for the ortho position is observed (Figure S8), which might be due to steric effects.

Intrigued by the surprisingly good control, we further examined whether the RAFT end group remains intact and is capable of reinitiating a chain extension.^[69] Therefore, another batch of PBA (P14) was prepared from the CTA L1, but the polymerization was stopped after 4 h to minimize the previously mentioned side reaction. A monomodal distribution ($\bar{D} = 1.10$) was obtained in this case and the polymer was purified by precipitation. Subsequently, this polymer was again dissolved in BA and a new initiator was added to initiate a potential chain extension of this macro-CTA. The comparison of the SEC traces (Figure 3) at each step reveals a clear and nearly complete shift of the signal for the macro-CTA (P14) after formation of the second block in the chain extension experiment. The newly formed polymer (P15) again features a monomodal distribution with narrow dispersity ($\bar{D} = 1.11$) if the reaction time was kept at 4 h. The reactivity or livingness of the chains seems therefore be mostly preserved during the polymerization underlining the good control provided by this RAFT agent, if extended polymerization times are avoided.

Another key question is whether the β -hydroxydithiocinnamic ester end group is still capable of fulfilling its second function, the complexation of metals. Therefore, we have exemplarily chosen the water-soluble polymers P1 and P6–P11 and added K_2PtCl_4 to form the corresponding complexes PtP1 and PtP6–11. NMR spectroscopy and inductively coupled plasma atomic emission spectroscopy (ICP-AES) revealed that all reactions yielded Pt(II) complexes. The ^1H NMR spectra of the resulting complexes PtP1 and PtP6–11 are very similar compared to the spectra of the

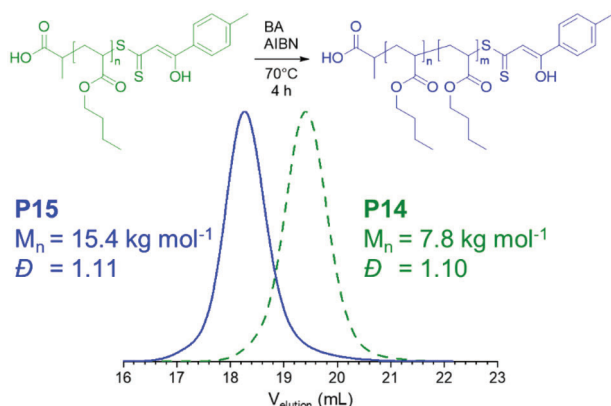


Figure 3. Scheme of the polymerization starting from the purified PBA (P14) using BA as monomer and the corresponding SEC traces of the macro-CTA P14 (dashed green line) and the resulting polymer P15 (solid blue line) after the chain extension (DMAc/LiCl, RI-detection, PMMA-calibration).

corresponding precursors polymer P1 and P6-11. However, the disappearance of the signal around 15 ppm indicates that the coordination occurred through the β -oxo-carbon atom. Furthermore, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of PtP1 and PtP6-11 display a downfield shift ($\approx 3\text{--}7$ ppm) for the methine carbon atom and a high field shift ($\approx 27\text{--}37$ ppm) for the quaternary thiocarbonyl carbon atom, which further corroborates that the coordination occurs through the β -hydroxydithiocinnamic ester moiety. We further used ICP-AES to quantify the amount of bound Pt in the polymers P1 and P6-11.^[70–73] Interestingly, in most polymers a Pt content was found, which is considerably higher than expected for a complexation of one equivalent of Pt, despite excessive washing steps and thorough purification. These calculations were based on average molar masses or number of repeating units, respectively, estimated from the ^1H NMR signals (aromatic protons vs protons of repeating units) of the precipitated polymers (Table 1). Although the M_n values might deviate from absolute molar masses (e.g., by the loss of the end group), this determination should still reflect the real content of active complexation sites in the sample independent of the molar masses. Therefore, these deviations cannot be related to false molar mass values. Instead, we assume that the additional binding of Pt is caused by the carboxylic acid groups present at the α end of the polymer chains (Figure 4a), which were initially chosen to simplify the purification of the β -hydroxydithiocinnamic esters. The SEC analysis of the exemplarily chosen complex PtP6 further corroborated our assumption, as a bimodal distribution is observed (Figure 4b), which reflects the expected composition comprising a polymer distribution close to the initial polymer P6 and second distribution representing a coupled species at double molar mass.

Given the proposed two structures, we estimated that PtP6 must consist of 42% A and 58% B considering a measured Pt content of 47.16 mg(Pt)/g(sample) and an M_n (NMR) of 6.6 kg mol⁻¹ for the polymer P6. Independent of the discrepancies in the expected and observed Pt content, the high amount of Pt bound in the polymers can only be explained if the β -hydroxydithiocinnamic ester moiety is still able to bind the metal.

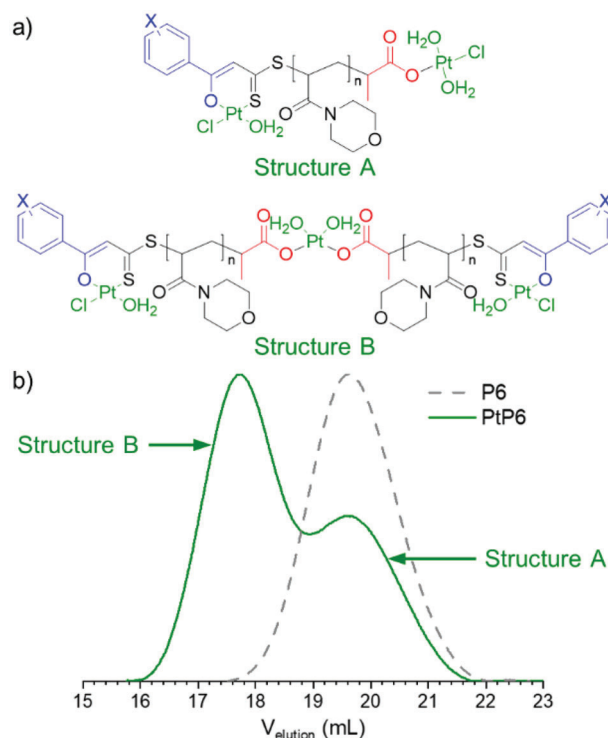


Figure 4. a) Scheme of the two potentially formed structures during the complexation of Pt by the RAFT-polymers based on NAM; b) corresponding SEC of the complex PtP1 (green solid line) in comparison with the initial polymer P1 (grey dashed line) (DMAc/LiCl, RI-detection, PMMA-calibration).

Therefore, this data confirms that the functionality of the end group is maintained during the polymerization and the desired Pt complexes can be formed. Considering the unexpected formation of the Pt-carboxylate complexes, we would like to emphasize that although these simple complexes appear quite robust, significantly higher binding constants can be expected for the Pt-complexes with β -hydroxydithiocinnamic esters considering the bidentate character of these O,S ligands.^[74] The carboxylic acid moiety at the R-group further represents a versatile group for additional modifications of the polymers with regard to potential applications. Further studies in this direction are under consideration in our groups, which should further underline the importance of the dual use of the presented CTAs.

3. Conclusion

In summary, we could demonstrate that derivatives of β -hydroxydithiocinnamic esters are suitable chain transfer agents to control the polymerization of various acrylic or styrene-based monomers. Detailed kinetic studies revealed a linear evolution of molar masses with conversion. It has however to be considered that the increased reactivity of the vinyl moiety in the Z-group might still cause side reaction, if extended reaction times are applied. Nevertheless, the resulting polymer chains can successfully be chain extended, if shorter polymerization times are applied, verifying a high-end group fidelity and the living character of the polymerization. The substitution pattern

on the adjacent benzene has overall only a minor impact on the polymerization behavior. Only in the case of the rather reactive bromine substituents reduced conversions and a broadening of the molar mass distribution was observed, which became particularly prominent for the meta and para-substituted compounds. Most interestingly, the polymers appear to be still capable of binding Pt (II) and afford the corresponding platinum complexes. These types of dual-function compounds are attractive candidates to directly prepare functional polymers for application as catalysts in a variety of organic reactions,^[62,64,65] anti-leishmanial agents,^[58] potential anti-cancer agent,^[56,57,59,60] inhibitors of amyloid aggregation,^[63] or in wastewater treatment due to the ability to act as chelating ligands for noble metals.^[75] Furthermore, such complexes might find use in bio-imaging by replacing the Pt element with Ti and Gd.^[76]

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

M.K.F. and F.V.G. contributed equally to this work. M.K.F. is grateful to the Katholischer Akademischer Ausländer-Dienst (KAAD) for a Ph.D. scholarship. J.C.B., F.V.G., and N.Z. further thank the German Science Foundation (DFG) for generous funding within the Emmy-Noether Programme (Project-ID: 358263073). Prof. U.S. Schubert is furthermore acknowledged for his continuous support and access to excellent research facilities. The authors would further like to thank Umicore AG & Co. KG Hanau-Wolfgang, Germany for donation of K₂PtCl₄.

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

controlled radical polymerization, ligands, platinum complexes, RAFT polymerization

Received: May 5, 2022
Revised: June 12, 2022
Published online: July 7, 2022

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