



In-Situ Analysis of Anionic Coordination Polymerizations by Electrospray-Ionization Mass Spectrometry

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Abstract: Anionic coordination polymerizations proceed via highly reactive intermediates, whose in situ analysis has remained difficult. Here, we show that electrospray-ionization mass spectrometry is a promising method to obtain detailed information on the polymerization process. Focusing on polymerization reactions of 1,3-dienes initiated by CoCl_2/RLi ($\text{R} = \text{Me}, n\text{Bu}, t\text{Bu}, \text{Ph}$), we directly observe the growing polymer chains and characterize the active anionic cobalt centers by gas-phase fragmentation experiments. On the basis of these results, we suggest a plausible mechanism for the polymerization reaction. Moreover, the ESI mass spectra permit the determination of molecular weight distributions, which are in good agreement with those derived from NMR-spectroscopic as well as MALDI mass-spectrometric measurements, and afford a wealth of kinetic data.

Synthetic polymers are of outstanding practical importance. To achieve full control of their formation, detailed insight into the polymerization reaction is required. Ideally, the nature of the active center, the molecular weight distribution of the growing polymer chains, and the reaction kinetics are known. It would be particularly convenient if this information could be obtained by in situ analyses. Such analyses are challenging due to the high reactivity of the growing polymers and the inherent difficulties in the determination of molecular weight distributions.

A promising method for the in situ analysis of polymerizations is given by electrospray-ionization (ESI) mass

spectrometry. Like other mass-spectrometric techniques,^[1] it affords stoichiometrically exact information and, thus, is able to determine at least approximate molecular weight distributions of the growing polymer.^[2] Moreover, it selectively detects charged species present in the sampled solution.^[3] The groups of Chen^[4] and Metzger^[5] have capitalized on these features of ESI mass spectrometry and successfully applied it to the investigation of cationic coordination polymerizations. More recently, this method has also been employed for monitoring radical-type polymerizations (by detecting Na^+ adducts of the neutral polymer chains).^[6] Here, we show that ESI mass spectrometry can also be used for the in situ analysis of anionic coordination polymerizations, whose active centers are even more reactive and elusive.^[7] As a model system, we consider the polymerization of buta-1,3-diene and isoprene mediated by organolithium reagents RLi ($\text{R} = \text{Me}, n\text{Bu}, t\text{Bu}, \text{Ph}$) and CoCl_2 in tetrahydrofuran (THF). Previous work in the context of cobalt-catalyzed cross-coupling reactions has already found evidence that these systems undergo efficient oligomerization.^[8,9] For comparison, we also use ^1H NMR spectroscopy and matrix-assisted laser-desorption/ionization (MALDI) mass spectrometry as well-established methods to characterize the isolated polymer products.^[10]

Analysis of solutions of CoCl_2 , MeLi , and buta-1,3-diene by negative-ion mode ESI mass spectrometry at different points in time (experimental details are given in the Supporting Information) showed the gradual build-up of several sets of equidistant peaks indicative of the formation of anionic polymers (Figures 1 and S1–S3 in the Supporting Information). The observed mass difference between neighboring peaks of the same series, $\Delta m = 54$, is fully in line with the expected iterative incorporation of buta-1,3-diene monomers. With increasing time, the peak distribution shifts to higher m/z ratios, thus reflecting the growth of the polymer chains. This marked time dependence rules out that the polymerization reactions occur predominantly in the microdroplets produced by the ESI process.^[11] At longer reaction times, the distributions remain almost constant (Figure S4). Analogous behavior was found for solutions of CoCl_2 , MeLi , and isoprene (Figures S5–S8).

It is the particular advantage of the present approach that it not only determines approximate molecular weight distributions, but also gives unprecedentedly detailed information on the active centers of the growing polymers. For the given system, the vast majority of anionic polymers belong to the series $\text{LiCo}_2(\text{DE})_x\text{R}_4^-$ ($\text{DE} = \text{diene}, \text{R} = \text{organyl}$). These species consist of two low-valent anionic

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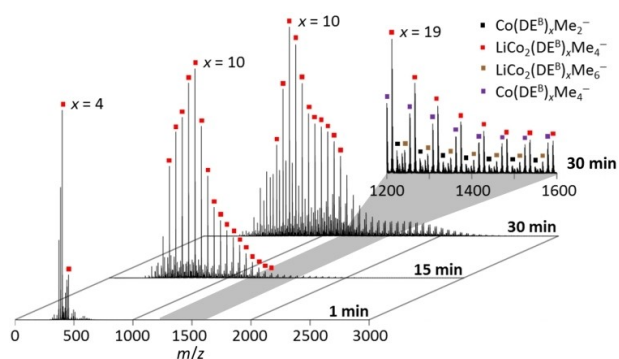


Figure 1. Negative-ion mode ESI mass spectrum of a solution of the products formed upon the reaction of CoCl_2 (13 mM) with MeLi (4 equiv) and buta-1,3-diene (20 equiv, DE^{B}) in THF at room temperature after reaction times of 1, 15, and 30 min. Inset: enlarged section from the mass spectrum recorded after a reaction time of 30 min.

cobalt(I) complexes of the type $\text{Co}(\text{DE})_x\text{R}_2^-$ held together by one Li^+ cation. The mononuclear $\text{Co}(\text{DE})_x\text{R}_2^-$ subunits were also directly observed, although in lower signal intensity than the $\text{LiCo}_2(\text{DE})_x\text{R}_4^-$ ions (Figures 1, S1–S3, S5–S8). The ratio between the detected mononuclear complexes and the higher aggregates depends not only on the concentration of the sample solution, but also on the ESI process. The increase of the effective concentration of the analyte ions during their transfer from solution into the gas phase favors the formation of higher aggregates, thus complicating kinetic analyses in these cases.^[12] Besides the $\text{Co}(\text{DE})_x\text{R}_2^-$ and $\text{LiCo}_2(\text{DE})_x\text{R}_4^-$ ions, anionic polymer chains of the types $\text{Co}(\text{DE})_x\text{R}_4^-$ and $\text{LiCo}_2(\text{DE})_x\text{R}_6^-$ ions were also observed (Figures 1, S1, S2, S5). These species contained cobalt centers in oxidation states of $> \text{I}$ and were prominent only at short reaction times. This finding suggests that these species are not directly involved in the actual polymerization.

Next, we investigated the effect of exchanging MeLi for *n*BuLi or *t*BuLi. In both cases, we again found anionic polymer chains bound to mono- and polynuclear cobalt(I) centers (Figures 2, S9–S19). However, these species contained not only organyl groups R, but also extra hydrogen atoms and displayed compositions of $\text{Co}(\text{DE})_x\text{H}_n\text{R}_{2-n}^-$ and $\text{LiCo}_2(\text{DE})_x\text{H}_n\text{R}_{4-n}^-$, respectively. These hydrogen atoms most likely originated from β -hydrogen eliminations. We have shown previously that butylcobaltate complexes easily decompose via this reaction.^[9] Even more abundant than these cobalt(I) anions were polymers of the type $\text{LiCo}_2(\text{DE})_x\text{H}_n\text{R}_{2-n}^-$. In line with previous results on related systems,^[9] we assign these species as mixed $\text{Co}^{\text{I}}/\text{Co}^{-\text{I}}$ complexes. This assignment is corroborated by the observation of the cobalt(–I) anions $\text{Co}(\text{DE})_x^-$ and $\text{LiCo}_2(\text{DE})_x^-$, $x=2$ –8, at long reaction times (Figures S12, S13, S15, S16, S18, S19). Apparently, these species result from the polymer chains being cleaved off the cobalt centers in processes that simultaneously reduce the latter, such as reductive eliminations.

When the polymerization was initiated by a mixture of CoCl_2 and PhLi, cobalt(I) complexes of the already known

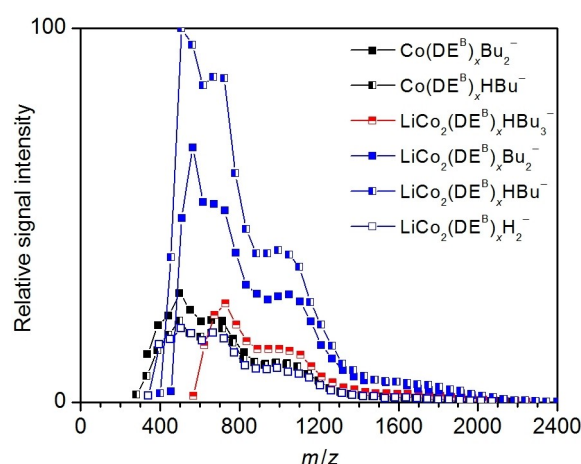


Figure 2. Envelopes of the anionic polymer peaks observed upon negative-ion mode ESI mass spectrometry of a solution of the products formed in the reaction of CoCl_2 (13 mM) with *n*BuLi (4 equiv) and buta-1,3-diene (20 equiv, DE^{B}) in THF at room temperature after a reaction time of 30 min.

types $\text{Co}(\text{DE})_x\text{R}_2^-$ and $\text{LiCo}_2(\text{DE})_x\text{R}_4^-$ predominated for the case of buta-1,3-diene (DE^{B} , Figures S20–S22) whereas the former largely prevailed for the polymerization of isoprene (DE^{I} , Figures 3, S23–S25). The $\text{Co}(\text{DE})_x\text{Ph}_2^-$ species grew in length during the first 15 min, after which time their relative abundances remained almost constant (Figure S26). This behavior resembles that of the $\text{CoCl}_2/\text{MeLi}/\text{DE}$ systems (see above). Increasing the amount of isoprene from 20 to 30 equiv resulted in a more than proportional increase of the average chain length (Figures S27 and S28). This behavior can be explained by a reversible chain propagation and the establishment of an equilibrium at longer reaction times.

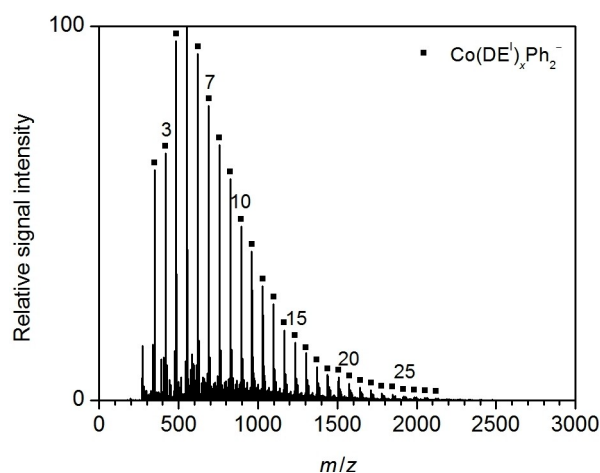
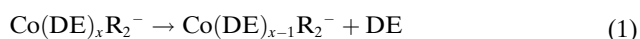


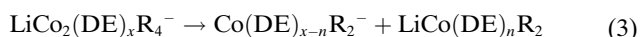
Figure 3. Negative-ion mode ESI mass spectrum of a solution of the products formed upon the reaction of CoCl_2 (13 mM) with PhLi (4 equiv) and isoprene (20 equiv, DE^{I}) in THF at room temperature after a reaction time of 20 min. The given numbers denote the number of isoprene units x .

Further evidence in support of a reversible chain propagation came from copolymerization experiments with isoprene and buta-1,3-diene. Here, we first allowed solutions of CoCl_2 , PhLi , and isoprene to react for 0, 15, or 30 min, respectively, before buta-1,3-diene was added (Figures S29–S34). Analysis by negative-ion mode ESI mass spectrometry after an additional reaction time of 30 min found mixed polymer anions of the types $\text{Co}(\text{DE}^{\text{B}})_x(\text{DE}^{\text{I}})_y\text{Ph}_2^-$, ($x=0-15$, $y=0-14$), whose exact compositions could be easily determined. For all experiments, the observed distributions of the two different diene monomers were rather broad. This finding suggests that after 30 min reaction time, the isoprene containing cobaltate species must have been still active. We also observed the formation of cobaltate complexes containing only buta-1,3-diene, but no isoprene ($\text{Co}(\text{DE}^{\text{B}})_x\text{Ph}_2^-$, $x=2-7$). This result strongly points to the reversibility of the chain propagation.

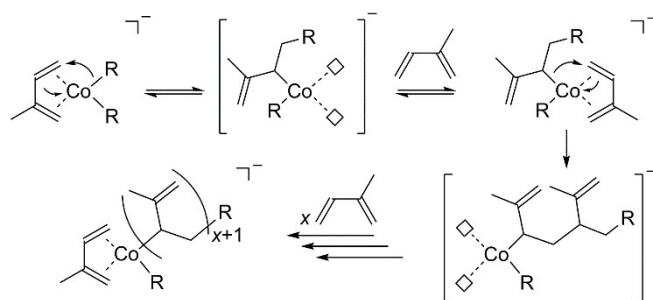
Additional insight into the unimolecular reactivity and structure of the cobalt-bound polymer anions could be obtained from gas-phase fragmentation experiments of $\text{Co}(\text{DE})_x\text{R}_2^-$ and $\text{LiCo}_2(\text{DE})_x\text{R}_4^-$ (Figures S35–S55). The former lost a single diene unit, Equation (1), but no longer fragments of the polymer chain. This finding suggests that the $\text{Co}(\text{DE})_x\text{R}_2^-$ species either contain single diene molecules not incorporated into the polymer chain or that they release such diene monomers in a step-wise fashion. In addition, the elimination of $\text{R}(\text{DE})_n\text{H}$ fragments occurred, Equation (2), for which reaction different mechanisms are conceivable (Schemes S1 and S2).



The $\text{LiCo}_2(\text{DE})_x\text{R}_4^-$ ions preferentially dissociate into mononuclear anions, Equation (3), in line with their composition of two mononuclear cobaltate subunits held together by a central Li^+ cation. Each fragmentation experiment affords extensive series of $\text{Co}(\text{DE})_{x-n}\text{R}_2^-$ fragment ions, which reflect the statistical nature of the polymerization process simultaneously proceeding at both cobalt centers. Smaller amounts of $[\text{Co}(\text{DE})_{x-n}\text{R}-\text{H}]^-$ fragment ions presumably resulted from consecutive dissociations of $\text{Co}(\text{DE})_{x-n}\text{R}_2^-$ according to Equation (2).



Most likely, the mechanism of the polymerization involves the coordination of a diene molecule as a π ligand in the first step to afford a 16-electron complex (Scheme 1), which resembles the behavior of cationic nickel and palladium catalysts used in olefin polymerizations.^[13] A reversible migratory insertion of the diene into the cobalt-bound polymer chain then regenerates a free coordination site at the metal. At the diene concentrations in the present experiments, this coordination site is expected to be filled fast by the coordination of another diene, thus reducing the chance of a competitive β -hydride elimination from the polymer chain. We found no clear evidence for this chain-



Scheme 1. Proposed mechanism for the propagation step during the polymerization of isoprene mediated by CoCl_2/RLi . Presumably, the intermediates with empty coordination sites are stabilized by interactions with double bonds from the growing polymer chains.

termination reaction under the present conditions,^[14] but had previously observed its occurrence at lower diene concentrations.^[9] Two-dimensional ^1H NMR spectroscopy of the isolated polymer product (Figures S56–62, Table S1) showed that an insertion in a 3,4 orientation (80 %, shown in Scheme 1) predominated over that in a 1,2 fashion (20 %). This result differs from the previously assumed preference of a 1,4 insertion.^[9]

Having thus characterized the active cobalt centers and obtained detailed mechanistic information, we went on to investigate whether the present approach could also be used for the determination of approximate molecular weights. To this end, we focused on the polymerization of isoprene initiated by $\text{CoCl}_2/\text{PhLi}$, which afforded particularly simple ESI mass spectra (see above). Terminating the reaction after 30 min, we analyzed the isolated product by ^1H NMR spectroscopy and MALDI mass spectrometry. From the NMR spectra, molecular weight distributions could be determined by comparing the signal intensity of the terminal alkene protons (2 per monomer) with that of the phenyl protons from the end group. Due to their limited m/z range, the recorded MALDI mass spectra (Figures S63 and S64) only afforded truncated molecular weight distributions, but at the same time showed the absence of any other end groups than Ph and H and, thus, suggested that chain-transfer reactions did not occur to a significant extent. The molecular weight distributions determined by NMR spectroscopy and MALDI mass spectrometry agreed well with that derived from our ESI-mass spectrometric experiments (Table 1). This agreement lends support to the reliability of ESI mass spectrometry for quantitative in situ analyses of anionic coordination polymerizations (at least for relatively narrow m/z ranges, for which mass-discrimination effects are small).

The MALDI and ESI mass spectra also permitted the determination of M_w/M_n ^[15] ratios. Here, the slightly lower value obtained from the truncated ESI mass spectra does not necessarily point to an inconsistency between both methods, but might reflect an asymmetric growth of the two polymer chains bound to one cobalt center. Furthermore, our present methodology offers the possibility to examine the polymer growth in more detail by analyzing its kinetics. We demonstrate the feasibility of this approach by again

Table 1: Molecular weight distributions for the reaction of CoCl_2 (13 mM) with PhLi (4 equiv) and isoprene (20 equiv, DE^1) in THF after 30 min at room temperature determined by ^1H NMR spectroscopy, ESI and MALDI mass spectrometry as well as a kinetic simulation.

	M_n [g mol^{-1}]	M_w [g mol^{-1}]	M_w/M_n
NMR	350–420	–	–
ESI ^[a]	383 ± 16	485 ± 9	1.27
ESI (simulated)	362	474	1.31
MALDI (truncated) ^[b]	695 ± 15	751 ± 23	1.08
ESI (truncated) ^[a,c]	635 ± 7	661 ± 10	1.04
ESI (truncated, simulated) ^[d]	650	688	1.06

[a] Average of 4 runs. [b] Includes all species $[\text{Ph}(\text{DE}^1)_x\text{H} + \text{M}]^+$ for $x = 6$ –18. [c] Includes all species $\text{Co}(\text{DE}^1)_x\text{Ph}_2^-$ for $x = 13$ –30. [d] Includes all species $\text{Co}(\text{DE}^1)_x\text{Ph}_2^-$ for $x = 13$ –40.

considering the system $\text{CoCl}_2/\text{PhLi}/\text{isoprene}$. We base our kinetic model on the proposed mechanism (Scheme 1) with a fast coordination of the diene to the cobalt center followed by a slower and reversible propagation step. We allow for individual rate constants for the first three propagation steps to account for possible differences in the reactivity of cobaltate ions binding very short polymer chains. The model does not include any chain transfer or termination reactions because we have not observed such processes. With this simplistic model, we can reproduce the observed temporal evolution of the abundances of the different $\text{Co}(\text{DE}^1)_x\text{Ph}_2^-$ species quite well (Figure 4). Moreover, the simulated mass distribution after a reaction time of 30 min closely resembles

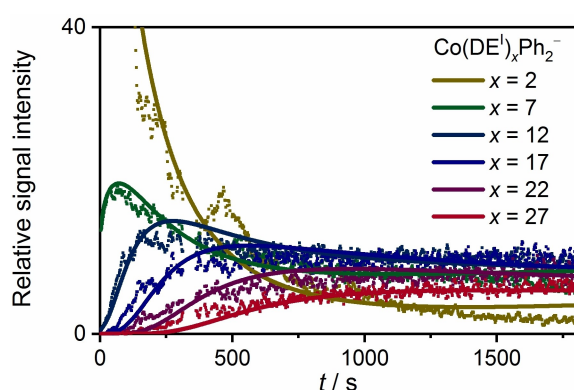


Figure 4. ESI mass spectrometric (dots) and simulated (lines) time profiles of the $\text{Co}(\text{DE}^1)_x\text{Ph}_2^-$ anions produced in the reaction of CoCl_2 (13 mM) with PhLi (4 equiv) and isoprene (30 equiv, DE^1) in THF at room temperature. Experimental data smoothed (average 5) for better visibility.

Table 2: Room-temperature rate constants for the propagation step $\text{Co}(\text{DE}^1)_x\text{Ph}_2^- \xrightarrow{\gamma} \text{Co}(\text{DE}^1)_{x+1}\text{Ph}_2^-$ and the back reaction derived from kinetic modeling.

$x/x+1$	2/3	3/4	4/5	$x/x+1$ ^[a]
k_{+1} [$\text{M}^{-1} \text{s}^{-1}$] ^[b]	0.023	0.12	0.11	0.20
k_{-1} [s^{-1}] ^[b]	0.004	0.013	0.011	0.032

[a] $5 \leq x \leq 40$. [b] $\Delta k/k < 3\%$ (standard deviation obtained from modeling).

the measured ones (Table 1). This agreement corroborates the postulated mechanism with a reversible propagation step.

The determined rate constants show that the first insertion steps proceed more slowly than the later ones (Table 2). This increase of the rate constants implies that the polymer chain first formed continues to grow before the second chain starts to form. Thus, the two polymer chains bound to one cobalt center typically will show an asymmetric growth, which explains the deviation in the M_w/M_n ratios determined by ESI and MALDI mass spectrometry. The rate constants for the back reactions are quite high. Accordingly, a relatively large excess of the diene is required to drive the equilibrium toward the side of long chains.^[16]

In conclusion, we have shown the high potential of ESI mass spectrometry for the in situ analysis of anionic coordination polymerization reactions. This method not only identifies the active anionic polymers, but by means of gas-phase fragmentation experiments also gives insight into their structure and reactivity. Even more detailed structural information can be expected from complementing the gas-phase characterization by ion-mobility measurements.^[17] Moreover, the present experiments determine approximate molecular weight distributions consistent with independent controls and provide extensive kinetic information. We have demonstrated the value of the present approach for the model system of diene polymerizations initiated by cobalt(II) chloride and organyl lithium reagents. Here, the polymerization is mediated by cobaltate(I) centers and involves reversible propagation steps with rate constants depending on the chain length. We expect our method to afford equally detailed mechanistic insight for other anionic polymerization reactions as well.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: Analytical Methods · Cobalt · Mass Spectrometry · Polymerization · Reaction Mechanisms

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