Are carbodiimide-quenched polyethylene distributions representative of bulk polymer samples? Analysis of metallocene-catalyzed ethylene polymerization by ESI-MS, MALDI, GPC and NMR†

Beth Moscato and Clark Landis

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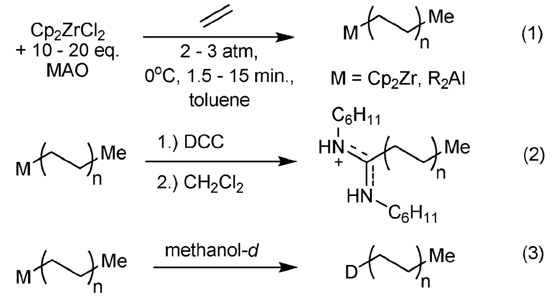
Polyethylene molecular weight distributions observed by ESI-MS following the quench of a Cp_2ZrCl_2/MAO-catalyzed ethylene polymerization with *N*,*N*′-dicyclohexylcarbodiimide do not agree with GPC or NMR analysis of methanol-d_1 quenched samples; factors contributing to the discrepant results include high sample polydispersities, polymer insolubility, and the incomplete quench of metal-polymer species. Kinetic analyses of molecular weight distributions obtained by ESI-MS are not representative of the predominate monomer-consuming pathways.

The study of metal-catalyzed olefin polymerizations and their products by mass spectrometry (MS) has been a longstanding challenge for both the analytical and polymerization communities. Although the development of "soft" ionization techniques, such as electrospray-ionization (ESI)[1] and matrix-assisted laser desorption/ionization (MALDI),[2] has assisted the analysis of more polar polymers, the hydrophobicity and low solubility of most polyolefins prevent effective ionization. Several approaches have been taken to combat these problems. MALDI-MS can ionize vinyl-terminated polyolefins, either directly,[3] or after post-polymerization chemical modification.[4] Other researchers have directly ionized the cationic metal catalysts employed in olefin polymerization, either after solution-phase polymerization[5] or prior to gas-phase polymerization of introduced monomer.[6,7]

We are currently investigating information-rich approaches for the rapid acquisition of metallocene polymerization kinetics. Recently, Chen and co-workers announced that *N*,*N*′-dicyclohexylcarbodiimide (DCC) can be employed as a quench-label reagent for a model metallocene-catalyzed polymerization (Scheme 1, eqn (1) and (2)).[8] Addition of DCC is believed to both kill all active polymerization catalysts and install a single ionizable endgroup upon the metal-bound polymer. The ensuing amidinium-terminated alkyl chains can be detected by ESI-MS. In principle, high-resolution MS of the quenched polymers provides active site counts, endgroup analysis, and molecular weight distributions, allowing rates of initiation, propagation, and termination to be computed from a single mass spectrum. The model used in this study was later refined[9] and expanded to include rates of chain walking.[10]



Scheme 1 Metal–alkyl chains produced during ethylene polymerization (eqn (1)) were quench-labeled with either DCC (eqn (2)) or methanol-d_1 (eqn (3)).

However, the results of carbodiimide quench-labeling studies rely on assumptions, such as a quantitative and rapid quench and quantitative ESI-MS analysis, that have not been proven. Quantitative quenches are notoriously rare and require external validation.[11] Herein we report the results of a *direct comparison* between ESI-MS analysis of carbodiimide quench-labeled samples and deuterated samples analyzed using conventional analytical techniques.

Amidinium-terminated polyethylene (PE) samples (Am-PE) were prepared as shown in eqn (1) and (2), with reaction conditions closely approximating those employed in earlier studies.[8] Gratifyingly, ESI-MS analysis of our samples yielded singly-charged distributions of methyl-terminated ethylene oligomers similar to previously published results (Fig. 1(a)).‡ No multiply-charged polymeryl ions were observed, confirming that ionization occurs exclusively at the amidinium ion terminus. Peak intensities were quantified relative to a linear alkyl amidinium internal standard, *N*,*N*′-dicyclohexyloctadecanimidamide (m/z = 461.5), which was added to solutions immediately prior to dilution in CH_2Cl_2. From the quantified data, number-average molecular weights (M_n), sample polydispersities (PDI; M_w/M_n), the number of polymer chains generated per zirconocene (N/Zr), and apparent catalyst activity could be computed (Table 1).

Polymer statistics can also be determined through conventional methods. Accordingly, polymerizations identical to the above were quenched with methanol-*d*, quantitatively and instantaneously yielding deuterium-labeled polyethylene (D-PE) (eqn (3)).[12] Dried samples were subjected to gel permeation chromatography (GPC), gravimetric analysis (Table 1) and, in some cases, ^{13}C NMR (*vide infra*).§

Data shown in Table 1 reveal that Am-PE distributions detected by ESI-MS are *not* influenced by reaction conditions.

Dept. of Chemistry, UW-Madison, 1101 University, Madison, WI, USA. E-mail: landis@chem.wixc.edu; Fax: 1 608 2626143; Tel: 1 608 2620362

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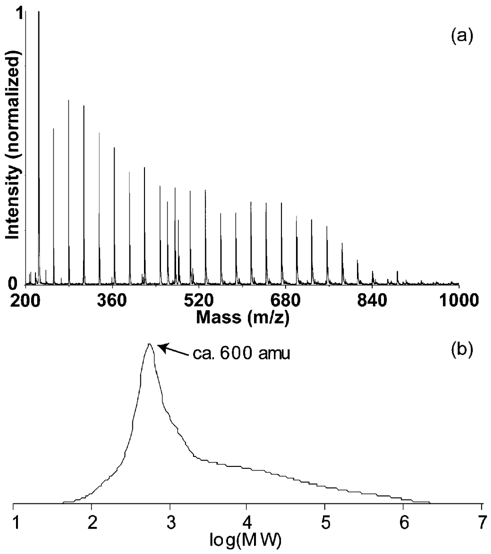

Fig. 1 Am-PE, as detected by ESI-MS, and deuterium-labeled polyethylene (D-PE) as detected by GPC, for samples produced according to the conditions of run 2, Table 1. (a) ESI-MS analysis of Am-PE oligomers. The maximum signal intensity is set to 5% of the methyl amidinium signal at $m/z = 223$. (b) GPC trace of bulk D-PE sample.

Increases in reaction time, ethylene pressure, and/or MAO concentration do *not* result in substantial increases in measured polymer statistics (M_n and PDI) and in fact apparently *decrease* catalyst activity. By contrast, GPC and gravimetric analysis show that bulk polymer properties do change as predicted. Under *all* reaction conditions, polymer statistics determined by ESI-MS are significantly lower than those obtained from bulk analysis. As these results show, Am-PE distributions are not reflective of reaction conditions, but are instead controlled primarily by the nature of ESI-MS analysis. Consequently, ESI-MS analysis of Am-PE distributions cannot yield meaningful kinetic parameters.

Fig. 1 is illustrative. The GPC trace (Fig. 1(b)) is bimodal and clearly shows a high molecular-weight distribution not detectable by ESI-MS (Fig. 1(a)); although only a minimal mole fraction of polymer, these high-mass PE chains account for a large fraction of consumed monomer. Similarly, no Am-PE oligomers of greater than 1000 Da are visible by ESI-MS, although these oligomers are detected by MALDI (*vide infra*). Finally, as shown in Table 1, ESI-MS analysis substantially underestimates the number of PE chains generated per zirconocene (0.5 *vs.* 6.8). Taken together, these results demonstrate that ESI-MS analysis alone does not provide the quantitative information needed for kinetic analysis.

It is known that molecular weight distributions observed by ESI or MALDI-MS are accurate only for samples with narrow polymer distributions (PDI $\leq$1.1–1.5).[13–15] Broader distributions suffer from increasing discrimination against higher molecular weight chains, resulting in lower measured molecular weights and polydispersities. These problems are intrinsic to soft ionization MS. GPC fractionation of high PDI samples prior to analysis is thus mandatory for quantitative results.[16] While the high PDI of the Am-PE distributions undoubtedly contributes to the observed discrepancies, preliminary experimental evidence suggests that other factors may also influence observed ESI-MS distributions.

PE has low solubility at room temperature. In contrast to prior reports,[8] we observed that carbodiimide quench-labeled solutions are opaque even at the shortest reaction times and produce a light yellow precipitate upon standing. Solid-phase MALDI-MS analysis of dried Am-PE samples isolated from unfiltered solutions revealed species with masses substantially greater than those observed by ESI-MS (Fig. 2(a)). In samples which were filtered prior to solvent removal, these heavier

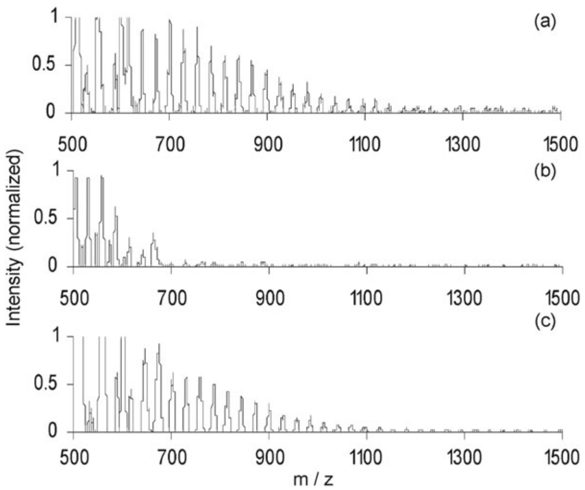

Fig. 2 MALDI-TOF spectra of dried Am-PE samples (all-*trans* retinoic acid matrix). PE samples generated under conditions listed in run 2. (a) MS of unfiltered crude Am-PE; (b) Am-PE remaining in filtrate; and (c) Am-PE recovered from the filtrant.

Table 1 Results from ESI-MS analysis of Am-PE and GPC and gravimetric analysis of D-PE (0 °C, toluene, [$CpZrCl_2$] = 2.6 mM)

Conditions				ESI-MS results					GPC results		
Run	Al/Zr	t/s	p/atm	Act.[ab]	M_n[c]	M_w/M_n	N/Zr[d]	Bulk activity[a]	M_n[c]	M_w/M_n	N/Zr[d]
1	10	90	2	3.1	310	1.3	0.5	26	350	2.9	3.6
2	10	300	2	0.9	290	1.3	0.5	28	680	51	6.8
3	10	900	2	0.1	400	1.1	0.1	24	1680	99	7.0
4	20	90	2	1.1	250	1.4	0.2	102	890	18	5.7
5	20	300	2	0.6	250	1.4	0.4	65	1400	32	9.1
6	20	90	3	0.8	230	1.4	0.2	104	1280	41	6.1
7	20	300	3	0.5	260	1.4	0.4	70	2200	44	9.9

[a] Catalyst activity is measured in g (mmol catalyst)$^{-1}$ h^{-1} (atm ethylene)$^{-1}$. [b] Computed as the total mass of all methyl-terminated polymer chains observed by ESI-MS. [c] Number-average molecular weight (M_n); g (mol PE)$^{-1}$. [d] Number of polymer chains per zirconium.

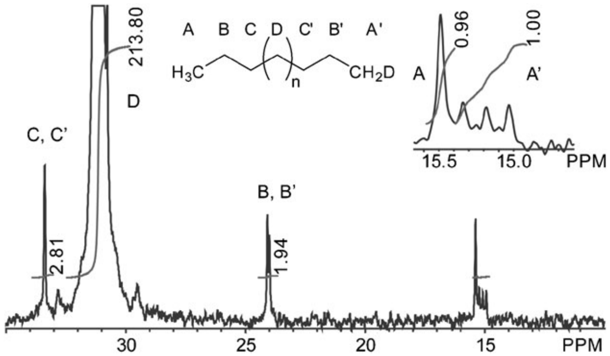

Fig. 3 Quantitative $^{13}C\{^1H\}$ NMR of selected D-PE samples ($C_2D_2Cl_4$, 120 °C) revealed quantitative deuteration of all PE chains.

oligomers are not present in the filtrate (Fig. 2(b)), but are seen in the filtrand (Fig. 2(c)). Thus, higher molecular weight Am-PE species may precipitate from solution prior to ESI-MS analysis, leaving only Am-PE oligomers to be detected.

PE chains that lack ionizable groups, such as the vinyl-terminated products of pre-quench chain transfer or metal–polymeryls that failed to insert carbodiimide, are undetectable by ESI-MS. ^{13}C NMR microstructure analysis of select D-PE samples shows clean deuteration of *all* PE chains: for each D-labelled terminal methyl group there is one unlabelled terminus (Fig. 3). Thus, all PE chains are metal-bound at the time of quench. Because the number of polymer chains formed per Zr is significantly greater than unity, most chains must be bound to aluminium.

It has been asserted that Am-PE distributions reflect polymeryl chains bound to both aluminium and zirconium,[9] but efficiencies of the quench-label reactions has not been established. We examined the quench-label reactions of DCC with two model species, $AlMe_3$ (**1**), a known chain transfer agent present in most commercially available MAO solutions,[17] and $Cp_2ZrMe(MeB(C_6F_5)_3)$ (**2**), a well-defined, catalytically active cationic zirconocene. At room temperature, the reaction of **1** with 10 eq. of DCC yields only dimethylmono(amidinate)-aluminium. Prior studies of the reaction between **1** and 1,3-diisopropylcarbodiimide have concluded that aluminium bis- and tris(amidinate) complexes are not formed below 70 °C, primarily due to steric inhibition of initial carbodiimide chelation.[18] Therefore, tripolymeryl or dipolymerylmethyl–aluminium species are expected to transfer at most only one alkyl to carbodiimide. Reaction of **2** with an excess of DCC (30 eq.) at room temperature is slow but quantitative. At short reaction times (<10 min), a transient intermediate, tentatively identified as $Cp_2ZrMe(DCC)^+$,[19] is detected by ^1H NMR. Consequently, it is unclear if all metal–polymeryls are quench-labeled through reaction with DCC.

In conclusion, distributions of amidinium-ion-terminated oligomers revealed by ESI-MS do not quantitatively represent the complete polymer distributions. Instead, apparent ESI-MS distributions are the products of non-linear ESI-MS sensitivity across wide mass ranges, the low solubility of high molecular-weight PE chains, and, possibly, the incomplete reaction of DCC with metal–alkyl species present in solution. Although ESI-MS analysis of polyolefins containing ionizable labels would greatly facilitate kinetic studies, current methods are not quantitative. Thus, kinetic interpretations of quench-labelled polymer distributions detected by ESI-MS require caution and must be externally validated. One approach to validating ESI-MS methods for characterizing polyolefin polymerization kinetics would use soluble polymers generated by well-defined single-site catalytic systems and analyzed with multiple techniques. Such efforts are currently underway.

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Notes and references

‡ Mass spectral appearance is highly dependant upon instrument settings, but observed variations do not influence the conclusions of this paper. See ESI† for details.

§ GPC distributions are multimodal and reveal that Cp_2ZrMe_2/MAO-catalyzed ethylene polymerization is quite complex. Further examination of this system is beyond the scope of this paper.

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