

GPC and ESI-MS Analysis of Labeled Poly(1-Hexene): Rapid Determination of Initiated Site Counts during Catalytic Alkene Polymerization Reactions

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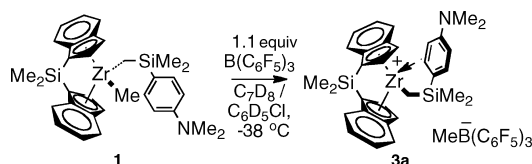
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Abstract: Accurate active-site counts are necessary for the establishment of olefin polymerization kinetics, yet current techniques are often tedious and limited in sensitivity. Herein, we describe the development of a novel method for determining the fraction of initiated catalyst using standard gel-permeation chromatography (GPC). The first insertion of monomer into the chromophore-bearing zirconocene **1** generates a single equivalent of a labeled polymer chain. The polymer-bound label can be quantified as a function of polymer molecular weight using a GPC with a UV detector; simultaneous RI detection allows both the extent of monomer conversion and the molecular-weight distribution to also be established. We estimate that monomer to catalyst ratios of as high as 10 000:1 can be measured using this technique.

The development of high-throughput organometallic synthesis and screening techniques has accelerated the discovery of highly active homogeneous olefin polymerization catalysts.¹ Modern metallocene and postmetallocene catalysts are exceedingly active and generate highly tailored polyolefins.² The mechanisms of catalytic polymerization can be complex,³ one important factor that limits mechanistic studies is practical determination of catalyst speciation under realistic conditions. Herein, we describe a novel approach to rapid catalyst-site counting that utilizes an ionizable chromophore to label polymer chains and is amenable to high throughput conditions using standard gel-permeation chromatography (GPC) and mass spectrometry techniques.

Accurate active site counts are a vital but often neglected element of polyolefin polymerization kinetic analysis.⁴ Most techniques require the reaction of propagating, polymeryl-bearing catalytic centers with an NMR-active⁵ or radioactive⁶ label, followed by tedious quantification. Alternative approaches, such as *in situ* NMR spectroscopy, can also be used but currently are limited to relatively slow processes at millimolar catalyst concentrations.⁷ We reasoned that selective labeling of polyolefins with a UV-chromophore would allow the concentration of an initiated catalyst to be directly quantified as part of standard polymer analysis by GPC with a UV detector.

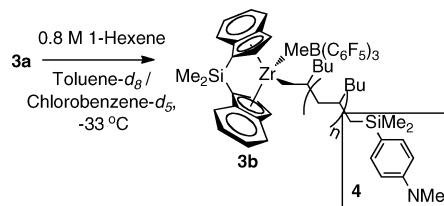
To test this approach, we designed a labeled catalyst system, *rac*-(SBI)Zr(Chrom)Me (**1**). **1** employs an industrially relevant *ansa*-metallocene backbone and a chromophore-bearing substituent, *N,N*-dimethylanilyldimethylsilyl-methylene. **1** can be readily synthesized in four steps from commercially available starting materials and is stable indefinitely under glovebox conditions.

Scheme 1. Activation of **1a**

Upon addition of excess $B(C_6F_5)_3$ (**2**; 9 μ mol in 0.2 mL of toluene- d_8) to a solution of **1** in toluene/chlorobenzene (8 μ mol of **1**, 0.5 mL of toluene-

d_8 /0.2 mL of chlorobenzene- d_5), clean activation is observed, generating the monomeric uninitiated catalyst **3a** (Scheme 1). This species has been extensively characterized by 1H and ^{19}F NMR. Spectral data indicate displacement of the $[MeB(C_6F_5)_3]^-$ counterion by coordination of the anilinyll ring to the zirconium center.

As anticipated, **3a** catalyzes the polymerization of 1-hexene (Scheme 2). At $-33^\circ C$, catalyst initiation can be readily monitored by NMR observation of the decrease in **3a**, which quantitatively generates a single equivalent of polymer-bound chromophore (**4**) upon initiation. 1-Hexene consumption also can be monitored as a function of time. Assuming that all of the initiated catalyst propagates, this permits *apparent* rates of catalyst initiation and propagation to be established ($k_i^{app} = 0.00017 \text{ mol}^{-1} \text{ L}^{-1} \text{ s}^{-1}$; $k_p^{app} = 0.399 \text{ mol}^{-1} \text{ L}^{-1} \text{ s}^{-1}$; both rate laws are first-order in zirconocene complexes and 1-hexene).⁸

Scheme 2. Polymerization Initiated by **3a**

Chromophore-labeled polymer samples (CPol) generated from polymerization reactions quenched with MeOD can be analyzed by ESI-MS, GPC, and NMR. Simple polyolefins are not easily ionized, precluding many mass spectral analyses.⁹ However, the first chain grown from **3a** contains an ionizable aniline group (Scheme 2). Although true polymer mass distributions cannot be obtained from ESI-MS of these polymers,^{9d} high mass resolution enables chain-end analysis through measurement of the ratio of deuterated to unsaturated chain ends, which differ by 3 amu (Figure 1); this ratio reflects the ratio, at the time of quench, of actively propagating catalytic polymeryls to chains liberated by β -hydride elimination. However, label decomposition under electrospray conditions and cumulative instrument damage induced by large amounts of un-ionized polyhexene discourage routine ESI-MS analyses.

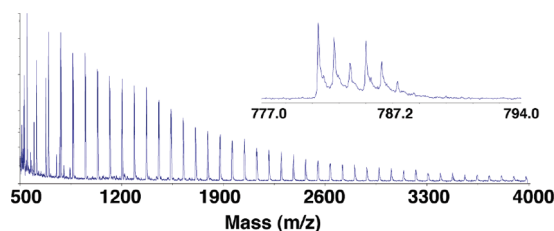


Figure 1. ESI-MS analysis of CPol sample. Conditions: [**1**] = 9.8 mM; [**2**] = 11.2 mM; [1-Hexene] = 0.47 M; 0.6 mL of toluene- d_8 /0.2 mL of chlorobenzene- d_5 , $-40^\circ C$, 3.5 h. Inset shows isotopic resolution.

Table 1. Results from Analysis of CPol Samples by NMR and GPC^a

Entry	[Zr] ^b (mM)	[B(C ₆ F ₅) ₃] (mM)	[Hexene] (M)	Time (min)	NMR Data		GPC Data		<i>M_w</i> ^c	PDI ^d
					% Init	% Conv	% Init	% Conv		
1	5	9	0.8	5	<i>e</i>	4 ^f	1.9	1.8	17 900	2.0
2	6	9	0.8	30	14	71	13	69	32 600	2.2
3	6	9	0.8	60	18	95	17	104	31 200	2.3
4	5	9	0.8	180	22	100	21	112	34 400	2.3
5	5	9	0.4	60	13	89	12	90	34 500	2.2
6	1.5	2.5	0.8	60	24	52	21	49	38 000	2.3
7	3.0	4.5	0.8	60	20	77	18	73	40 500	2.2

^a Reaction conditions: −33 °C in toluene-*d*₈/chlorobenzene-*d*₅ (0.7 mL/0.2 mL), with 5.45 mM diphenylmethane present as an internal standard. Analysis procedures are described in the Supporting Information. ^b Absolute catalyst concentrations were established by NMR prior to initiation. ^c Weight-average molecular weight. ^d Polydispersity index (*M_w*/*M_n*). ^e Peak could not be detected. ^f Reported percent conversion is uncertain due to low value.

Alternatively, GPC analysis of quenched CPol samples yields substantial, quantitative information. Unlike simple polyolefin samples, two-detector GPC analysis of CPol samples yields two distinct traces: an RI trace, which shows the *mass* concentration of bulk polymer, and a UV–vis trace, which reflects the *molar* concentration of polymers derived from **4** as a function of molecular weight (Figure 2). Because each initiated catalyst must produce a chromophore-labeled polymer, this technique uniquely enables simultaneous monitoring of how much catalyst has undergone initiation, the mass distribution of the first chain grown at a catalyst, and mass distribution of the bulk polymer using standard equipment.

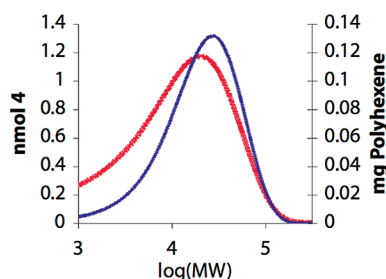


Figure 2. GPC analysis of CPol sample. Conditions are described in Table 1, entry 3. Red line: UV trace (left axis); blue line: RI trace (right axis).

To test the quantitative accuracy of this labeling technique, results from GPC analysis were directly compared to those from NMR analysis of quench-labeled polymer samples (Table 1). At the specified time of quench, samples intended for GPC analysis were quenched with a mixture of methanol-*d*₄ and NEt₃ and then transferred to a precooled NMR probe, where the concentration of **4** and the remaining hexene concentration were established via quantitative ¹H NMR. Following workup, samples were diluted into 10 mL of THF and analyzed on a Viscotek GPC equipped with refractive index and UV–vis detectors. As shown in Table 1, results from NMR and GPC analysis agree well, uniquely demonstrating determination of the concentration of initiated sites of an alkene-polymerization catalyst directly from GPC analysis of bulk polyolefin samples.

The sensitivity of the GPC technique was compared with that of other site counting methods. Previously, we estimated that ²H labeling, through use of a labeled catalyst or through quench-labeling with MeOD, was sensitive to samples with more than one active site per 3000 monomer insertions, at best.^{5a} At minimum, samples shown above contain a **4**/monomer ratio of 1:1200. Dilution experiments demonstrate that as little as 0.1 nmol of **4** can be detected and roughly quantified by GPC; this corresponds to a **4**/monomer ratio of ca. 10 000:1 for GPC analysis at a polymer concentration of 1 mg/mL. Unlike common NMR techniques,

sensitivity can be readily improved using this technique by either increasing the concentration of polymer or developing better chromophores.

The significance of this approach is twofold. First, initiated catalyst concentrations and molecular weight distributions as a function of time are among the two crucial components necessary for detailed kinetic studies (the other components, such as end group analysis, can be readily determined using standard NMR techniques or mass spectrometry).¹⁰ At short reaction times the UV-detected mass distributions are particularly sensitive to initiation kinetics. Second, the method is practical: it uses common instrumentation, is suitable for very active catalysts, and can be automated for high throughput.

Although experiments with **1** establish that careful choice of catalyst precursors generates polymers suitable for ESI-MS detection and quantitative GPC analysis, this chromophore is not ideal. First, the label, which bears a *N,N*-dimethylanilinyll group, is susceptible toward reaction with cationic metallocenes. Additionally, **4** decomposes in the presence of acid and is slightly unstable even in the presence of base. Tentative evidence suggests this may be due to cleavage of the Si–phenyl bond. Even with added NEt₃, reaction workup must be relatively rapid and sample analysis must occur within a week or inaccurate concentrations of **4** will be measured. Furthermore, **4** is expected to have different initiation rates (but not propagation or chain transfer rates) than other common initiating alkyl groups such as methyl and benzyl. In the presence of additives such as MAO, aluminum alkyls, or diethyl zinc that can undergo transmetalation reactions with polymerization catalysts, the chromophore-labeled polymer may not reflect the total initiated catalyst.¹¹

In conclusion, we have shown that GPC analysis of polyolefins synthesized from a labeled catalyst can provide highly accurate initiated site counts and bulk polymer mass distributions. This technique is rapid and versatile, can detect as little as 0.1 nmol of chromophore, and uses common instrumentation. In order to facilitate routine application of these methods we are developing more chemically inert chromophores.

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Supporting Information Available: Synthesis of **1**; characterization of **1**, **3a**, and **4**; conditions and preliminary apparent kinetic information for **3a**-catalyzed 1-hexene polymerization, procedure for ESI-MS and

GPC analysis of CPol, and supplemental NMR and GPC spectra and data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) We note that, should transalkylation with other metal alkyls occur, this presents a mechanism for introducing the chromophore label *in situ*.

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