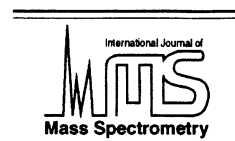




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Mass spectrometric assay of polymerization catalysts for combinational screening

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Abstract

Electrospray ionization mass spectrometry of a homogeneous Ziegler-Natta polymerization catalyzed by a Pd(II) diimine complex shows two distinct distributions of metal-bound oligomeric ions corresponding to catalytic centers which have not undergone chain transfer and those that have. A fit of two distributions by numerical integration of the kinetic equations describing the polymerization gives the absolute rates for initiation, propagation, and chain transfer in the polymerization reaction, from which the bulk polymer properties can be predicted. The mass spectrometric method requires mg quantities of catalyst, requires only a few minutes, and is suitable for both pooled and parallel screens of catalyst libraries. (Int J Mass Spectrom 195/196 (2000) 377–383) © 2000 Elsevier Science B.V.

Keywords: Mass spectrometric assay; Polymerization catalysts; Combinational screening; Ziegler-Natta

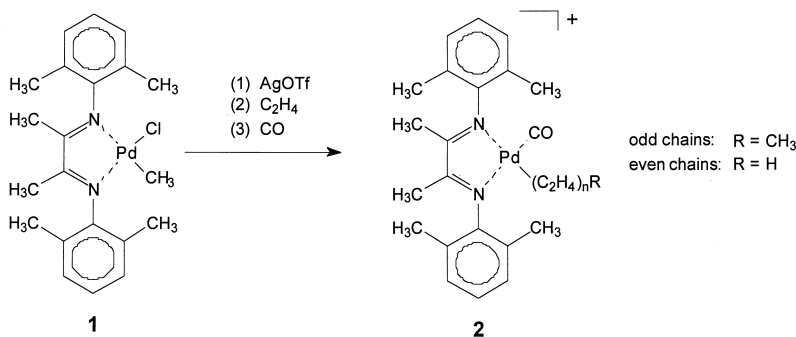
1. Introduction

Methods for high-throughput screening of organo-metallic catalysts occupy a central position in the emerging area of combinatorial materials science [1]. There have been a variety of strategies employed to correlate some aspect of catalysis to a measurable quantity that can be, moreover, measured quickly on very small samples. Chromatographic [2], thermographic [3], fluorescence quenching [4], microwell parallel reactions [5], and polymer-supported “bead” methods [6] have been tried with varying degrees of success. The strategies typically assay reaction rate or turnover number. For example, rate is correlated with

heat release in the thermographic assay, which is appropriate for assays of overall catalytic activity. For polymerization reactions [7], on the other hand, catalytic activity is only one of several important catalyst properties for which high-throughput screens would be needed. The key properties of average molecular weight [8], M_w or M_n , and molecular weight distribution, M_w/M_n are currently not accessible in any fast assay. The usual methods of size-exclusion chromatography (also termed gel permeation chromatography or gpc), light scattering, viscosity, or colligative property measurement require bulk samples and/or careful calibration, and are poorly suited to high-throughput screening. In a previous report [9], we showed that electrospray ionization tandem mass spectrometry could screen according to chain length for metal-bound polymer chains. We report here further development of the mass spectrometric

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Dedicated to Professor Robert R. Squires.



Scheme 1.

method for high-throughput screening of catalysts [10] according to the likely M_w of the resulting bulk polymer, including polymer chains that do not remain on the catalyst. The screen, demonstrated for a homogeneous Ziegler-Natta polymerization, requires a few milligrams of catalyst, assay times measured in minutes, and can work for either a pooled, simultaneous screen of multiple catalysts, or a parallel, sequential screen of one catalyst at a time.

2. Results

As a test system, the Brookhart Pd(II) system [11,12], precatalyst 1, was chosen, although the method is general to most classes of polyolefin catalysts. As in many of the Ziegler-Natta catalysts, the final polymer molecular weight is largely determined by chain-transfer with monomer (or polymer if the concentration becomes high enough). The elementary steps in the polymerization [13] have been explored computationally by Ziegler and co-workers [14], and experimentally for this particular family of catalysts by Brookhart. Because of very fast monomer complexation, the resting state of the Pd(II) diimine catalysts is the ethylene complex; the ethylene consumption rate was found accordingly to be zero-order in ethylene [11].

A thermostatted CH₂Cl₂ solution (5 ml, 9.8 °C), presaturated with ethylene, in which 2 mg (<5 μmol) of 1 was dissolved, was activated by AgOTf, allowed

to polymerize for 26 minutes, and then quenched by saturation with CO gas [15]. A sample was removed, diluted to fifty-fold, and analyzed by electrospray in a modified Finnigan MAT TSQ-7000 mass spectrometer. The instruments and operating parameters have been previously described [9,16]. The resulting mass spectrum is shown in Fig. 1. Examination of the $m/z = 1000-2500$ region reveals two distinct distributions of oligomeric ions. Metal-bound oligomer chains with methyl endgroups, designated odd chains, correspond to chains built on a catalytic center that has not undergone chain-transfer. Metal-bound oligomer chains with hydrogen endgroups, designated even chains, correspond to chains built on a catalytic center that has undergone chain-transfer at least once. Although both the odd and even chains are built by addition of ethylene units, they are displaced from one another by 14 mass units. Using the general kinetic scheme for Ziegler-Natta polymerization, with adaptations to the specific class, in this case Brookhart catalysts, the two distributions can be fitted, by integration of the differential rate equation, to yield unique, absolute rates for initiation, propagation, and chain-transfer for the particular set of conditions in the reaction. The fit for $k_{\text{init}} = 0.01$, $k_{\text{prop}} = 0.044$, and $k_{\text{trans}} = 0.00045 \text{ s}^{-1}$, for initiation, propagation, and chain-transfer rates, respectively, is shown in Fig. 2.

The entire procedure can be repeated at several temperatures to obtain rates for Arrhenius plots. A preliminary attempt in this direction finds non-Arrhe-

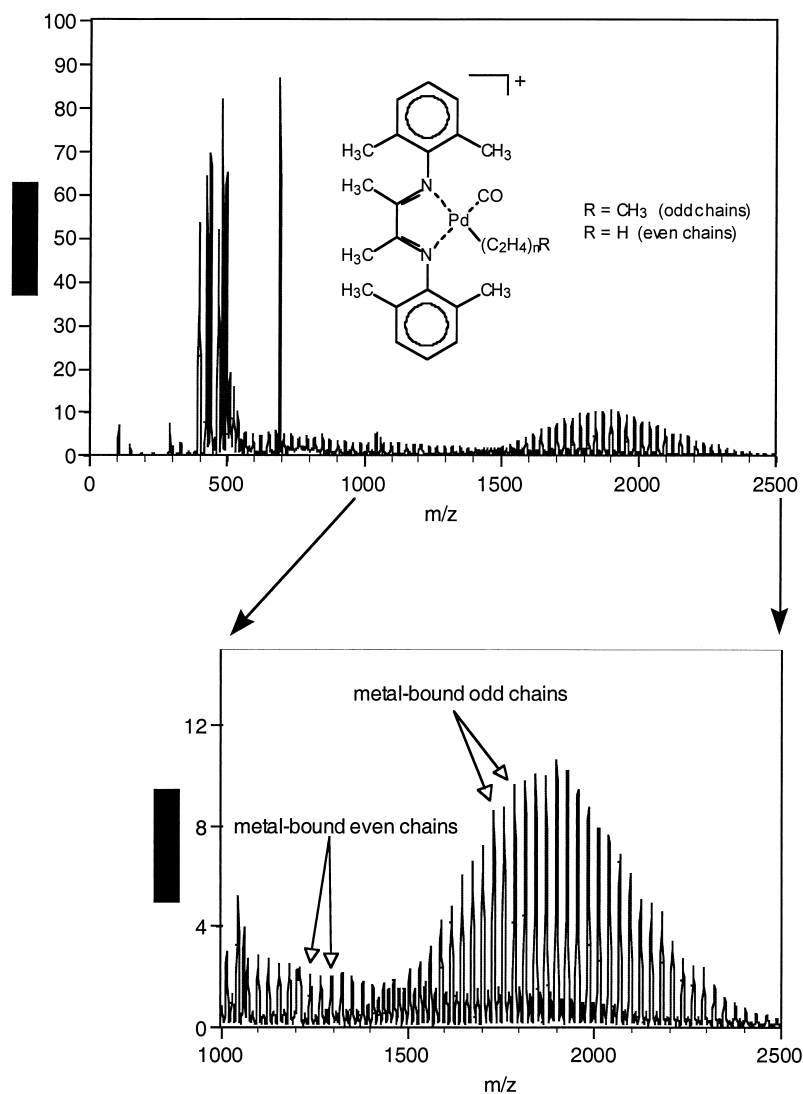


Fig. 1. Electrospray mass spectrum of **1**, after activation, reaction with ethylene, and quenching with CO. The expanded region shows the odd and even-chain distributions.

nius behavior for the initiation rate, understandable because it is heterogeneous; we find, on the other hand, $E_a^{\text{prop}} = 18.9$ and $E_a^{\text{trans}} = 21.4$ kcal/mol. The rates can also be used to compute the average molecular weight and extent of polymerization as a function of time, shown in Fig. 3, under the assumption of constant ethylene concentration and dilute polymer

solution. With these assumptions, the polydispersity is $M_w/M_n = 2$, as expected from theory. In the event that more realistic conditions, e.g. high polymer concentration, need to be simulated, the rate expressions with chain-transfer to either monomer or polymer can be integrated. One expects in such a case that $M_w/M_n > 2$.

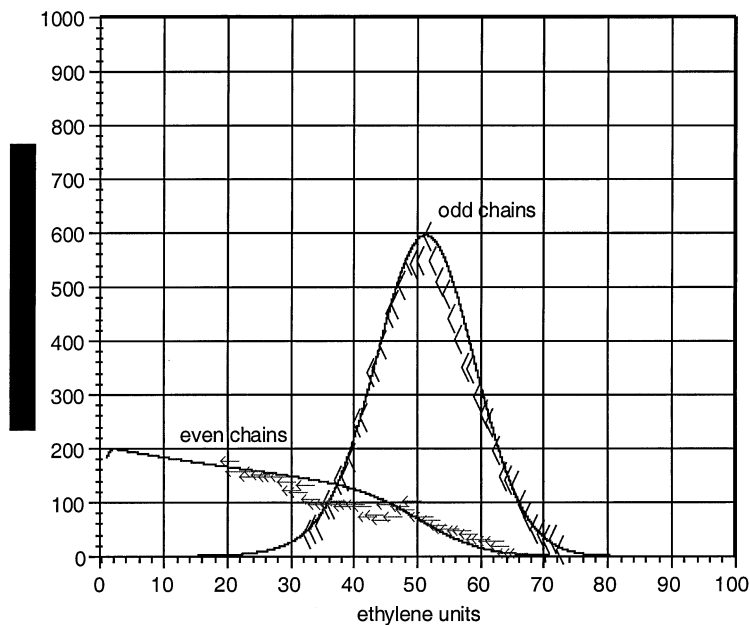


Fig. 2. Fit of the odd and even-chain distributions to the rates for initiation, propagation, and chain transfer.

3. Discussion

In the general mechanism for homogeneous Ziegler-Natta polymerization, the limiting chain

length, and therefore the polymer molecular weight, is determined primarily by the ratio of the propagation to chain-transfer rates. Whereas the former rate can be measured by a number of techniques, there are ex-

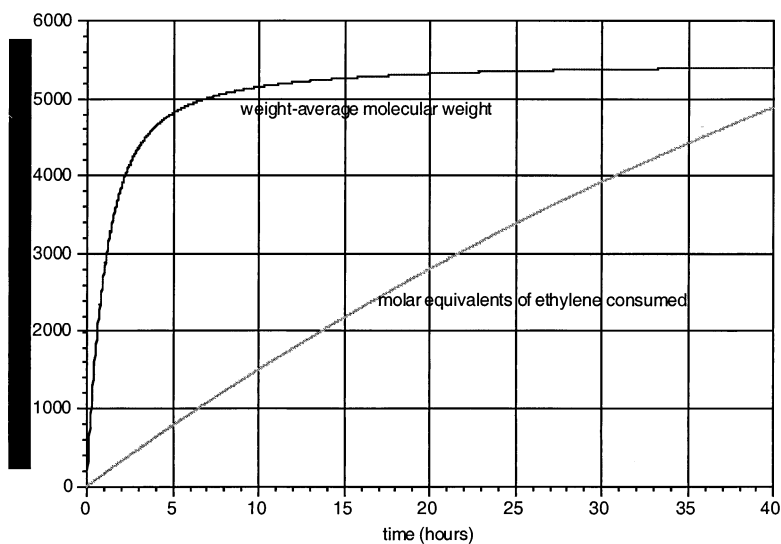


Fig. 3. Computed average molecular weight and extent of polymerization at 9.8 °C, calculated using the rates determined from the fit to the odd- and even-chain distributions.

tremely limited ways to obtain the latter. Brookhart reported propagation rates [11] for catalysts related to **1**. In control experiments on these catalysts, our propagation rates were approximately a factor of two slower than that in the literature. Given that the mode of activation was different, giving triflate as the counterion in the present work, as opposed to tetrakis(pentafluorophenyl)borate, the factor of two is completely understandable. Brookhart reports no chain-transfer rates, so no direct comparison can be made. One could proceed to compute the polymer molecular weight to compare to the M_w reported in the literature, but that value was measured under conditions which are far from ideal for the comparison, e.g. 45 g polymer formed in 100 ml solvent, making a direct test again difficult. Nevertheless, one should note that **1** was not rated as one of the better catalysts in the Brookhart work, consistent with the modest M_w seen in Fig. 3.

Procatalyst **1** was chosen for the test because it gave odd-chain and even-chain distributions which are easily seen in Fig. 1. If a better catalyst were to be used [17], the same exercise could be done to extract the three rates, but the difference in magnitude between the odd-chain and even-chain distribution would have been greater. With commercial quadrupole or sector instruments delivering a dynamic range of $\sim 10,000$ to 1, one can estimate that the present screening method should function up to $M_w \sim 500,000$. The upper-bound applies only if one is in fact concerned with using the mass spectrometric method to quantify M_w . In practice, as a screening method, only trends and gross magnitudes need to be measured, because the actual polymer molecular weight would be determined conventionally for a “hit” anyway. This same argument applies in case the actual rates for propagation and chain-transfer, contrary to assumption, do in fact depend on chain length. As long as the variation is smooth and slow as a function of chain length, the integrity of the mass spectrometric screen is not impaired.

Ideally, one would want the three rates in the fit to the odd- and even-chain distributions to be linearly independent so that a unique fit can be achieved.

Although an analytical proof of linear independence has not been done, an examination of the behavior of the fitting functions as the parameters are varied suggests that the three rates can be uniquely determined. Qualitatively, the absolute propagation rate is primarily responsible for the position of the maximum and the shape of the leading edge of the odd distribution. The ratio of propagation to initiation rate determines the width and the shape of the trailing edge of the odd-chain distribution. The ratio of the propagation to chain-transfer rate determines the relative magnitude of the odd versus even chain distribution. The shapes, bell-shaped for the odd-chain distribution, and monotonically decreasing with a sharper drop at the leading edge for the even-chain distribution—are consequences of the kinetic model and not otherwise adjustable. The good fit of these shapes with the three rates suggests that the model is adequate for the deconvolution.

Important for the interfacing of the assay to a complete screening procedure is the ability of the assay to handle a pooled screen, i.e. multiple simultaneous catalysts at once, and the facility by which the assay can be automated for a parallel screen. For both kinds of screens, the mass spectrometric method is well-suited. We have already shown that, for a pooled screen, the implementation of a parent ion scan on the β -hydride elimination daughter ion produced by collision-induced dissociation of the metal-bound oligomers generates the equivalent to Fig. 1 for a single catalyst in the presence of many others [9]. For a parallel screen, automation can be done with autosamplers available for the commercial spectrometers. Compared to conventional methods for polymer molecular weight determination, the present mass spectrometric method is faster, requires much less sample, and is more amenable to automation. Other mass spectrometric approaches [18] suffer from the disadvantage that they operate directly on the polymer rather than on the metal-bound oligomers, meaning that the ionization process (in the case of electrospray) and/or the mass range of the spectrometer (for electrospray or MALDI), become problematic, especially for polyethylene and polypropylene.

4. Experimental

CH_2Cl_2 was distilled from CaH_2 before use. Electrospray ionization was conducted with flow rates of 5 to 15 $\mu\text{L}/\text{min}$, N_2 sheath-gas, and a spray-voltage of 5.0 kV. Very mild desolvation-conditions (heated capillary 150 °C, tube lens potential 52 V) were employed.

4.1. $(\text{ArN}=\text{C}(\text{Me})-\text{C}(\text{Me})=\text{NAr})\text{PdMeCl}$ ($\text{Ar} = 2,6\text{-C}_6\text{H}_3(\text{Me})_2$) [11]

The precatalyst **1** was prepared as described in the literature. The free diimine ligand, biacetyl-bis-(2,6-dimethylphenylimine) [19], 73.1 mg (0.25 mmol), and 66.3 mg (0.25 mmol) (1,5-cyclooctadiene)Pd(Me)Cl [20] were suspended in 3 mL ether and stirred for 18 h. The orange precipitate that formed was filtered off and washed thoroughly with ether and dried in vacuo. Yield 101.0 mg orange solid (90%). $^1\text{H-NMR}$ (300 MHz, CDCl_3) δ 7.17–7.05 (m, 6 H, Ar), 2.25 (s, 6 H, Ar- CH_3), 2.22 (s, 6 H, Ar- CH_3), 2.03 (s, 3 H, N=C- CH_3), 1.98 (s, 3 H, N=C- CH_3), 0.44 (s, 3 H, Pd- CH_3).

4.2. Polymerization experiments

2.0 mg (4.45×10^{-3} mmol) **1** were dissolved in 5 mL CH_2Cl_2 in a 20 mL Schlenk tube fitted with a thermocouple to measure internal temperature and cooled to the reaction temperature 9.8 °C. The solution was saturated with ethylene by stirring vigorously under an ethylene atmosphere for 30 min. Approximately 10 mg AgOTf were then added to activate the catalyst. Vigorous stirring was continued under one bar ethylene; the polymerization reaction was allowed to proceed for 26 min. The reaction was then quenched by bubbling a vigorous stream of CO through the solution. An aliquot of the solution was filtered through a plug of glass wool to remove silver salts, diluted 50-fold with CH_2Cl_2 , and analyzed by electrospray ionization mass spectrometry.

5. Conclusion

A mass spectrometric assay for polymerization catalysts is introduced that provides the connection between the microscopic world of ion distributions and the macroscopic world of bulk polymers properties. The procedure is fast, robust, and adapts readily to a variety of screening strategies.

References

- [1] A general review of screening for catalysts has recently appeared: B. Jandeleit, H.W. Turner, T. Uno, J.A.M. van Beck, W.H. Weinberg, *CatTech* 2 (1998) 101.
- [2] M.B. Francis, E.N. Jacobsen, *Angew. Chem* 111 (1999) 987.
- [3] S.J. Taylor, J.P. Morken, *Science*, 280 (1998) 267; M.T. Reetz, M.H. Becker, K.M. Kühling, A. Holzworth, *Angew. Chem.* 110 (1998) 2792.
- [4] A.C. Cooper, L.H. McAlexander, D.H. Lee, M.T. Torres, R.H. Crabtree, *J. Am. Chem. Soc.* 120 (1998) 9971.
- [5] K. Burgess, H.J. Lim, A.M. Porte, G.A. Sulikowski, *Angew. Chem.* 108 (1996) 192; S.M. Senkan, *Nature*, 394 (1998) 350.
- [6] B.M. Cole, K.D. Shimizu, C.A. Krueger, J.P.A. Harrity, M.L. Snapper, A.H. Hoveyda, *Angew. Chem.* 108 (1996) 1776; T.R. Boussie, C. Coutard, H. Turner, V. Murphy, T.S. Powers, *Angew. Chem.* 110 (1998) 3472.
- [7] Recent advances in new homogeneous Ziegler-Natta catalysts have been reviewed: G.J.P. Britovsek, V.C. Gibson, D.F. Wass, *Angew. Chem.* 111 (1999) 448.
- [8] M_n is the number-average molecular weight. M_w is the weight-average molecular weight. M_w/M_n quantifies the polydispersity—the distribution of molecular weights—because M_w emphasizes the heavier chains, whereas M_n emphasizes the lighter ones.
- [9] C. Hinderling, P. Chen, *Angew. Chem. Int. Ed. Engl.* 38 (1999) 2253.
- [10] Two previous electrospray ionization mass spectrometric studies of active polymerization catalysts did not produce data on oligomers suitable for kinetic analysis or screening, although one did perform an endgroup determination for a ROMP oligomer: R. Saf, R. Schitter, C. Mirtl, F. Stelzer, K. Hummel, *Macromol.* 29 (1996) 7651; Z.M. Dzhabieva, V.P. Kozlovskii, Yu. M. Shul'ga, A.F. Dodonov, G.P. Belov, *Russ. Chem. Bull.* 45 (1996) 474.
- [11] L.K. Johnson, C.M. Killian, M. Brookhart, *J. Am. Chem. Soc.* 117 (1995) 6414.
- [12] Further work on related catalysts is described: L.K. Johnson, S. Mecking, M. Brookhart, *J. Am. Chem. Soc.* 118 (1996) 267; C.M. Killian, D.J. Tempel, L.K. Johnson, M. Brookhart, *J. Am. Chem. Soc.* 118 (1996) 11664; B.L. Small, M. Brookhart, A.M.A. Bennett, *J. Am. Chem. Soc.* 120 (1998) 4049; B.L. Small, M. Brookhart, *Organometallics* 32 (1999) 2120.
- [13] A complete overview of Ziegler-Natta polymerization can be

- found: Ziegler Catalysts, G. Fink, R. Mülhaupt, H.H. Brintzinger, Ed., Springer-Verlag, Berlin, 1995.
- [14] P. Margl, L. Deng, T. Ziegler, *J. Am. Chem. Soc.* 121 (1999) 154, and references therein.
- [15] Several neutral two-electron ligands, such as DMSO and pyridine, were tried as quenchers. CO gave the most reliable results.
- [16] C. Hinderling, D.A. Plattner, P. Chen, *Angew. Chem.* 109 (1997) 272; C. Hinderling, D. Feichtinger, D.A. Plattner, P. Chen, *J. Am. Chem. Soc.* 119 (1997) 10793; D. Feichtinger, D.A. Plattner, *Angew. Chem.* 109 (1997) 1796; D. Feichtinger, D.A. Plattner, P. Chen, *J. Am. Chem. Soc.* 120 (1998) 7175; C. Hinderling, C. Adlhart, P. Chen, *Angew. Chem.* 110 (1998) 2831; Y.M. Kim, P. Chen, *Int. J. Mass Spec.* 185 (1999) 871.
- [17] The catalyst with *o,o'*-diisopropyl rather the *o,o'*-dimethyl groups on the aromatic moieties gives exceedingly small peaks corresponding to even-chain distribution, consistent with it being the best of the reported catalysts.
- [18] Mass spectrometric approaches to polymer characterization have been characterized: S.A. Lorenz, P.E. Maziarz, T.D. Wood, *Appl. Spec.* 53 (1999) 18A; R. Festag, S.D. Alexandratos, D.C. Joy, B. Wunderlich, B. Annis, K.D. Cook, *J. Am. Soc. Mass. Spectrom.* 9 (1998) 299; S.M. Hunt, M.M. Sheil, M. Belov, P.J. Derrick, *Anal. Chem.* 70 (1998) 1812; C.A. Jackson, W.J. Simonsick, *Curr. Opin. Solid State Mater. Sci.* 2 (1997) 661.
- [19] H.T. Dieck, M. Svoboda, T. Greiser, *Z. Naturforsch.* 32b (1981) 823.
- [20] R.E. Rülke, J.M. Ernsting, A.L. Spek, C.J. Elsevier, P.W.N.M. van Leeuwen, K. Vrieze, *Inorg. Chem.* 32 (1993) 5769.