

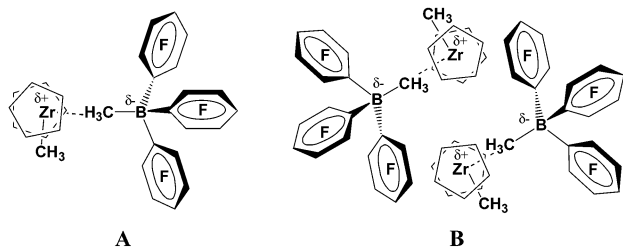
Metalloocene Polymerization Catalyst Ion-Pair Aggregation by Cryoscopy and Pulsed Field Gradient Spin–Echo NMR Diffusion Measurements

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The generally accepted structural model for homogeneous metallocene-based Ziegler–Natta polymerization catalysts¹ consists of a highly electrophilic group 4 metallocene cation paired with a weakly coordinating anion (e.g., **A**), usually derived from an activator such as a neutral organo-Lewis acid (e.g., perfluoroarylborane, MAO) or perfluoroarylmatalloid/metalate reagent.^{1,2} In the low-polarity solvents typically used in polymerizations, the cation and anion have been shown to be strongly associated both by experimental measurements over broad concentration and solvent polarity ranges (primarily by NMR)³ and by theoretical studies.⁴ Several investigations into the energetics of ion-pair formation and reorganization have been reported,³ ion-pairing sensitive polymerization processes studied over a broad concentration range,⁵ kinetics of initiation, propagation, and termination quantified,⁶ and numerous crystal structures analyzed.^{1,2} In all cases the data are consistent with a model in which cation and anion exist in solution primarily as 1:1 ion-pairs (e.g., **A**).



Recently, Geyer et al. reported⁷ the diffusion coefficients in benzene of $[\text{Cp}_2\text{ZrMe}]^+\text{X}^-$ and $[\text{rac-Me}_2\text{Si}(2\text{-Me-benz}[e]\text{indenyl})_2\text{-ZrMe}]^+\text{X}^-$ ($\text{X}^- = [\text{MeB}(\text{C}_6\text{F}_5)_3]^-$, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$) ion-pairs measured by a pulsed field gradient spin–echo (PGSE) NMR technique⁸ in the 1.6–4.7 mM concentration range. Employing the Stokes–Einstein relationship, an idealized model relating the translational diffusion coefficient, D , to phenomenological hydrodynamic radii (r_H ; eq 1 where $k = \text{Boltzmann's constant}$, $T = \text{absolute temperature}$, $\mu = \text{solution viscosity}$),^{8,9} they presented evidence that these ion-pairs are aggregated into ion-quadruples (e.g., **B**). Subsequent work has again invoked the importance of metallocenium ion-pair aggregates.¹⁰

$$D = \frac{kT}{6\pi\mu r_H} \quad (1)$$

While precedent exists for the aggregation of 1:1 organic salts in low-dielectric media,¹¹ such effects are not expected to be important when the cation and anion are similar in size and shape or at concentrations below 10^{-4} – 10^{-5} M, where single-site polymerizations are typically conducted.^{1,2} For these reasons we have carried out a detailed investigation of ion-pairing in a series of typical metallocenium salts by both a straightforward colligative method (freezing point depression)^{11a–c} and by PGSE NMR. We

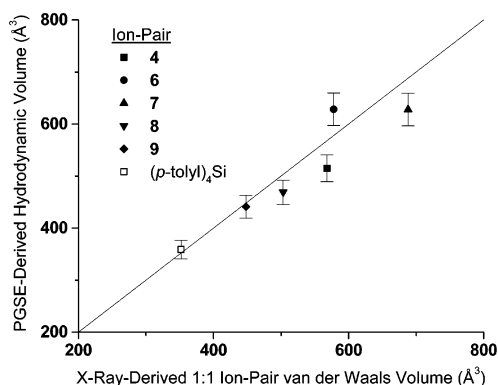


Figure 1. Plot of PGSE-derived metallocenium ion-pair hydrodynamic volumes versus van der Waals volumes computed for 1:1 ion-pairs from the corresponding crystal structures. The straight line represents the equation $\text{Vol}_{\text{PGSE}} = \text{Vol}_{\text{x-ray}}$. The uncertainty bars are shown at 5%.

restricted our study to ion-pairs which can be isolated and purified by crystallization and vacuum-drying rather than by generation in situ (inexact metallocene:activator stoichiometries can lead to polynuclear species^{2f}), and avoided unstable $\text{B}(\text{C}_6\text{F}_5)_4^-$ salts which frequently undergo decomposition to polynuclear species.^{2f,12} We report here that any aggregation is below the detection limits.

Table 1. Aggregation Numbers at the 90% Confidence Interval Measured by Cryoscopy for a Series of Metallocenium Ion-Pairs in Benzene

ion-pair ^a	molality (10^{-3} mol kg ⁻¹)	aggregation
1 $[(\text{Me}_5\text{Cp})_2\text{ZrMe}]^+\text{X}^-$	14.1	0.99(0.11)
2 $[\text{rac-Et}(\text{Indenyl})_2\text{ZrMe}]^+\text{X}^-$	12.8	0.94(0.16)
3 $[(1,2\text{-Me}_2\text{Cp})_2\text{ZrCH}_2\text{TMS}]^+\text{X}^-$	12.4	0.92(0.12)
4 $[\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(t\text{-BuN})\text{TiMe}]^+\text{X}^-$	18.3	1.15(0.13)
5 $[\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(t\text{-BuN})\text{ZrMe}]^+\text{X}^-$	13.8	0.76(0.07)
6 $[\text{Me}_2\text{C}(\text{Fluorenyl})(\text{Cp})\text{ZrMe}]^+\text{X}^-$	10.2	0.94(0.25)

^a $\text{X}^- = [\text{MeB}(\text{C}_6\text{F}_5)_3]^-$.

Cryoscopic molecular weight measurements were carried out in benzene solution under rigorously anhydrous/anaerobic conditions in a microprocessor-interfaced system and were calibrated with ferrocene.¹³ Measurements were limited to those ion-pairs having sufficient solubility for accurate results, with applicable concentrations well above the aforementioned 10^{-4} – 10^{-5} M range. As can be seen in Table 1, there is no evidence for significant aggregation for a range of ion-pair ancillary ligation, from relatively “open” to sterically hindered. To the extent that $\text{Zr-CH}_2\text{TMS}$ in **3** better simulates the steric characteristics of a growing polyolefin chain vs Zr-Me , it can be seen that this species also behaves as a 1:1 ion-pair.

PGSE experiments were also carried out under rigorously anhydrous/anaerobic conditions using the Stejskal–Tanner pulse

Table 2. Comparison of PGSE-Derived Ion-Pair Radii and Volumes in C₆D₆ with Those Computed from X-ray Crystallographic Data¹⁵

	ion-pair	concentration ^a (10 ⁻³ mol L ⁻¹)	radius ^b		volume ^b	
			PGSE	crystal	PGSE	crystal
1	[(Me ₅ Cp) ₂ ZrMe] ⁺ [MeB(C ₆ F ₅) ₃] ⁻	5.6	5.0(1)	5.2	523(26)	596
4	[Me ₂ Si(Me ₄ Cp)(<i>t</i> -BuN)TiMe] ⁺ [MeB(C ₆ F ₅) ₃] ⁻	9.9	5.0(1)	5.1	515(26)	568
6	[Me ₂ C(Fluorenyl)(Cp)ZrMe] ⁺ [MeB(C ₆ F ₅) ₃] ⁻	4.3	5.3(1)	5.1	628(31)	566
7	[(Me ₅ Cp) ₂ ThMe] ⁺ [B(C ₆ F ₅) ₄] ⁻	0.8	5.3(1)	5.5	628(31)	682
8	[(Me ₂ SiCp ₂)ZrMe] ⁺ [MeB(C ₆ F ₅) ₃] ^{-c}	2.8	4.8(1)	5.0	469(23)	532
9	[Cp ₂ ZrMe] ⁺ [MeB(C ₆ F ₅) ₃] ⁻	2.5	4.7(1)	4.7	441(22)	448
	(<i>p</i> -tolyl) ₄ Si	0.1	4.4(1)	4.4	359(18)	352

^a All measurements performed with 1 mM (*p*-tolyl)₄Si internal diffusion standard. ^b See Supporting Information for derivation of uncertainties. ^c Radius and volume estimated from the analogous [μ -(CH₂CH₂)Cp₂ZrMe]⁺[MeB(C₆F₅)₃]⁻ crystal structure (ref 15f).

sequence⁸ and (*p*-tolyl)₄Si as an internal diffusion calibrant¹⁴ (it exhibits a sharp ¹H singlet and obeys the Stokes–Einstein relationship well).¹³ Measured hydrodynamic radii (eq 1; pragmatically assuming a spherical shape) for six typical ion-pairs are summarized in Table 2, and compared to van der Waals radii and volumes computed from crystallographic diffraction data.^{1f,12,15} The results are depicted graphically in Figure 1 where it can be seen that there is good agreement between solution experimental data and those estimated for unaggregated 1:1 cation–anion pairs. Interestingly, the thermally stable, crystallographically characterized B(C₆F₅)₄⁻ derivative, **7**,¹² is not aggregated, although it would be premature to assume that this behavior extends to all B(C₆F₅)₄⁻-containing ion-pairs.

We show elsewhere that ¹H, ¹⁹F–HOESY measurements are also consistent with 1:1 ion-pairs in that close NOE interactions are only observed between MeB(C₆F₅)₃⁻ methyl protons or *o*-fluorines and the metallocenium cation.¹⁶ In an aggregate, anion aryl *p*- and *m*-fluorine–metallocenium cation NOE interactions are also expected.

In summary, the present results, employing two complementary solution-phase physicochemical techniques and a representative series of stable, well-characterized, single-site metallocenium ion-pair polymerization catalysts, provide no evidence of significant aggregation at concentrations in the ~1–18 millimolar regime. While it is conceivable that metallocene ion-pair aggregates may be important at yet higher concentrations, in other solvents, with other ligands or anions, or as fleeting intermediates/transition states, their relevance to actual olefin enchainment and propagation processes seems unlikely.

Acknowledgment. This research was supported by the U.S. Department of Energy (DE-FG 02-86 ER13511). C.Z. thanks the Italian CNR for a postdoctoral research fellowship. We thank Mr. B. Stubbart for a sample of complex **7** and Mr. J. Roberts for help with the X-ray structure data.

Supporting Information Available: Details of ion-pair synthesis, cryoscopic and PGSE measurement details (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0346375