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Self-Aggregation Tendency of Zirconocenium Ion Pairs Which Model Polymer-Chain-Carrying Species in Aromatic and Aliphatic Solvents with Low Polarity

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Olefin polymerizations catalyzed by cationic Group IV metallocenes[1] are usually carried out in solvents with very low polarity such as toluene, benzene, hexanes and isoparaffins. It is now generally accepted that the counteranion plays a fundamental role in the catalytic process,[2–4] and, consequently, it is not possible to exclude the ion pair in its entirety from consideration. On the contrary, there is still an unresolved controversy whether aggregates higher than ion pairs, particularly ion quadruples, can be formed in appreciable amounts under catalytic conditions[5] and take part in the process.[6]

In 1999, Beck, Geyer and Brintzinger reported the first diffusion NMR evidence for the formation of ion quadruples from zirconocenium ion pairs in [D$_6$]benzene at millimolar levels.[5a] Successively, in collaboration with Marks and coworkers, we showed[5c] that ion pairs bearing weakly coordinating anions [$\mathrm{MeB(C_6F_5)_3}^-$] in the first coordination sphere, that is, ISIPs (Inner Sphere Ion Pairs),[2c] do not exhibit any tendency to associate. In ion pairs with more weakly coordinating anions [such as $\mathrm{B(C_6F_5)_4}^-$], the counterion usually resides in the second coordination sphere leading to OSIPs (Outer Sphere Ion Pairs)[2c] that have a marked tendency to self-aggregate. Despite this, OSIPs also generate a negligible percentage of ion quadruples at catalytic concentration values ($<10^{-4}$ M) in [D$_6$]benzene.[5c–d]

One aspect that seems to be a general characteristic is the direct correlation between the charge separation and the tendency of ion pairs to form ion quadruples is that the higher the charge separation in the ion pairs, the higher their tendency is to form ion quadruples.[7,8] As a consequence, the ongoing search for large counteranions with a dispersed charge, which are less and less coordinating,[9] on the one hand, reduces the possibility that the anion competes with the substrate for the coordination at the metal, while, on the other hand, it increases the charge separation and the possibility of forming ion quadruples. Clearly, also an enhanced dimension of the cation may contribute to reduce the ion-pair strength thereby increasing the charge separation and the tendency to form ion quadruples.

During the polymerization process, a rapid growth of the polymer chain occurs that necessarily unwinds in the proximity of the catalytic site. This could lead to the removal of the counterion, an enlarged charge separation and a higher tendency to form ion quadruples. An increase of the dipole moment as a function of the isotactic propylene chain length in a silicon-bridged zirconocene ion pairs was predicted by Klesing and Bettonville through DFT calculations.[10]

With the aim of obtaining information about the position of the counterion during the growth of the polymer chain and the tendency of ion pairs bearing a polymer chain to self-aggregate, we decided to synthesize model zirconocenium ion pairs with alkylic chains of variable length and investigate them through advanced NMR techniques. The presence of long chains made zirconocenium ion pairs soluble in aliphatic solvents with relative permittivity (ε_r) values lower than benzene. This provided the unique possibility to explore their self-aggregation tendency in a reaction medium that is closer to that used in industrial plants (normally isoparaffins).

The introduction of a suitable aliphatic chain in zirconium ion pairs was achieved by the reaction of the ISIP [$\mathrm{Cp_2Zr^{\delta+}Me{\cdots}MeB^{\delta-}(C_6F_5)_3}$] (**1**) with tertiary amines (Scheme 1). Initially, the amine displaces the counteranion from the first coordination sphere, forming the transient species **I** that spontaneously transforms into **2**–**4** ISIPs (Supporting Information) through methane evolution (Scheme 1).[11] From the reactions of the ISIPs **2**–**4** with THF, OSIPs **5**–**7** were obtained, which contain the alkyl chains R^1 and R^2 that mime

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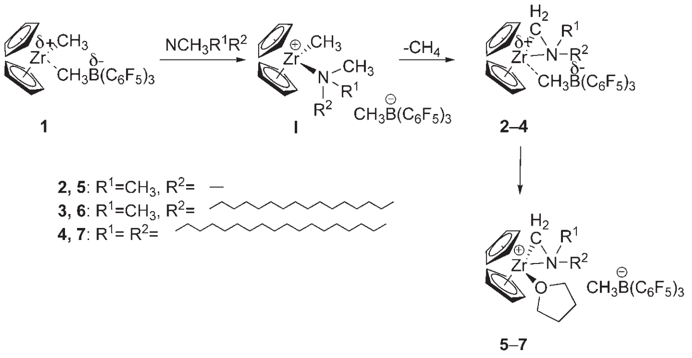

Scheme 1. Syntheses of ISIPs **2**–**4** and OSIPs **5**–**7**.

the polymer chain growing at the metal site (Supporting Information).

In ISIPs **2**–**4** and OSIPs **5**–**7** the N-functionality is oriented inside toward $MeB(C_6F_5)_3^-$ or THF,[11] respectively, as indicated by ^{1}H-NOESY and ^{19}F,^{1}H-HOESY NMR spectra (Supporting Information). The latter allow the relative cation/counterion orientation within ion pairs to be determined.[12] The ^{19}F,^{1}H-HOESY spectrum recorded for compound **6** in [D$_6$]benzene is illustrated as an example in Figure 1.

In addition to a strong intramolecular NOE interaction between B-Me and *o*-F nuclei, NOE interionic interactions between *o*-F, *m*-F and, in some cases, *p*-F nuclei and Cp (with higher intensity with the Cp^u moiety where N-Me points), THF and N-Me protons are observed. The central protons of the aliphatic chain overlap with the β protons of THF. A quantification of the NOE contacts indicates that they only interact weakly with the *o*-F and *m*-F nuclei of the counterion. These observations and the absence of NOE between the anion and the protons of the cyclometalated carbon suggest that the counterion is located between the Cps and THF as shown in Figure 1. It is import to note that the same relative anion–cation orientation is observed for all OSIPs **5**–**7** independent of the aliphatic chain length.

The self-aggregation tendency of ISIPs **2**–**4** and OSIPs **5**–**7** was investigated by means of PGSE (pulsed field gradient spin-echo) diffusion NMR spectroscopy.[13] PGSE NMR allows the translational self-diffusion coefficient (D_t) to be determined; the latter is related to the hydrodynamic radius (r_H) of the diffusing particle through the Stokes–Einstein equation.[14] In order to obtain accurate hydrodynamic dimensions of the diffusing species, the D_t data were treated as described in our recent paper.[14] The hydrodynamic volume (V_H) of the aggregates was determined by r_H assuming that they had a spherical shape. Finally, the aggregation number (N), defined as the ratio of the experimental hydrodynamic volume of cation or anion and the hydrodynamic volume of the ion pair (V_H), was derived. V_H^{IP0} for **2**–**4** was assumed to be equal to V_H extrapolated at infinite dilution. For **5**–**7** V_H^{IP0} was evaluated by adding the measured V_H of free THF to the V_H^{IP0} of the parent ISIP (Supporting Information).

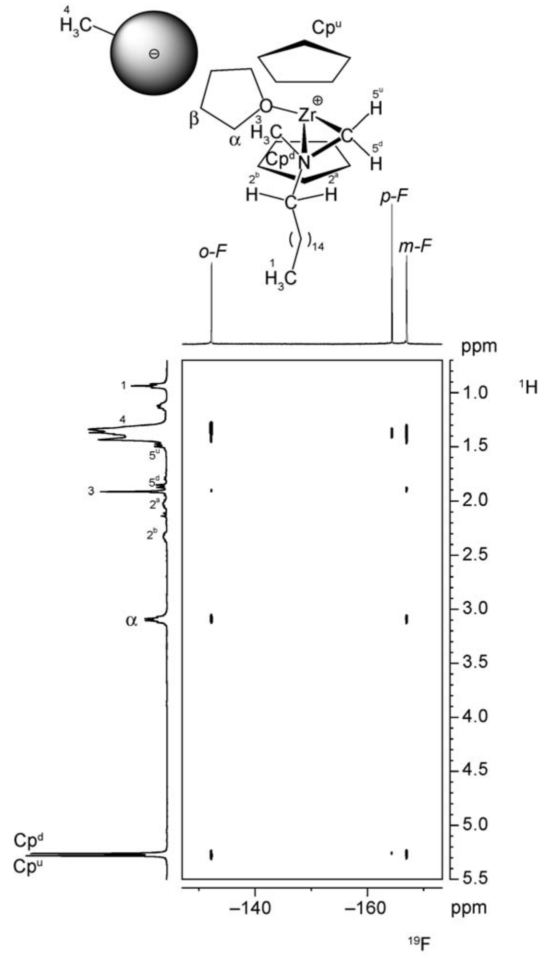

Figure 1. ^{19}F,^{1}H-HOESY NMR spectrum of OSIP **6** recorded in [D$_6$]benzene at 298 K.

Diffusional and hydrodynamic data are reported in Table 1. The graphical trends of N versus the concentration (c) in [D$_6$]benzene are shown in Figure 2. The value of N deviates very little from 1 for **2**–**4** over the entire concentration range, consequently, the latter are mainly present as single ion pairs. On the contrary, N increases rapidly as the concentration of the **5**–**7** increases; nevertheless, the trends of N do not substantially depend on the aliphatic chain length. OSIPs with longer chains are more soluble and exhibit the highest N values at elevated concentrations (Figure 2) but a single N versus c "master" trend describes their self-aggregation tendency. Importantly, the value of N approaches 1 for all OSIPs at low concentration values (ca. 10^{-5} M) (Table 1); this indicates that the presence of ion quadruples is negligible.[5c–d]

A coherent picture is derived from the NOE and PGSE measurements in [D$_6$]benzene: since the position of the counterion, particularly its distance from the metal site, is affected little by the chain length, OSIPs roughly have the same dipolar moment and, consequently, the same self-aggregation tendency.

Table 1. Diffusion coefficient (D_t in $10^{-10}\,m^2s^{-1}$), hydrodynamic radius (r_H in Å), hydrodynamic volume (V_H in Å^3) and aggregation number (N) at various concentrations (c in 10^{-3}M) for ISIPs and OSIPs in [D$_6$]benzene ($\varepsilon_r=2.28$) and [D$_{12}$]cyclohexane ($\varepsilon_r=2.04$).

Compound	c	D	r_H	V_H	N
[D$_6$]benzene					
2	0.9	6.31	5.82	825	1.0
$V_H^{IP0}=829$ Å^3	2.7	6.14	5.88	851	1.0
	6.4	6.08	5.91	864	1.0
	13.6	5.76	6.20	998	1.2
3	0.6	5.27	6.75	1290	1.0
$V_H^{IP0}=1284$ Å^3	2.7	5.15	6.95	1410	1.1
	7.4	5.07	6.92	1390	1.1
	13.4	4.85	7.18	1550	1.2
4	0.6	4.40	7.94	2100	1.0
$V_H^{IP0}=2088$ Å^3	1.1	4.37	7.94	2100	1.0
	2.6	4.26	7.98	2130	1.0
	25.0	3.82	8.39	2470	1.2
5	0.1	5.91	6.06	932	1.0
$V_H^{IP0}=899$ Å^3	0.2	5.76	6.18	988	1.1
	0.4	5.15	6.78	1300	1.5
	1.0[a]	4.81	7.23	1580	1.8
6	0.1	4.72	7.34	1660	1.2
$V_H^{IP0}=1354$ Å^3	0.3	4.26	7.81	1990	1.4
	0.6	4.29	8.04	2180	1.6
	1.6	3.82	8.90	2950	2.2
	1.8	3.79	8.95	3000	2.2
	3.9	3.39	9.89	4050	3.0
	6.2	3.07	10.7	5190	3.8
	8.5[a]	2.82	11.6	6570	4.9
7	0.1	4.14	8.28	2380	1.1
$V_H^{IP0}=2158$ Å^3	0.5	3.76	8.91	2960	1.4
	1.1	3.45	9.73	3860	1.8
	3.0	3.01	10.9	5420	2.5
	6.6	2.69	12.3	7795	3.6
	7.1	2.55	12.5	8160	3.8
	11.7	2.26	14.0	11600	5.4
[D$_{12}$]cyclohexane					
6	0.04[a]	0.27	8.82	2870	2.1
7	0.05	0.21	11.2	5910	2.7
	0.90	0.15	15.4	15400	7.1
	1.60	0.13	18.2	25200	11.7
	2.47	0.12	19.8	32700	15.2
	4.75	0.10	22.8	49800	23.1
	11.8	0.08	28.3	94700	43.9
	19.0	0.07	32.3	141000	63.3
	23.2	0.06	33.8	162000	75.0

[a] Saturated solution.

The enhanced solubility of OSIPs with long chains prompted us to explore their self-aggregation tendency in solvents with ε_r values lower than that of benzene. This aspect is important since in industrial plants olefin polymerizations are often carried out in isoparaffins having an ε_r close to 2,[15] which is slightly lower than that of [D$_6$]benzene ($\varepsilon_r=2.24$). OSIP **7** bearing two aliphatic C_{18} chains was soluble enough in [D$_{12}$]cyclohexane ($\varepsilon_r=2.04$, practically identical to that of several isoparaffins)[15] to allow a PGSE study as a function of the concentration. Diffusional and hydrodynamic data are reported in Table 1. OSIP **7** exhibits a self-aggregation tendency that is enormously higher in [D$_{12}$]cyclohexane than in [D$_6$]benzene (Figure 3). While for a 1.1 mM solution of **7** in [D$_6$]benzene N is equal to 1.8, at almost the same concentration (1.6 mM) in [D$_{12}$]cyclohexane, N amounts to 11.7. At the highest concentration in [D$_{12}$]cyclohexane, aggregates containing an average of 75 ion pairs are present while, at the lowest concentration (0.05 mM), N is 2.7 (Table 1); thus, ion quadruples and even higher aggregates are surely present. Although **6** was not soluble enough in [D$_{12}$]cyclohexane to allow a complete PGSE study as a function of the concentration, its saturated solution (0.04 mM) was measured. The N value (2.1, Table 1) fits perfectly in the N versus c trend of **7** indicating that the chain length also does not affect the self-aggregation tendency of OSIPs in [D$_{12}$]cyclohexane.

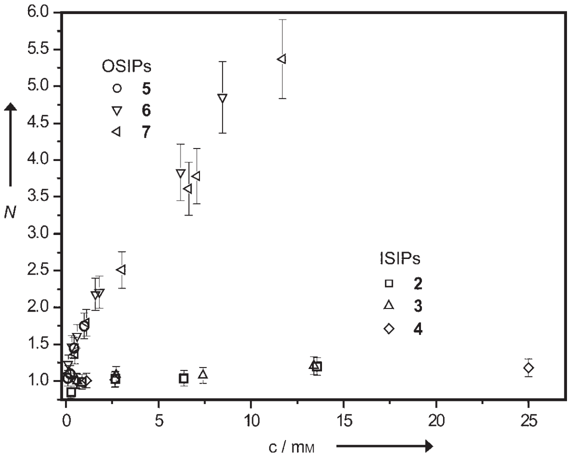

Figure 2. Trends of the aggregation number (N) as a function of the concentration (c) in [D$_6$]benzene showing the markedly different self-aggregating behavior of ISIPs and OSIPs.

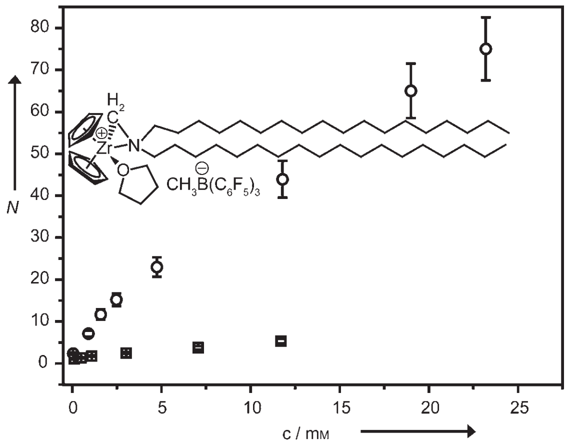

Figure 3. Trends of the aggregation number (N) as a function of the concentration (c) for OSIP **7** showing its markedly different tendency to self-aggregate in [D$_6$]benzene (□) and [D$_{12}$]cyclohexane (○).

The standard free energy (ΔG^0) for the self-aggregation process of ion pairs was estimated by elaborating the N versus c data according to the isodesmic model of indefinite association called Equal K (EK, K=equilibrium constant).[16] Plotting $N(N-1)$ versus c generates a linear trend the slope of which is equal to K (Supporting Information).[14,17] The K and ΔG^0 values for the self-aggregation process of **5**–**7** OSIPs in [D_6]benzene and **7** in [D_{12}]cyclohexane are reported in Table 2. In agreement with the above qualitative considerations, K and ΔG^0 for **5**–**7** in [D_6]benzene are the same within the experimental error (Table 2). In contrast, there is a considerable increase of K and $|\Delta G^0|$ for **7** OSIP on passing from [D_6]benzene to [D_{12}]cyclohexane (Table 2). It can be estimated that with a $K = 1.11 \times 10^5\,\text{M}^{-1}$ there is a notable concentration of ion quadruples and higher aggregates (up to 40%) even at concentrations between 10^{-5} and $10^{-6}\,\text{M}$.

Table 2. Thermodynamic parameters for the self-aggregation of **5**–**7** in [D_6]benzene and **7** in [D_{12}]cyclohexane.

Compound	K [M^{-1}]	ΔG^0 [kJ mol^{-1}]
[D_6]benzene		
5	1482 ± 200	−18.09 ± 0.30
6	1492 ± 30	−18.10 ± 0.05
7	1479 ± 42	−18.08 ± 0.07
[D_{12}]cyclohexane		
7	111200 ± 8500	−28.79 ± 0.20

In conclusion, we have shown that the presence of an aliphatic chain of variable length, that mimics the growth of a polymer chain, does not alter the intrinsic tendency of a zirconocenium ion pair to self-aggregate. This is substantially due to the fact that anion position is not affected by the length of the chain. The presence of the aliphatic chain allowed an unprecedented investigation of the tendency of zirconocenium ion pairs to self-aggregate in cyclohexane having an ε_r value less than benzene and similar to those of isoparaffins used in industrial plants. Although the variation of ε_r is marginal, the results of the PGSE measurements indicate that the tendency to self-aggregate results enhanced enormously to the point that the percentage of ion quadruples is noticeable even at the concentration level used in the olefin polymerizations. Hence, ion quadruples are thermodynamically accessible species in aliphatic solvents with low polarity; further studies will have to be conducted in order to establish their kinetic relevance.

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