Supporting Information for Comparison of PGSE NMR and ESI-MS Measurements on Methylaluminoxane

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Table S-1 Energies (a.u.) of Aluminoxane Structures at M06-2X/TZVP Level in Gas Phase at 298.15 K

Structure[a]	E	H	H-qh[b]	TS	TS-qh[b]
8,4 tube (minimum)	-4310.519479	-4309.672842	-4309.683715	0.167432	0.161239
8,4 4-coordinate (4-C) sheet	-4310.501147	-4309.655035	-4309.668384	0.177468	0.166466
8,4 5-C sheet	-4310.507978	-4309.662171	-4309.675058	0.174864	0.165447
8,4 cage	-4310.510188	-4309.662249	-4309.672536	0.164480	0.158620
12,5 4-C sheet (minimum)	-6103.636485	-6102.483864	-6102.499551	0.223473	0.212524
12,5 cage	-6103.639281	-6102.484586	-6102.498500	0.215628	0.204449
16,4 cage (minimum)	-7172.428805	-7171.206203	-7171.221971	0.236063	0.223733
16,4 chiral 3,1 tube	-7172.421734	-7171.200061	-7171.215038	0.231075	0.221863
16,4 armchair 2,2 tube	-7172.407751	-7171.183874	-7171.199386	0.231114	0.220697
16,4 zigzag 4,0 tube	-7172.393121	-7171.174640	-7171.189847	0.230776	0.223506
16,6 4-C sheet (minimum)	-7896.765367	-7895.307476	-7895.328801	0.281349	0.263429
16,6 cage	-7896.768968	-7895.307820	-7895.325950	0.264867	0.251867
23,7 cage (minimum)	-10763.114990	-10761.207472	-10761.231037	0.338757	0.324307
23,7 4-C sheet	-10763.094507	-10761.189946	-10761.217916	0.357717	0.336484

a. See Table S-1.xyz for coordinates of unreported structures in Figure 4. b. Enthalpy and entropy corrected for low energy vibrations using a quasi-harmonic approximation see a) R. F. Ribeiro, A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2011**, *115*, 14556–14562; b) Y.-P. Li, J. Gomes, S. M. Sharada, A. T. Bell, M. Head-Gordon, *J. Phys. Chem. C*, **2015**, *119*, 1840−1850.

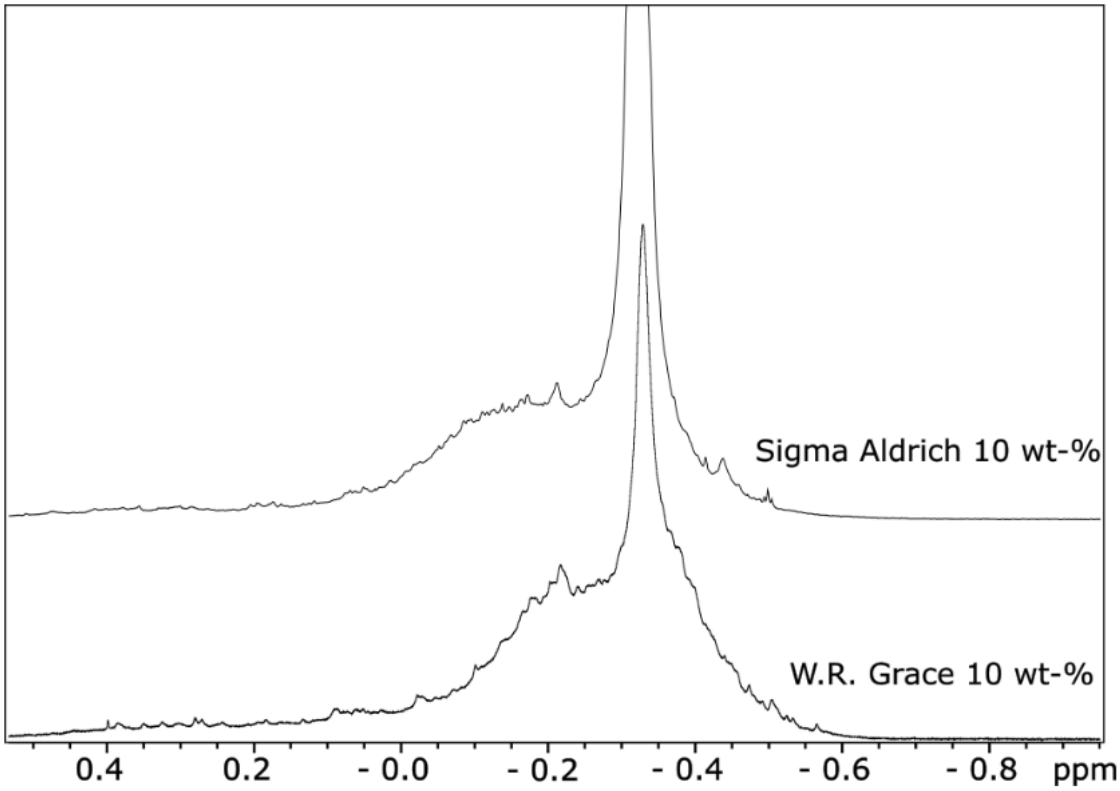


Figure S-1 – ^{1}H NMR spectra of W. R. Grace and Sigma Aldrich MAO showing the different Me_3Al contents (sharp signal at ca. -0.32 ppm).

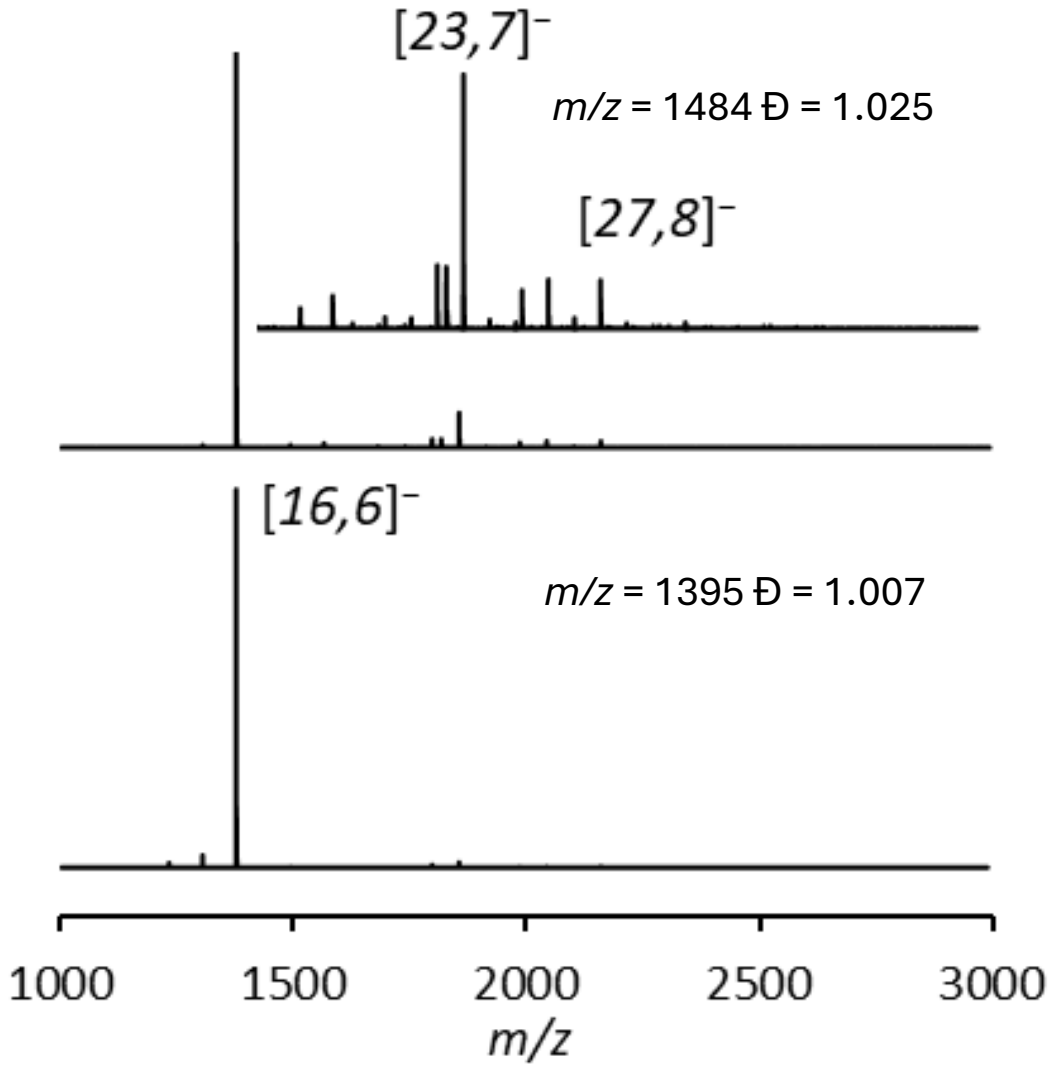


Figure S-2 – Negative ion-mass spectra of 10 wt% MAO and Cp_2ZrMe_2 in PhF with [Al] = 0.05 M. Top: Al:Zr = 1000:1. Bottom: Al:Zr = 100:1 with average *m/z* ratio and polydispersity (Đ) calculated from the raw MS data files. Inset is a vertical expansion to show weaker higher *m/z* anions.

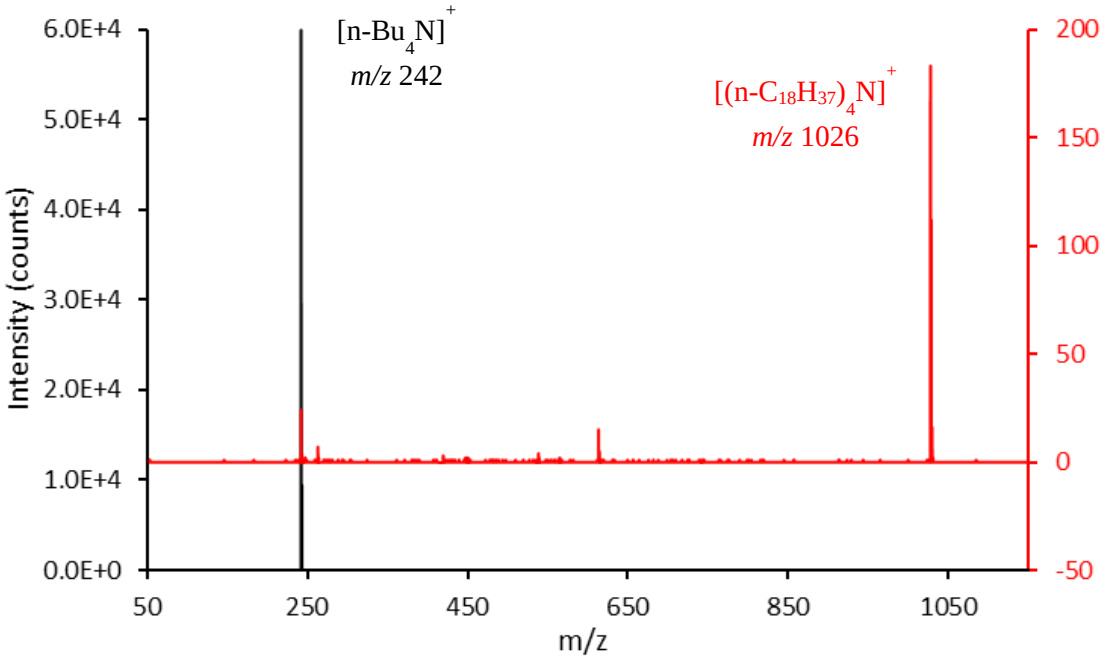


Figure S-3 – Positive ion mass spectra of $[nBu_4N][B(C_6F_5)_4]$ (0.19 mM in PhF, black spectrum and vertical axis) and $[(n\text{-}C_{18}H_{37})_4N][B(C_6F_5)_4]$ (0.10 M in PhF, red spectrum and vertical axis). Note that $[nBu_4N]^+$ is present as an impurity ion in the red spectrum.

From the number of counts for the two spectra (which were both averaged over the same number of data points) the sensitivity is very different - ca. 150:1 in favour of $[nBu_4N]^+$ (*m/z* 242) vs. $[(n\text{-}C_{18}H_{37})_4N]^+$ (*m/z* 1026) after correction for the difference in concentration.

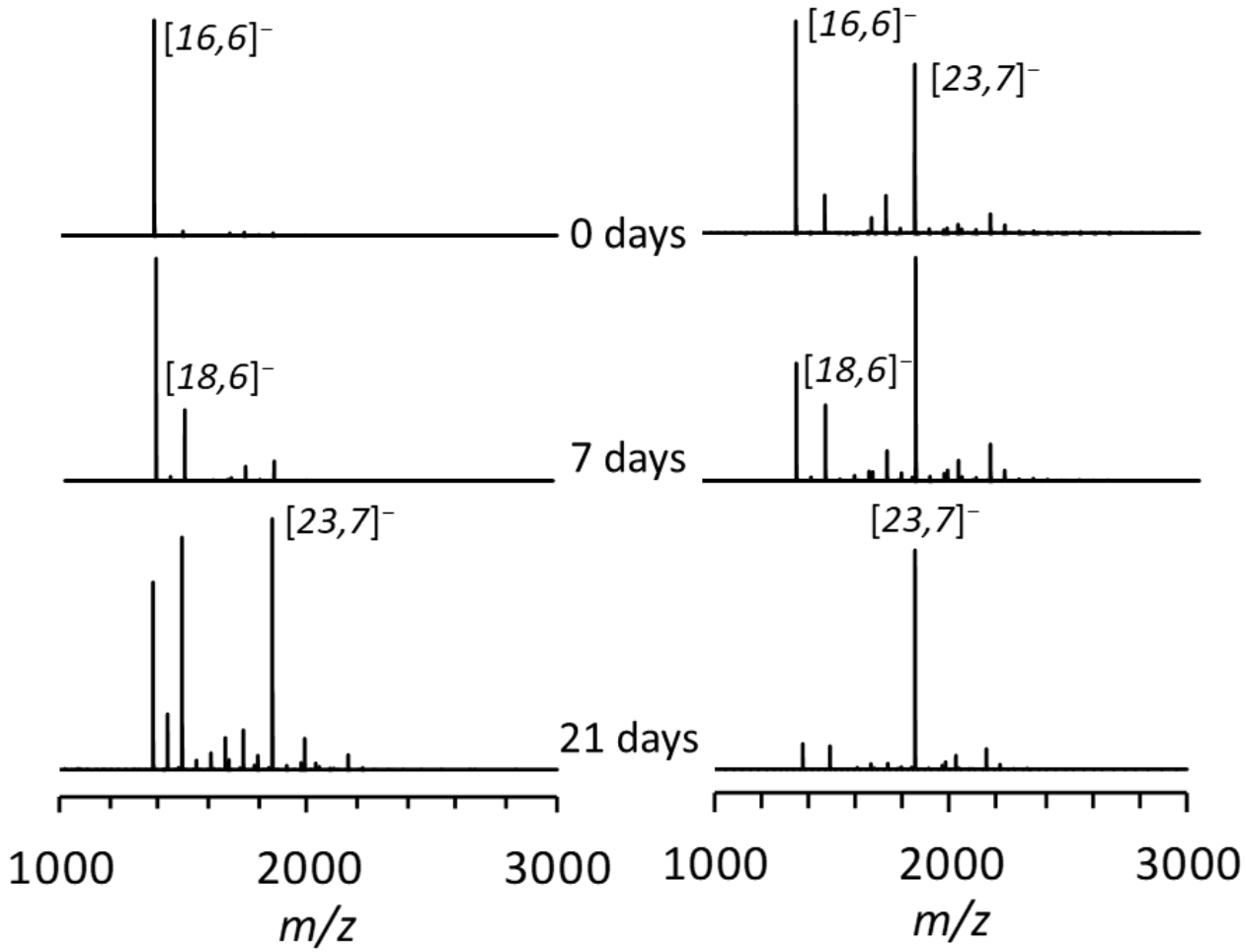


Figure S-4. Negative ion ESI-MS spectra of a commercial (left) and proprietary (right) 30 wt% MAO formulations as a function of storage time at room temperature. Samples were prepared by adding 2.0 mol% OMTS after the indicated time at room temperature and diluting with PhF prior to analysis.

Table S-2 Analysis of MAO Samples by ^{1}H NMR Spectroscopy[a]

Sample		30 wt% Proprietary			30 wt% Commercial		
		Component			Component		
t (days)	Amount	MAO	Me_3Al-THF	$[Me_2Al(THF)_2]^+$	MAO	Me_3Al-THF	$[Me_2Al(THF)_2]^+$
0	mol% Al	87.1	11.1	1.86	85.2	13.4	1.44
	wt%	25.7	4.05[b]	0.54[b]	25.3	4.92[b]	0.42[b]
0[c]	mol% Al	86.5	11.4	2.09	84.8	13.8	1.40
	wt%	25.5	4.16	0.60	25.1	5.08	0.41
7	mol% Al	88.7	9.44	1.86	86.9	11.5	1.59
	wt%	25.7	3.40	0.53	27.4	4.50	0.49
14	mol% Al	89.4	8.61	2.01	86.9	11.4	1.74
	wt%	29.4	3.52	0.65	26.6	4.33	0.52
21	mol% Al	90.3	7.92	1.81	87.5	11.1	1.47
	wt%	30.5	3.32	0.60	28.3	4.45	0.47

a. Samples were prepared by adding 0.25 mL of MAO solution to 1.0 mL THF-d_8 with stirring in a vial at room temperature after storage of the MAO solution for the indicated time at room temperature in a sealed vial. After one hour, the sample was analyzed by ^{1}H NMR spectroscopy (30° pulse width, 5 sec relaxation delay, 64 transients) integrating the signals due to toluene, MAO, Me_3Al-THF and $[Me_2Al(THF)_2]^+$ before and after manual baseline subtraction. For details see ref. 21. The estimated error in integration is ±10% but is larger for the weak signal due to $[Me_2Al(THF)_2]^+$ which overlaps completely with the broad resonance due to MAO. For representative spectra see Figure S-5. b. Expressed as wt% Me_3Al. c. Same sample but baseline was corrected using a cubic spline polynomial for comparison purposes.

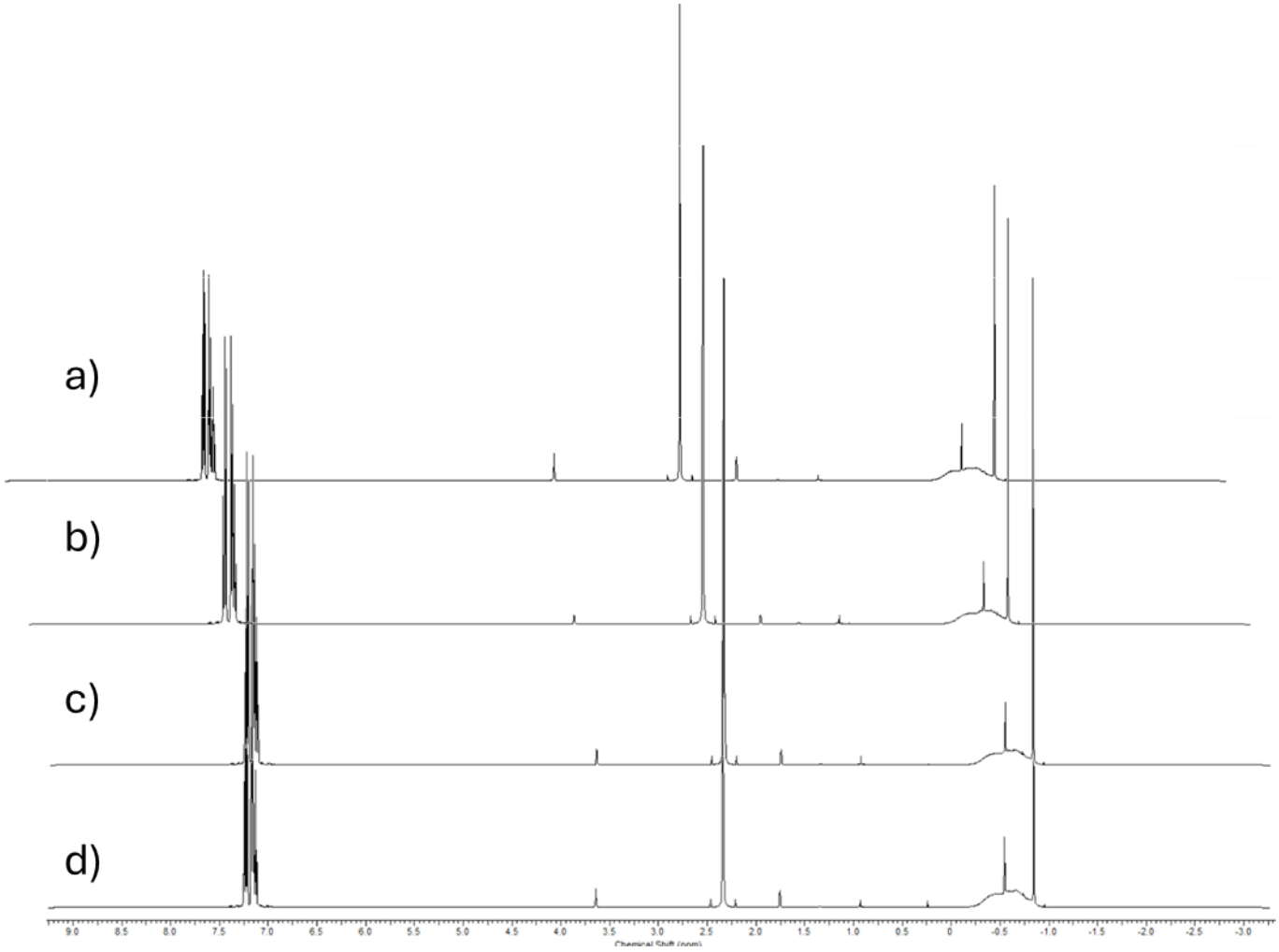


Figure S-5 – a) to c) ^{1}H NMR spectra 30 wt% commercial MAO in toluene at three-, two- and one-weeks storage at room temperature after dilution with 1.0 mLTHF-d_8.

The spectra are plotted such that the broad envelope due to MAO has the same intensity while the Me signal due to toluene is off scale in all spectra. From the relative intensity of the Me_3Al and toluene aromatic signals, both materials have evaporated over this time, at least with respect to non-volatile material. The vapor pressure of these two volatile materials at 20 °C are 12 and 28 mmHg, respectively. Sample d) is the same sample as c) but stored for over a week at -30 °C in the glove-box freezer. Since any water in the glove-box atmosphere would condense under such conditions, the formation of methane is expected and observed (singlet at ca. 0.25 ppm).

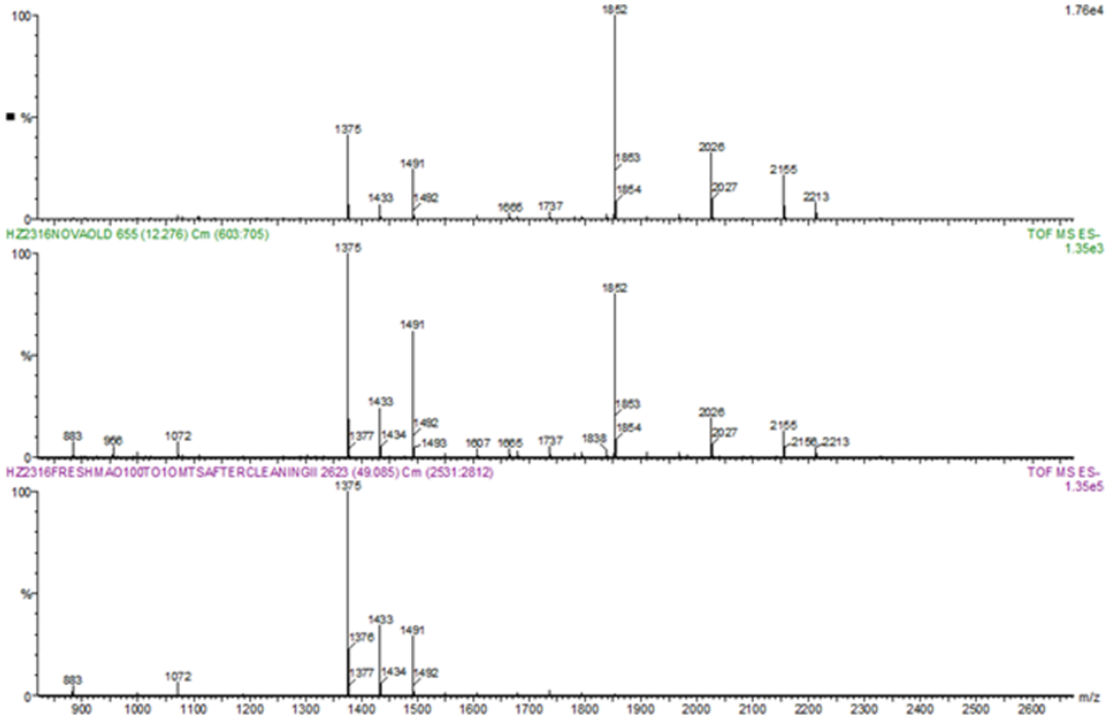


Figure S-6 Negative ion spectrum of a 10 wt% MAO sample from W. R. Grace (ca. 2.0 mol% OMTS[34]) directly from the freezer (bottom), the same spectrum after 6 weeks at room temperature (middle) and the sample aged for 6 months (top). Average *m/z* ratio ~ 1750 Da at six months.

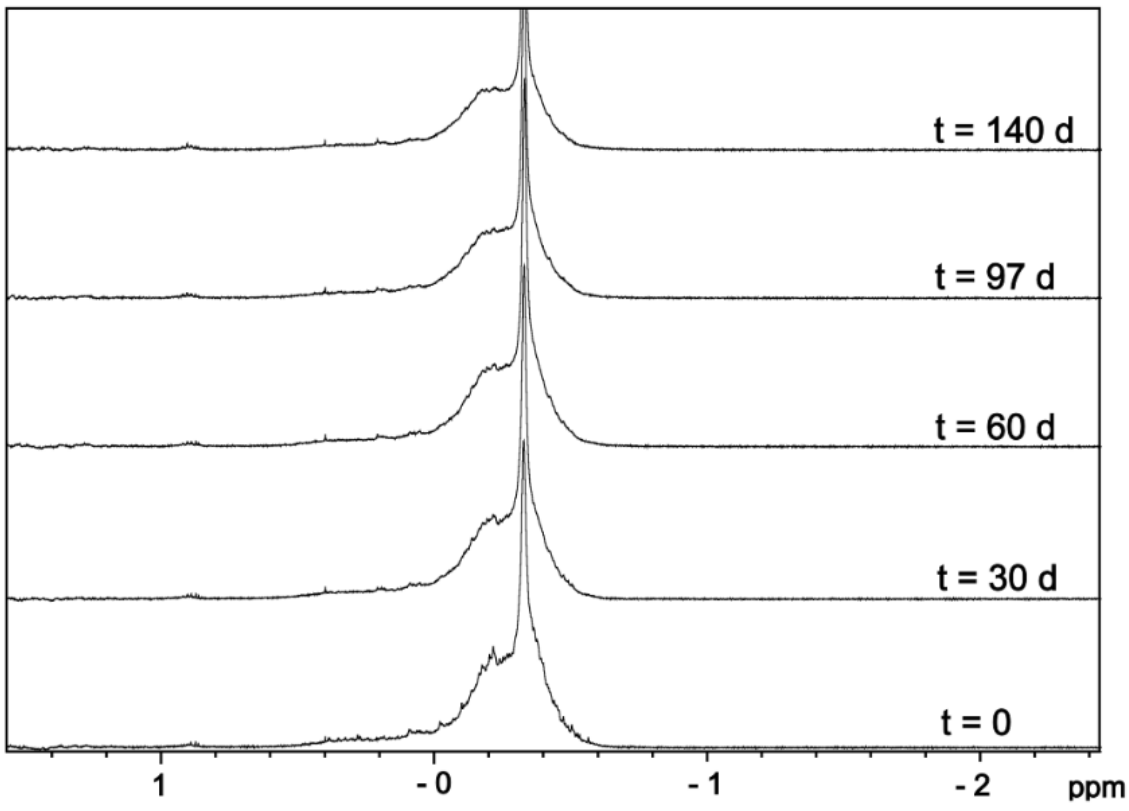
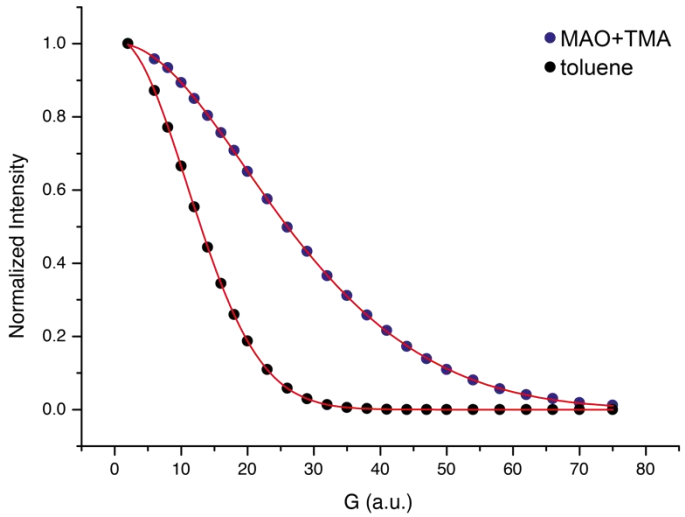


Figure S-7 – Evolution of the ^{1}H NMR spectrum of neat 10%wt MAO in toluene upon aging at RT for 140 days.

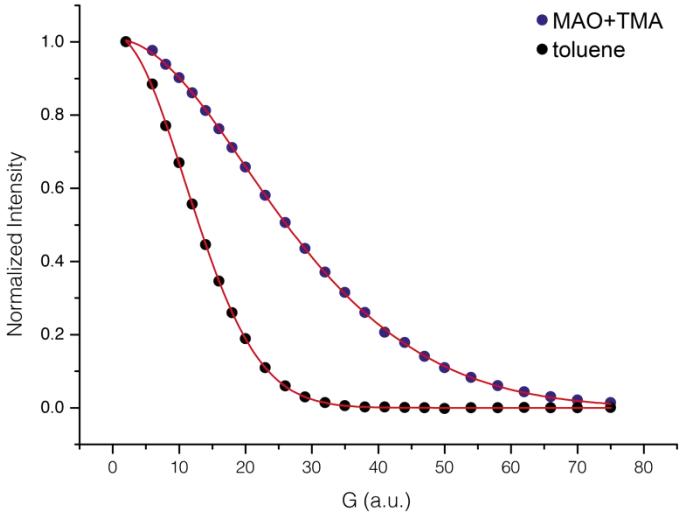
PGSE NMR Experimental Decay Data and Non-linear Regression/Error Analyses for all Samples



Equation	y = A01*exp(-m1*(x^2))		
Adj. R-Square	0,99999		
		Value	Standard Error
Toluene	A01	1,01499	6,25383E-4
Toluene	m1	0,00422	5,31113E-6

Equation	y = A01*exp(-m1*(x^2))+A02*exp(-m2*(x^2))		
Adj. R-Square	0,99996		
		Value	Standard Error
MAO	A01	0,75625	0,02135
TMA	A02	0,24585	0,02083
MAO	m1	7,66294E-4	1,22362E-5
TMA	m2	0,00236	1,42592E-4

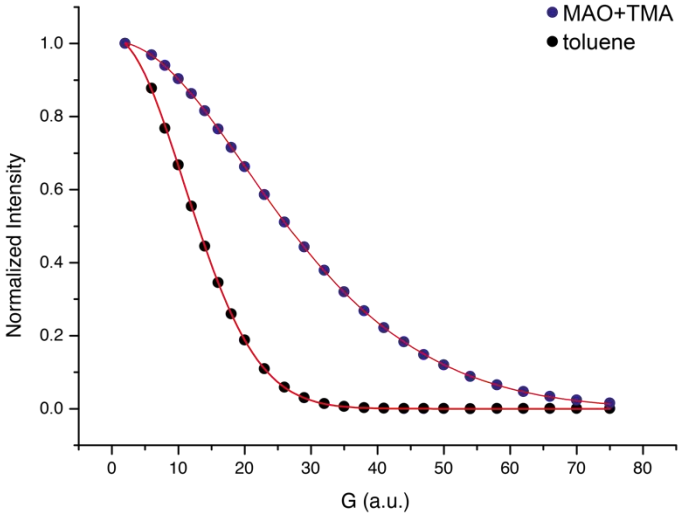
Figure S-8 – Normalized Intensity vs. G plot obtained by 1H PGSE NMR for a 10 wt% MAO solution diluted with toluene-d8 (C = 11.0 mM, 298K).



Equation	y = A01*exp(-m1*(x^2))		
Adj. R-Square	0,99993		
		Value	Standard Error
Toluene	A01	1,01968	0,00187
Toluene	m1	0,00422	1,57881E-5

Equation	y = A01*exp(-m1*(x^2))+A02*exp(-m2*(x^2))		
Adj. R-Square	0,99992		
		Value	Standard Error
TMA	A01	0,29724	0,03977
MAO	A02	0,71148	0,04054
TMA	m1	0,00206	1,73215E-4
MAO	m2	7,40896E-4	2,16824E-5

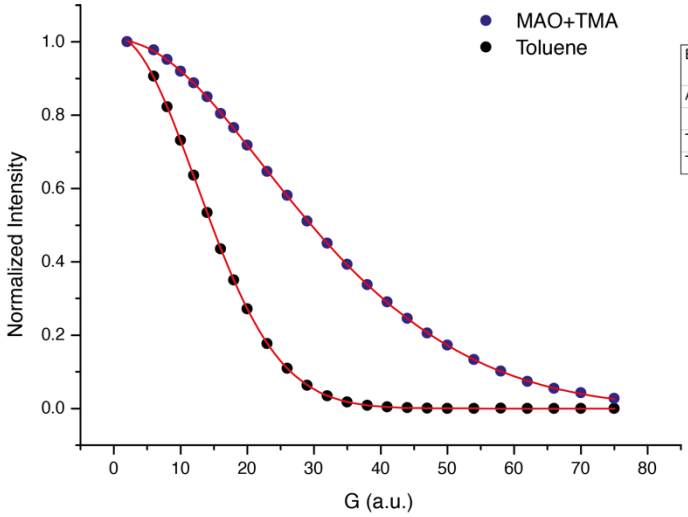
Figure S-9 – Normalized Intensity *vs.* G plot obtained by ^{1}H PGSE NMR for a 10 wt% MAO solution diluted with toluene-d_8 (C = 85.5 mM, 298K).



Equation	y = A01*exp(-m1*(x^2))		
Adj. R-Square	0,99996		
		Value	Standard Error
Toluene	A01	1,01634	0,00136
Toluene	m1	0,00422	1,15141E-5

Equation	y = A01*exp(-m1*(x^2))+A02*exp(-m2*(x^2))		
Adj. R-Square	0,99999		
		Value	Standard Error
TMA	A01	0,32164	0,01528
MAO	A02	0,68489	0,01557
TMA	m1	0,00196	5,86019E-5
MAO	m2	7,01797E-4	8,24751E-6

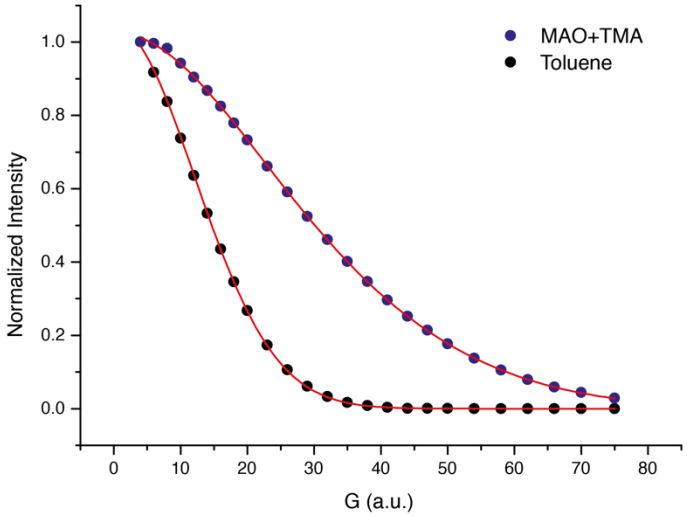
Figure S-10 – Normalized Intensity *vs.* G plot obtained by ^{1}H PGSE NMR for a 10 wt% MAO solution diluted with toluene-d_8 (C = 376.8 mM, 298K).



Equation	y = A01*exp(-m1*(x^2))		
Adj. R-Square	0,99998		
		Value	Standard Error
Toluene	A01	1,01685	9,55624E-4
Toluene	m1	0,0033	6,60016E-6

Equation	y = A01*exp(-m1*(x^2))+A02*exp(-m2*(x^2))		
Adj. R-Square	0,99997		
		Value	Standard Error
MAO	A01	0,76563	0,0184
TMA	A02	0,2407	0,01799
MAO	m1	6,02847E-4	8,15264E-6
TMA	m2	0,00182	9,36703E-5

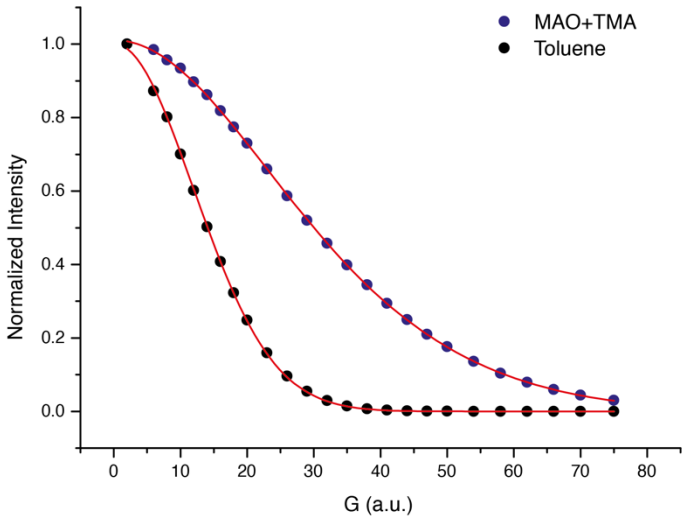
Figure S-11 – Normalized Intensity *vs.* G plot obtained by ^{1}H PGSE NMR for a 10 wt% MAO solution diluted with chlorobenzene-d_5 (C =31.2 mM, 298K).



Equation	y = A01*exp(-m1*(x^2))		
Adj. R-Square	0,99992		
		Value	Standard Error
Toluene	A01	1,04457	0,00213
Toluene	m1	0,00342	1,45822E-5

Equation	y = A01*exp(-m1*(x^2))+A02*exp(-m2*(x^2))		
Adj. R-Square	0,99988		
		Value	Standard Error
MAO	A01	0,74687	0,04536
TMA	A02	0,27947	0,04441
MAO	m1	5,84112E-4	1,91192E-5
TMA	m2	0,00169	1,75379E-4

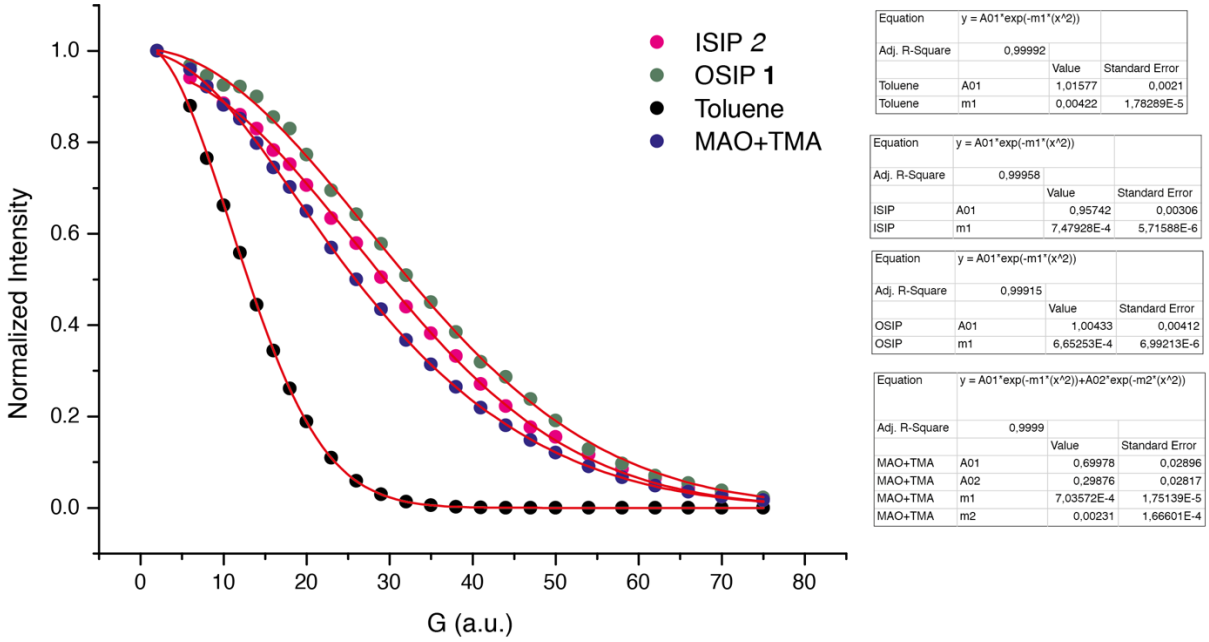
Figure S-12 – Normalized Intensity *vs.* G plot obtained by ^{1}H PGSE NMR for a 10 wt% MAO solution diluted with chlorobenzene-d_5 (C = 241.8 mM, 298K).



Equation	y = A01*exp(-m1*(x^2))		
Adj. R-Square	0,99987		
		Value	Standard Error
Toluene	A01	1,00197	0,0025
Toluene	m1	0,00351	1,84576E-5

Equation	y = A01*exp(-m1*(x^2))+A02*exp(-m2*(x^2))		
Adj. R-Square	0,99995		
		Value	Standard Error
TMA	A01	0,3458	0,0446
MAO	A02	0,66541	0,04519
TMA	m1	0,0014	9,7112E-5
MAO	m2	5,58066E-4	1,77085E-5

Figure S-13 – Normalized Intensity *vs.* G plot obtained by ^{1}H PGSE NMR for a 10 wt% MAO solution diluted with chlorobenzene-d_5 (C = 521.3 mM, 298K).



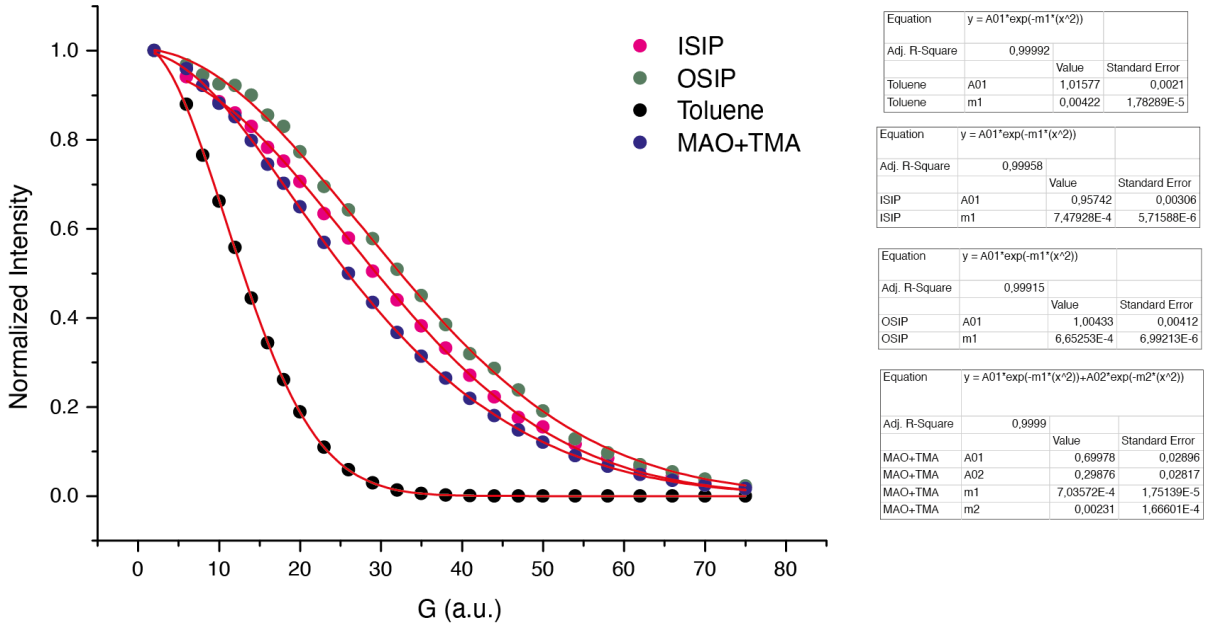
Equation	y = A01*exp(-m1*(x^2))		
Adj. R-Square	0,99992		
		Value	Standard Error
Toluene	A01	1,01577	0,0021
Toluene	m1	0,00422	1,78289E-5

Equation	y = A01*exp(-m1*(x^2))		
Adj. R-Square	0,99958		
		Value	Standard Error
ISIP	A01	0,95742	0,00306
ISIP	m1	7,47928E-4	5,71588E-6

Equation	y = A01*exp(-m1*(x^2))		
Adj. R-Square	0,99915		
		Value	Standard Error
OSIP	A01	1,00433	0,00412
OSIP	m1	6,65253E-4	6,99213E-6

Equation	y = A01*exp(-m1*(x^2))+A02*exp(-m2*(x^2))		
Adj. R-Square	0,9999		
		Value	Standard Error
MAO+TMA	A01	0,69978	0,02896
MAO+TMA	A02	0,29876	0,02817
MAO+TMA	m1	7,03572E-4	1,75139E-5
MAO+TMA	m2	0,00231	1,66601E-4

Figure S-14 – Normalized Intensity *vs.* G plot obtained by ^{1}H PGSE NMR for a solution obtained upon activating Cp_2ZrMe_2 with 100 equivalents (Zr:Al = 1:100) of 10 wt% MAO and diluted in toluene (C_{Zr} = 1.35 mM, 298K).



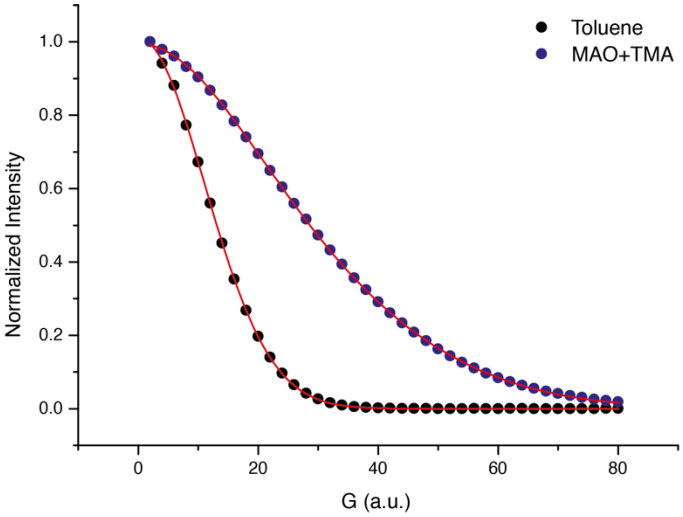
Equation	y = A01*exp(-m1*(x^2))		
Adj. R-Square	0,99992		
		Value	Standard Error
Toluene	A01	1,01577	0,0021
Toluene	m1	0,00422	1,78289E-5

Equation	y = A01*exp(-m1*(x^2))		
Adj. R-Square	0,99958		
		Value	Standard Error
ISIP	A01	0,95742	0,00306
ISIP	m1	7,47928E-4	5,71588E-6

Equation	y = A01*exp(-m1*(x^2))		
Adj. R-Square	0,99915		
		Value	Standard Error
OSIP	A01	1,00433	0,00412
OSIP	m1	6,65253E-4	6,99213E-6

Equation	y = A01*exp(-m1*(x^2))+A02*exp(-m2*(x^2))		
Adj. R-Square	0,9999		
		Value	Standard Error
MAO+TMA	A01	0,69978	0,02896
MAO+TMA	A02	0,29876	0,02817
MAO+TMA	m1	7,03572E-4	1,75139E-5
MAO+TMA	m2	0,00231	1,66601E-4

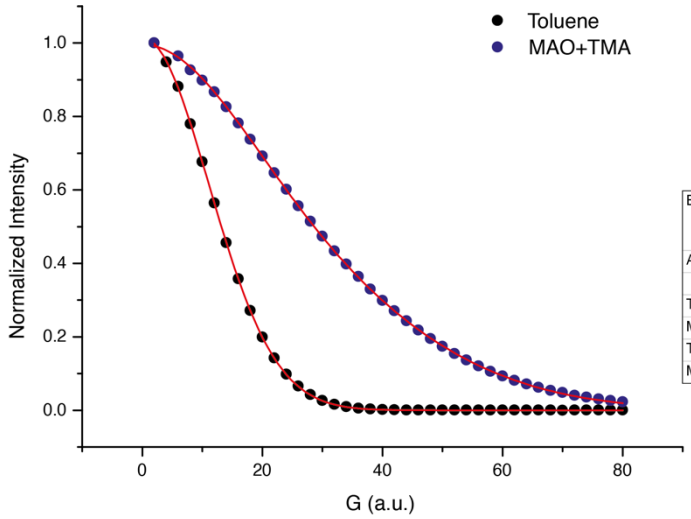
Figure S-15 – Normalized Intensity *vs.* G plot obtained by ^{1}H PGSE NMR for a solution obtained upon activating Cp_2ZrMe_2 with 100 equivalents of 10wt% MAO (Zr:Al = 1:100) and diluted in chlorobenzene-d_5 (C_{Zr} = 1.1 mM, 298K).



Equation	y = A01*exp(-m1*(x^2))		
Adj. R-Square	0,99995		
		Value	Standard Error
Toluene	A01	1,01217	0,0013
Toluene	m1	0,0041	1,15332E-5

Equation	y = A01*exp(-m1*(x^2))+A02*exp(-m2*(x^2))		
Adj. R-Square	0,99995		
		Value	Standard Error
MAO	A01	0,72212	0,01569
TMA	A02	0,2727	0,01528
MAO	m1	5,95672E-4	7,4136E-6
TMA	m2	0,00192	8,35915E-5

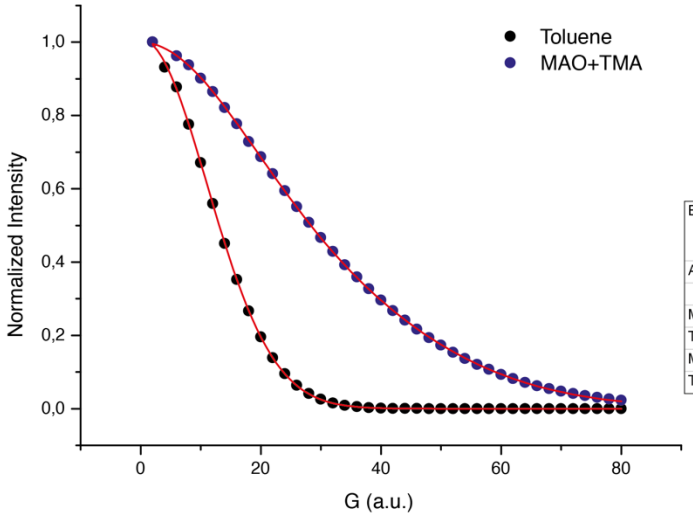
Figure S-16 – Normalized Intensity *vs.* G plot obtained by ^{1}H PGSE NMR for a fresh aliquot of neat 10%wt MAO in toluene.



Equation	y = A01*exp(-m1*(x^2))		
Adj. R-Square	0,99999		
		Value	Standard Error
Toluene	A01	1,01541	6,50042E-4
Toluene	m1	0,00407	5,72382E-6

Equation	y = A01*exp(-m1*(x^2))+A02*exp(-m2*(x^2))		
Adj. R-Square	0,99992		
		Value	Standard Error
TMA	A01	0,28755	0,0131
MAO	A02	0,70811	0,01364
TMA	m1	0,00206	8,66992E-5
MAO	m2	5,61435E-4	6,89818E-6

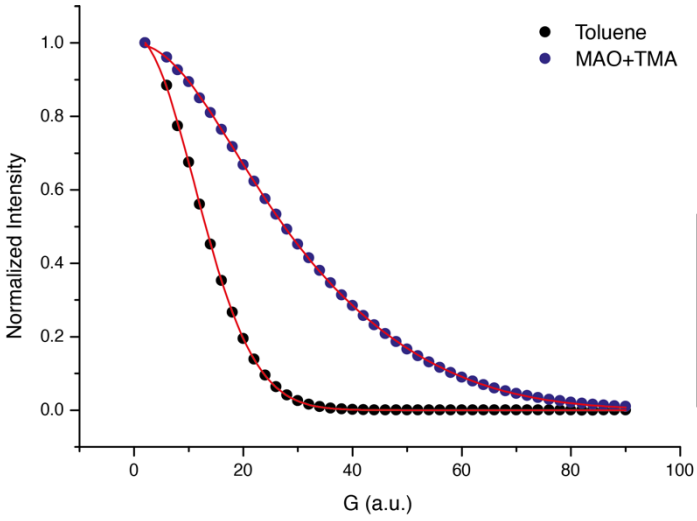
Figure S-17 – Normalized Intensity *vs.* G plot obtained by ^{1}H PGSE NMR for aged neat 10%wt MAO in toluene (t = 30 days).



Equation	y = A01*exp(-m1*(x^2))		
Adj. R-Square	0,99992		
		Value	Standard Error
Toluene	A01	1,00929	0,00164
Toluene	m1	0,0041	1,46684E-5

Equation	y = A01*exp(-m1*(x^2))+A02*exp(-m2*(x^2))		
Adj. R-Square	0,99996		
		Value	Standard Error
MAO	A01	0,69822	0,00869
TMA	A02	0,30151	0,00831
MAO	m1	5,57027E-4	4,61991E-6
TMA	m2	0,00216	5,86171E-5

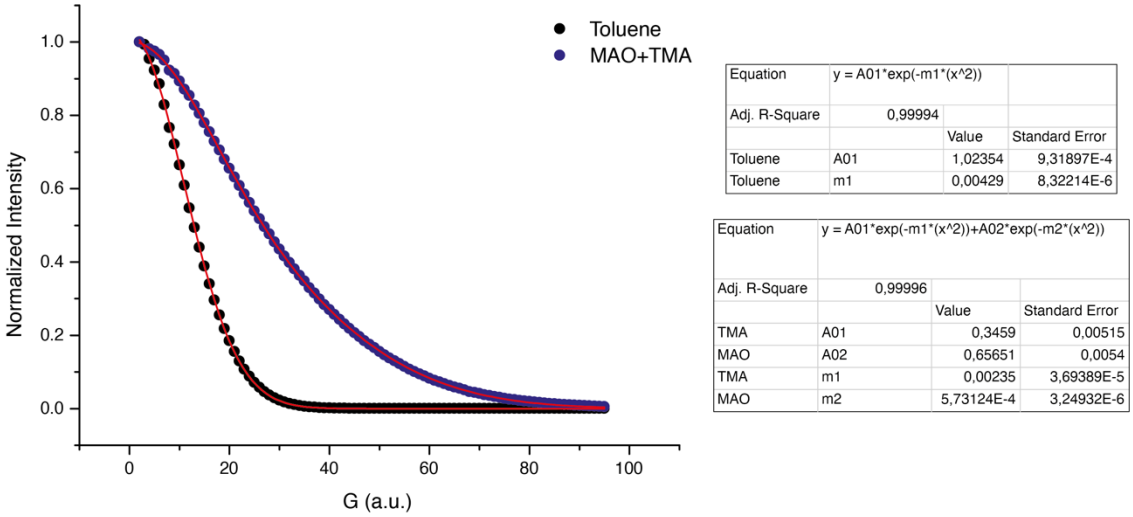
Figure S-18 – Normalized Intensity *vs.* G plot obtained by ^{1}H PGSE NMR for aged neat 10%wt MAO in toluene (t = 60 days).



Equation	y = A01*exp(-m1*(x^2))		
Adj. R-Square	0,99996		
		Value	Standard Error
Toluene	A01	1,01797	0,00116
Toluene	m1	0,00413	9,2808E-6

Equation	y = A01*exp(-m1*(x^2))+A02*exp(-m2*(x^2))		
Adj. R-Square	0,99994		
		Value	Standard Error
TMA	A01	0,31928	0,00848
MAO	A02	0,67902	0,00891
TMA	m1	0,00232	6,59704E-5
MAO	m2	5,59381E-4	5,11104E-6

Figure S-19 – Normalized Intensity *vs.* G plot obtained by ^{1}H PGSE NMR for aged neat 10%wt MAO in toluene (t = 97 days).



Equation	y = A01*exp(-m1*(x^2))		
Adj. R-Square	0,99994		
		Value	Standard Error
Toluene	A01	1,02354	9,31897E-4
Toluene	m1	0,00429	8,32214E-6

Equation	y = A01*exp(-m1*(x^2))+A02*exp(-m2*(x^2))		
Adj. R-Square	0,99996		
		Value	Standard Error
TMA	A01	0,3459	0,00515
MAO	A02	0,65651	0,0054
TMA	m1	0,00235	3,69389E-5
MAO	m2	5,73124E-4	3,24932E-6

Figure S-20 – Normalized Intensity *vs.* G plot obtained by ^{1}H PGSE NMR for aged neat 10%wt MAO in toluene (t = 140 days).

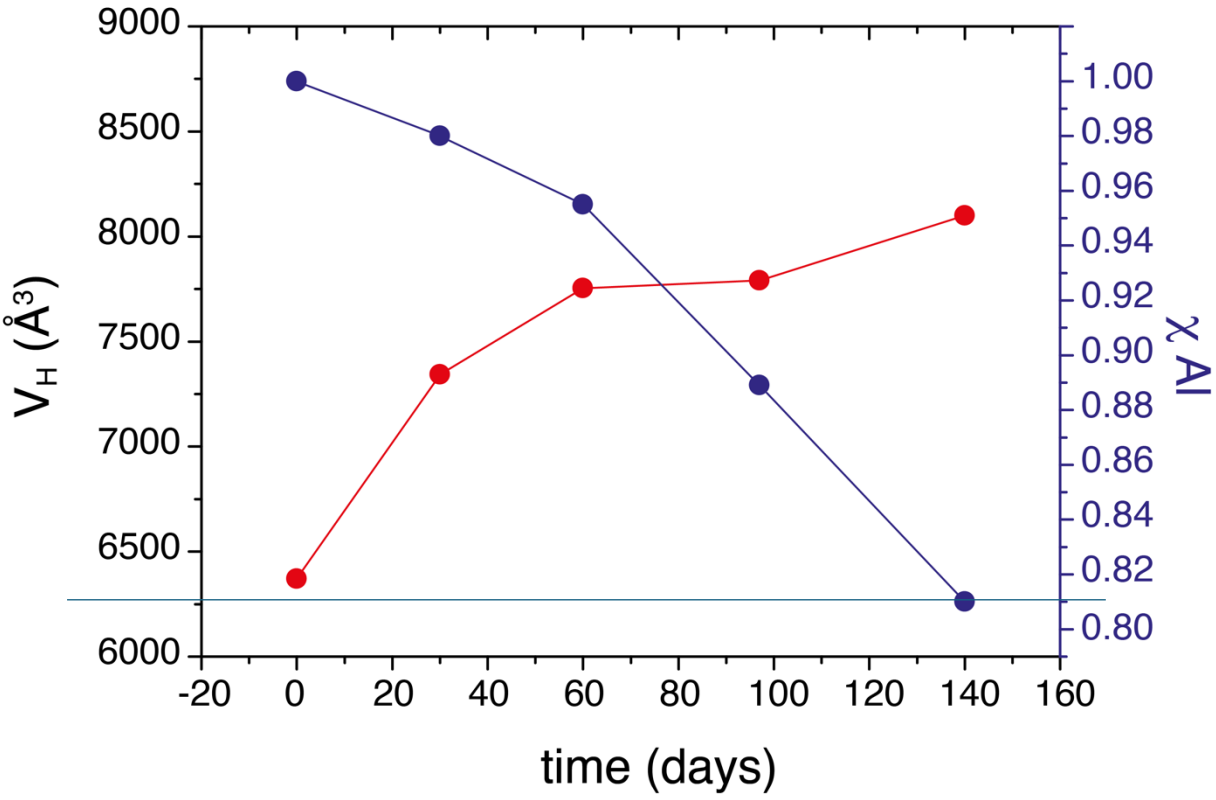


Figure S-21 – Evolution of the hydrodynamic volume (red) and soluble Al content (blue) of neat 10 wt% MAO in toluene upon aging at RT for 140 days.

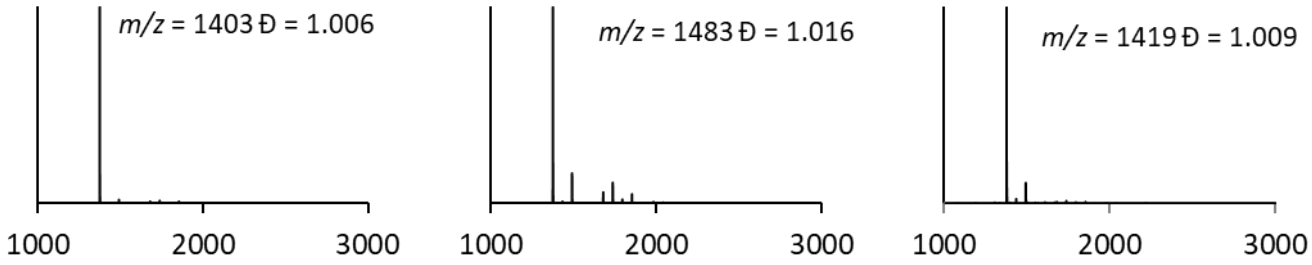


Figure S-22 -Negative ion ESI-MS spectra of left: 30 wt% W. R. Grace MAO sample plus 1.0 mol% OMTS, middle: the same material after 21 hours of storage at room temperature and right: a sample of 10 wt% W. R. Grace MAO and 1.0 mol% OMTS after storage in a glove-box freezer for about one year. Though these materials can obviously be distinguished by ESI-MS, no other mass-sensitive experimental technique could distinguish between these materials, especially for unaged 10- and 30-wt% samples.

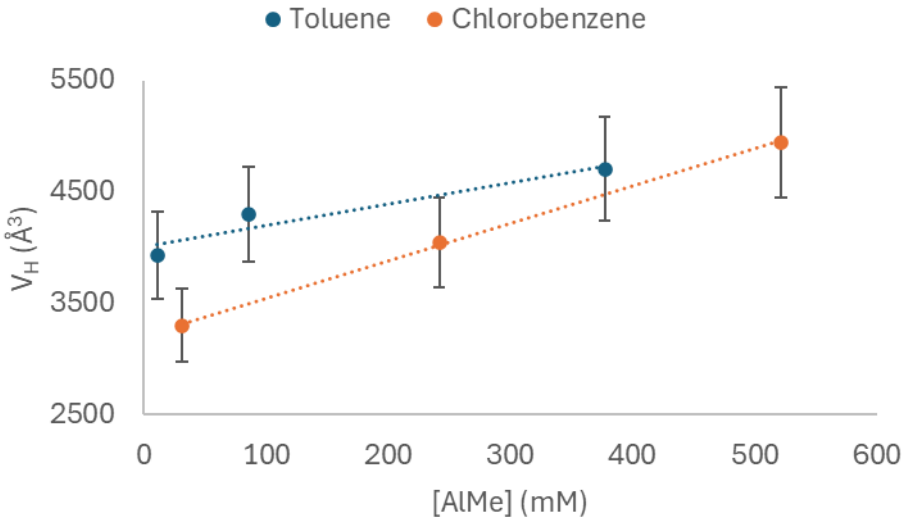


Figure S-23 – Hydrodynamic volume vs. [AlMe] concentration for 10 wt% h-MAO from W. R. Grace (Data in Table 2 with estimated error in V_H of ±10%). The slopes are different indicating the tendency towards aggregation is higher in the more polar solvent.