catalysts

MDPI

Supporting Information

Modified Magnesium Alkyls for Ziegler–Natta Catalysts

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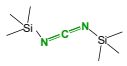
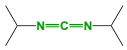
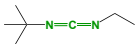
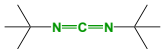
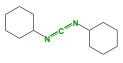
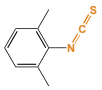
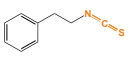
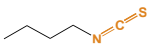
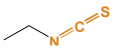
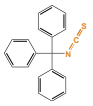
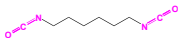
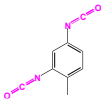
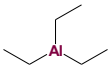
1. Effect of heterocumulenes and butyl octyl magnesium (BOMAG)

In Table S1 the observations and exact values of the BOMAG amount, additive concentration and viscosities are listed.

Table S1. Exact values for the used magnesium alkyl butyl octyl magnesium (20.4% in heptane), the values for the additive concentration, the viscosities and visual observations.

Entry	m_{BOMAG} (g)	Additive	w_{mol} (mol%)	$T_{increase}$ (°C)	Color	Sold formation	η (mPa s)
1	-	no additive	-	-	colorless	x	40.0
2	19.37		2.51	1.1	colorless	x	7.7
3	14.59		2.66	2.5	colorless	x	10.2
4	21.06		2.49	0	colorless	x	10.3
5	18.50		2.28	1.9	colorless	x	10.7
6	24.30		2.50	3.3	colorless	x	12.6
7	25.27		2.50	-0.3	yellow	x	18.2
8	23.68		2.80	1.6	yellow	x	24.5
9	13.68		2.42	1.8	yellow	x	32.8
10	26.86		2.55	2.5	yellow	x	36.0
Entry	**m_{BOMAG} (g)**	**Additive**	**w_{mol} (mol%)**	**$T_{increase}$ (°C)**	**Color**	**Sold formation**	**η (mPa s)**

11	25.53		2.90	2.3	yellow	x	37.0
12	22.62		4.10	3.1	yellow	x	40.0
13	20.22		2.25	0.4	yellow	x	49.0
14	23.39		2.39	1.7	colorless	yes	39.3
15	24.44		4.26	3.7	colorless	yes	47.8
16	22.22		4.7	-0.2	colorless	x	25.9
17	21.50		2.48	2.4	colorless	x	8.3

[1] polymer bonded, 200-400 mesh, 2 % cross-linked with divinylbenzene, 0.139 g were used

2. Viscosity data

In Table S2 the viscosity data for the magnesium alkyls BOMAG and BEM are listed, unmodified and modified with trimethylsilyl carbodiimide and triethylaluminum (each 2.5 mol%) at different alkyl concentrations in heptane.

Table S2. Viscosity data for butyl ethyl magnesium (BEM) and butyl octyl magnesium (BOMAG) with and without additives (2.5 mol% each) at different alkyl concentrations. The graphic can be seen in Figure 3 of the article.

Entry	Alkyl	Additive	w_{Mg} (wt%)	w_{Alkyl} (wt%)	η (mPa s)
1	BEM	-	1.10	4.98	2.46
2	BEM	-	2.18	9.93	8.33
3	BEM	-	3.38	15.37	26.73
4	BEM	-	4.39	19.95	61.8
5	BEM	-	5.50	25.01	147.0
6	BEM	-	6.81	30.95	385.5
7	BEM	-	7.30	33.20	609.0
8	BOMAG	-	1.50	10.31	8.28
9	BOMAG	-	2.22	15.26	17.08
10	BOMAG	-	3.00	20.41	40.20
11	BOMAG	-	3.64	25.02	72.38
12	BOMAG	-	4.32	29.69	142.6
13	BOMAG	-	5.25	36.08	305.3
14	BEM	trimethylsilyl carbodiimide	1.10	5.00	1.43
15	BEM	trimethylsilyl carbodiimide	2.20	10.02	2.54
16	BEM	trimethylsilyl carbodiimide	3.28	14.90	4.82
17	BEM	trimethylsilyl carbodiimide	4.40	20.01	9.68
18	BEM	trimethylsilyl carbodiimide	5.48	24.93	17.68
19	BEM	trimethylsilyl carbodiimide	6.59	30.00	32.83

20	BEM	trimethylsilyl carbodiimide	7.30	33.20	47.4
21	BOMAG	trimethylsilyl carbodiimide	0.73	5.00	1.14
22	BOMAG	trimethylsilyl carbodiimide	1.45	10.00	2.27
23	BOMAG	trimethylsilyl carbodiimide	2.18	14.95	4.04
24	BOMAG	trimethylsilyl carbodiimide	2.90	19.91	7.62
25	BOMAG	trimethylsilyl carbodiimide	3.63	24.97	14.05
26	BOMAG	trimethylsilyl carbodiimide	4.37	30.01	24.99
27	BOMAG	trimethylsilyl carbodiimide	5.13	35.26	46.32
28	BEM	triethylaluminum	1.10	5.00	1.10
29	BEM	triethylaluminum	2.20	9.99	2.28
30	BEM	triethylaluminum	3.30	14.98	4.37
31	BEM	triethylaluminum	4.17	18.95	7.23
32	BEM	triethylaluminum	5.50	24.99	15.74
33	BEM	triethylaluminum	6.59	29.96	28.71
34	BEM	triethylaluminum	7.30	33.20	38.94

Entry	**Alkyl**	**Additive**	w_{Mg} **(wt%)**	w_{Alkyl} **(wt%)**	η **(mPa s)**
35	BOMAG	triethylaluminum	0.73	5.05	1.10
36	BOMAG	triethylaluminum	1.42	9.73	3.06
37	BOMAG	triethylaluminum	2.16	14.86	3.45
38	BOMAG	triethylaluminum	2.91	20.02	6.33
39	BOMAG	triethylaluminum	3.63	24.97	11.37
40	BOMAG	triethylaluminum	4.36	29.98	20.37
41	BOMAG	triethylaluminum	5.13	35.26	37.74

In Table S3 the effect of the additive concentration on the viscosity of a 33.2% BEM solution in hepatane is given.

Table S3. Viscosity data for figure 4 in the article for a 33.2% BEM solution in heptane and different additive concentrations.

Entry	**Additive**	$w_{addiive}$ **(mol%)**	η **(mPa s)**	**Entry**	**Additive**	$w_{addiive}$ **(mol%)**	η **(mPa s)**
1	trimethylsilyl carbodiimide	0	609	9	triethyl aluminum	0	609
2		1.04	156.4	10		0.93	150
3		2.48	47.4	11		2.46	38.95
4		2.04	89.3	12		3.85	19.41
5		3.88	31.8	13		5.81	10.23
6		5.58	17.22	14		7.64	6.75
7		7.38	11.22	15		9.10	4.91
8		9.17	7.5				

3. Polymerization data

Figure S1 shows the molecular weight distributions of the obtained polymers and Figure S2 displays the schematic drawing of the used 0.5 L polymerization reactor.

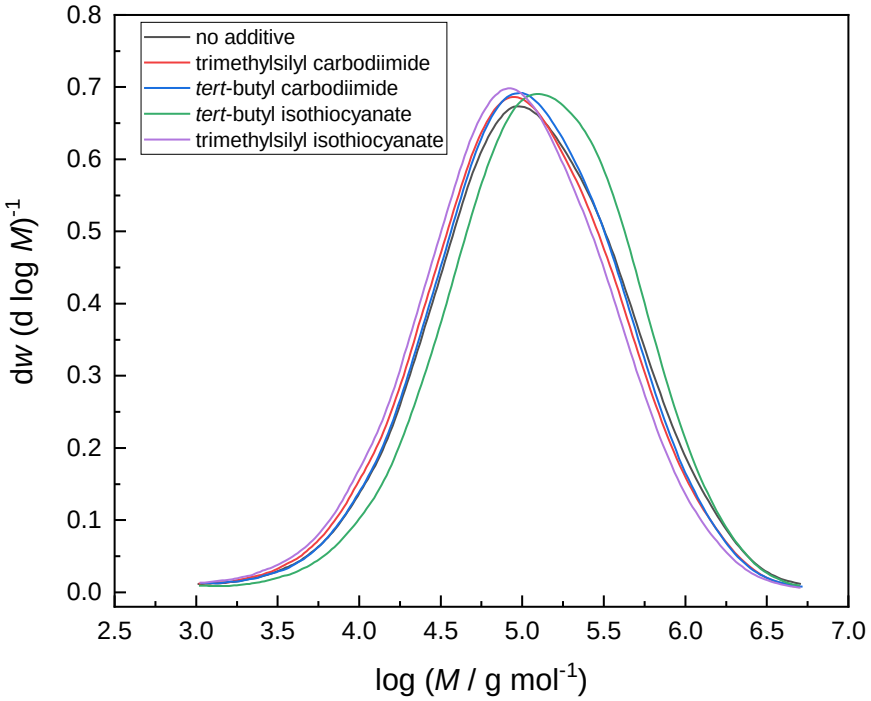


Figure S1. Molecular weight distributions for the obtained polymers measured with HT-SEC.

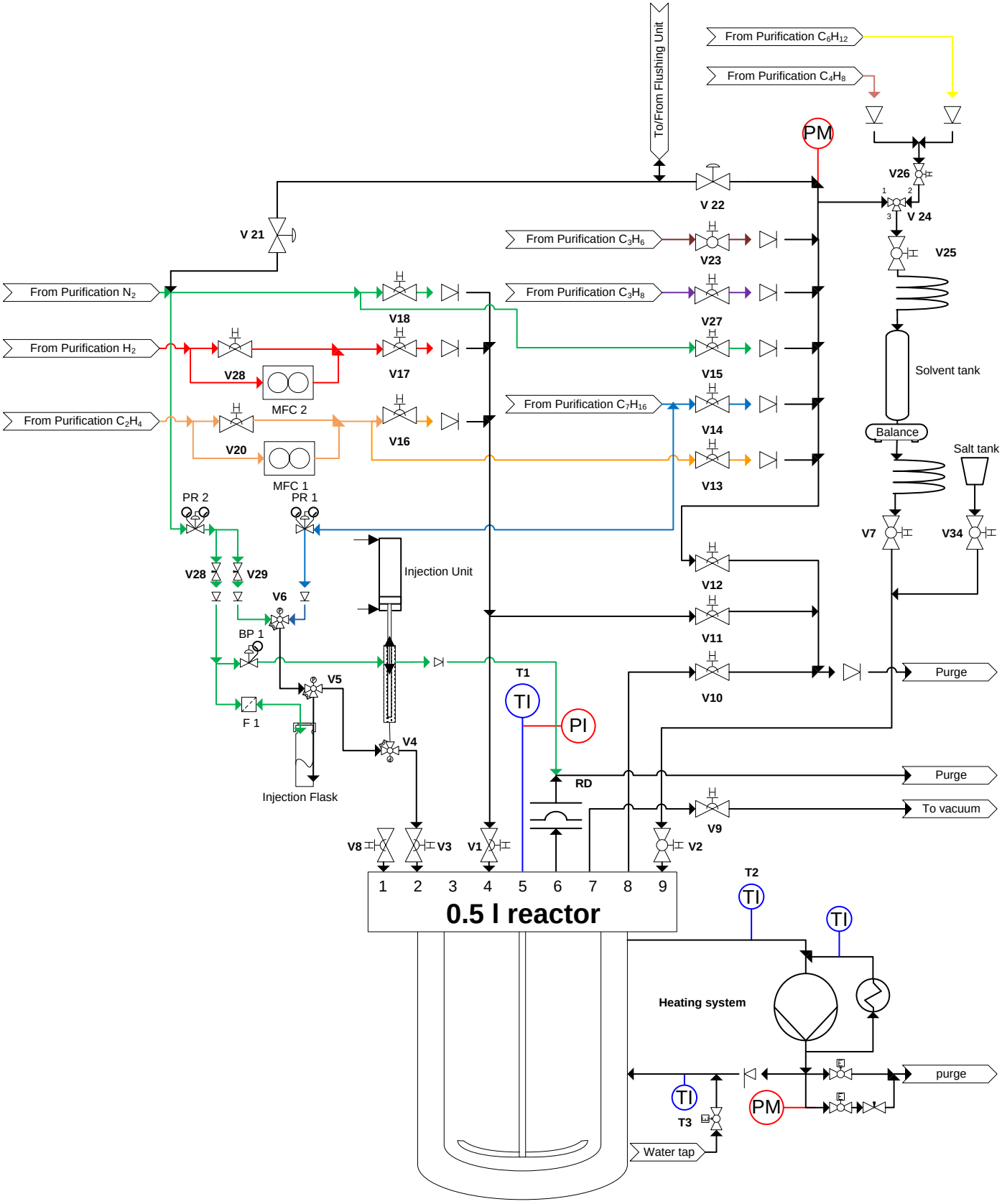


Figure S2. Schematic drawing of the 0.5 L reactor setup used for the polymerization experiments.