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Syndio-rich poly(methyl methacrylate) from the anionic polymerisation of methyl methacrylate in the presence of novel organoaluminium amides

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New organoaluminium amide complexes have been designed and exploited as additives to produce syndio-rich poly(methyl methacrylate) (PMMA) in good yield and low polydispersity from the anionic polymerisation of methyl methacrylate (MMA) at 0 °C.

The properties of PMMA are strongly dependent on polymer microstructure and tacticity. The glass transition temperature is one of the most important properties of PMMA, and this is influenced by chain length, backbone rigidity and tacticity. For example, estimates for the T_g of syndiotactic PMMA are in the range 130–165 °C whilst the isotactic variant has a T_g of about 45 °C.[1] The clear advantage of the high optical quality of PMMA would be much improved if the glass transition temperature could be raised. One such approach is the design of new material which has a high syndiotactic content. In this manuscript, we show how anionic polymerisation of MMA can be modified to control polymer microstructure. Anionic polymerisation has been found to be an excellent method for the preparation of PMMA of controlled tacticity.

Yasuda[2] and Nodono[3] have used organolanthanides to synthesise highly syndiotactic PMMA, in a living polymerisation, over a range of temperatures. Recently chiral metallocenes have been used to promote the formation of isotactic PMMA,[4] whereas a zircocenium aluminate complex strongly favored syndio-rich material.[5]

The use of alkylaluminium compounds as additives in the anionic polymerisation of methacrylates was first demonstrated by Hatada. Highly isotactic,[6] syndiotactic[7] and heterotactic[8] poly(methyl methacrylate) were obtained at low temperatures. Polymerisation with high stereocontrol at ambient temperature is a strategic objective of the present work. Ballard[9] showed that syndiotactic PMMA (~60% rr) can be obtained using organoaluminium additives such as i-Bu$_2$Al(BHT) (BHT = 2,6-di-*tert*-butyl-4-methylphenolate). The strong influence of the Lewis acidity of the aluminium species was demonstrated by Schlaad and Müller,[10] and also by Bolig and Chen.[5] More recently, Müller and coworkers undertook a study in which additives such as caesium[11] and tetraalkylammonium halides[12] and lithium salts[13] were used to modify the kinetics and resulting polydispersity of the organoaluminium-mediated anionic polymerizations of methacrylates. A Density Functional Theory (DFT) study taking into account solvation effects in THF showed that solvated dimers were the most stable state of lithium ester enolates except when a cryptand ligand was present in which case the ligand-separated triple ion pair was of comparable stability.[14]

Jenkins, Nyathi and Smith[15] demonstrated that organoaluminium amides, such as [Et$_2$Al(NHi-Pr)]$_3$ and [Et$_2$Al(NMe$_2$)]$_2$, initiated the polymerisation of MMA and aldehydes. Unfortunately no data concerning the tacticity were described. Hatada[16] studied the polymerisation of MMA using organolithium (t-BuLi) as initiator with organoaluminium amides Et$_2$AlNPh$_2$ as additives at low temperature. He concluded that aluminium amides were acting as additives and not as initiators, when lithium initiators were used. Recently Fraser[17] has used copper ATRP (atom transfer radical polymerization) catalysts with quadridentate amine ligands to synthesise PMMA in which tacticity followed Bernoullian statistics. Highly syndiotactic PMMA was obtained by Kanetaka,[18] using enamine initiators in combination with MeAl(BHT)$_2$.

We have previously defined the criteria for tacticity control in the anionic polymerisation of MMA in the presence of organoaluminium additives.[19] It was demonstrated that the nature of the ligands on the aluminium controlled the microstructure of the resulting polymer. There was a strong correlation between complexation of the organoaluminium additives with either the enolate initiator or the monomer and the outcome of the tacticity of the resulting polymer. When the organoaluminium reagent failed to complex to the monomer and/or the enolate, we obtained isotactic PMMA. We now demonstrate that these general design principles can be employed with a new class of organoaluminium amides, and that the resulting complexation of monomer and enolate can lead to polymer which is highly syndiotactic.

All polymerisations were initiated with ethyl α-lithioisobutyrate **2** preformed by deprotonation of the corresponding ester **1** with lithium diisopropylamide (LDA) (Fig. 1). The steric and electronic effect of the ligands attached to the aluminium atom were then evaluated. The use of an enolate as initiator reduces side reactions and results in greater control.[10]

The aluminium catalysts were prepared by adding triisobutylaluminium to the required number of equivalents of N-containing ligand in toluene, in order to form i-Bu$_2$Al(NRR′)

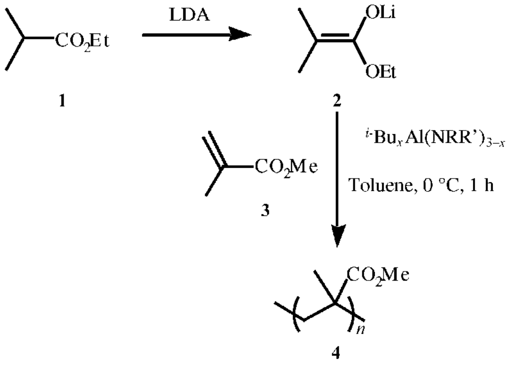

Fig. 1 Anionic polymerisation of MMA initiated by the enolate anion **2** in the presence of organoaluminium amides.

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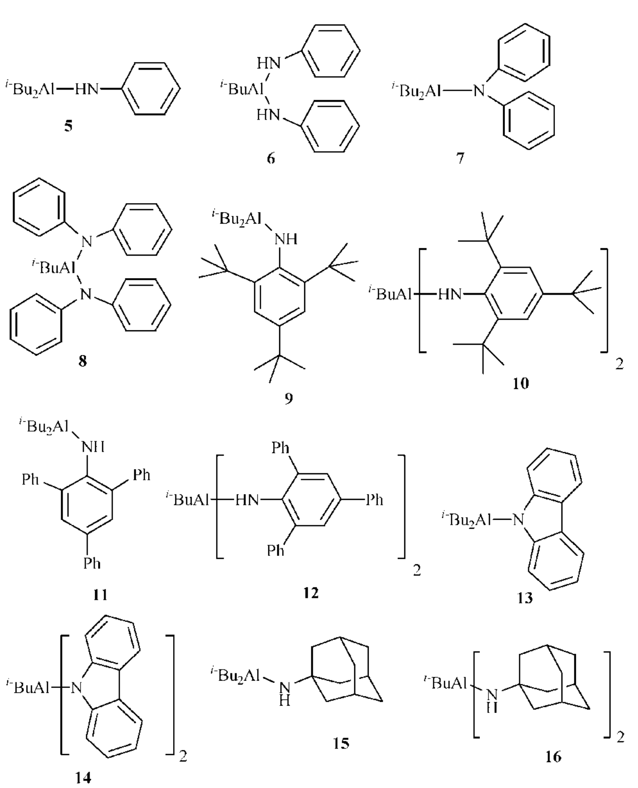

Fig. 2 Organoaluminium amide additives used in the present study.

or i-BuAl(NRR$'$)$_2$. Complexes **5–16** were evaluated (Fig. 2). The molecular weight, polydispersity and tacticity of the final polymer were highly dependent on the structure of the particular *N*-containing ligand (Table 1).[20]

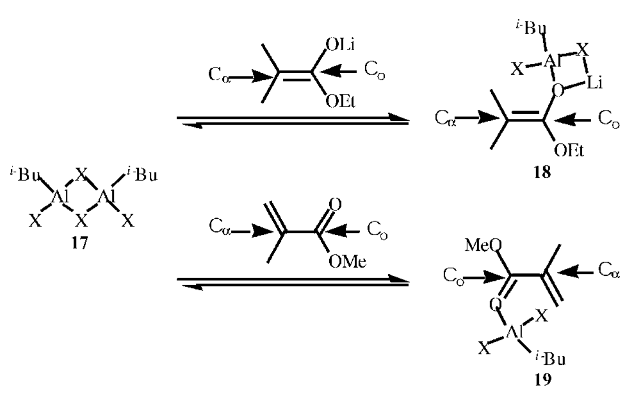

Fig. 3 Complexation of the enolate initiator **2** and the monomer **3** with the organoaluminium additive **17**.

It is first noted that a control experiment (Table 1, entry 1) without any Al additive afforded isotactic rich polymer with poor molecular weight control.[19] Significant improvements in polydispersity and variation of tacticity are possible using the nitrogen-based additives reported in this study. Additives based on aniline were generally ineffective in promoting polymerisation with the exception of entry 2 in which a low yield of isotactic polymer was produced. By contrast, syndio-rich polymers were obtained with low polydispersity when the additives **7** and **8** were used (entries 7, 9). Furthermore, 3 equivalents of the catalyst (Al/Li) were required to obtain high syndiotacticity, and we concentrate our discussion on these examples. According to our general observation, it would appear that monomer activation is necessary to obtain high syndiotactic PMMA.

The use of bulky amine ligands [*e.g.* the amino-analogue of i-Bu$_2$Al(BHT) **9** and also **10**] does not improve the characteristics of the PMMA obtained (entries 10–13). These additives gave even lower syndiotactic polymer than complexes **7** and **8** (67% compared with 73% for the best examples). A better syndiotactic content was obtained with complexes **11** and **12** (entries 15, 17). Higher molecular weight and excellent polydispersity were also observed. The presence of the *tert*-butyl and phenyl groups may increase the living nature of the polymerisation as the polydispersity improved in changing from complexes **7** and **8** to **9–12**. We assume (and demonstrate) that monomer activation correlates with the achievement of high syndiotacticity.

In the case of additives **13** and **14** syndio-rich PMMA was obtained (71–75%) with high molecular weight and (mostly) narrow polydispersity (entries 18–21). The aluminium reagent

Table 1 Effect of the organoaluminium complexes **5–16** on the tacticity, polydispersity and yield in the anionic polymerisation of MMA (Fig. 1)

			Triad tacticity					
Entry	Al complex	Al/Li	mm	mr	rr	M_n	M_w/M_n	Yield (%)
1	None	—	69	21	10	18,700	8.18	77
2	**5**	1	73	20	7	16100	1.60	32
3	**5**	3	No polymer					
4	**6**	1	No polymer					
5	**6**	3	No polymer					
6	**7**	1	24	36	40	12300	1.32	100
7	**7**	3	2	22	73	7100	1.34	100
8	**8**	1	21	36	43	13700	1.35	100
9	**8**	3	6	26	68	6900	1.40	100
10	**9**	1	10	34	56	9800	1.15	100
11	**9**	3	3	30	67	11800	1.15	100
12	**10**	1	10	36	54	9800	1.14	100
13	**10**	3	4	31	65	11700	1.15	100
14	**11**	1	5	29	66	14500	1.18	100
15	**11**	3	2	26	72	22000	1.24	100
16	**12**	1	5	32	63	12500	1.17	100
17	**12**	3	2	26	71	12000	1.22	100
18	**13**	1	2	24	74	12300	1.15	100
19	**13**	3	2	26	71	32200	1.22	100
20	**14**	1	No polymer					
21	**14**	3	3	22	75	23000	4.29	30
22	**15**	1	42	36	22	36200	2.18	89
23	**15**	3	64	26	10	20400	2.76	74
24	**16**	1	72	21	7	20900	1.90	53
25	**16**	3	71	22	7	18400	1.77	35

Table 2 ^{13}C NMR study of the complexation of the aluminium species **5–16** with either the enolate **2** or methyl methacrylate **3** (Fig. 3)

Al complex	Enolate **2**		Methyl methacrylate **3**			
δ C_0/ppm	δ C_α/ppm	δ C_0/ppm	δ C_α/ppm	δ CH_2/ppm	δ OCH_3/ppm	
None	159.0	77.0	167.3	136.7	125.0	51.3
i-Bu_3Al[a]	150.2	91.6	173.0	134.1[b]	132.9[b]	55.3
5	—[c]	—[c]	167.0	136.4	124.7	51.0
7	152.1	92.7	153.1	133.5	—[d]	55.4
8	150.6	92.7	153.1	133.5	—[d]	55.5
9	153.6	71.3	168.3	135.8	126.6	52.0
10	145.1	86.1	172.5	133.9	132.5	54.9
11	156.3	90.6	171.2	—[d]	125.3	54.0
12	156.3	90.5	170.8	—[d]	125.1	53.7
13	—[c]	—[c]	—[c]	139.6	—[c]	54.1
14	147.6	89.7	167.1	136.4	124.9	51.0
15	159.0	77.0	167.0	136.4	124.8	51.0
16	—[c]	—[c]	167.0	136.4	124.8	51.0

[a]These data are taken from reference 21. [b]The assignment of these two signals may be exchanged. [c]No signals observed. [d]Assignment of these peaks is ambiguous due to other signals in the same region.

14 gave poor polydispersity (entry 21) or no PMMA (entry 20), presumably owing to its low solubility in toluene. Unfortunately the solubility could not be improved when the reagent was prepared in a mixed solvent.

Bulky alkylamine complexes **15** and **16** gave isotactic PMMA with high molecular weight and moderate polydispersity (entries 22–25). The isotactic content and polydispersity improved when two adamantanamine ligands were used, but at the expense of the yield.

By considering ethyl α-lithioisobutyrate **2** as a model for the enolate at the propagating chain end of the polymer, Müller has studied the complexation of the living chain with aluminium alkyls by ^{13}C NMR spectroscopy, and has provided valuable information on the nature of this propagating species.[21,22]

As well as coordination to the enolate, aluminium alkyls can also complex with unreacted monomer, activating it towards nucleophilic attack. Hatada has postulated that such coordination of methacrylates to organoaluminiums is implicated in the mechanism for the formation of heterotactic polymers in anionic polymerisation. We have also investigated potential monomer activation and enolate complexation by the additives **5–16** by ^{13}C NMR, using the chemical shifts of the C_0, C_α, $=CH_2$ and OCH_3 carbons relative to those for free MMA and the enolate **2**,[19] to reveal complexation to the aluminium centre (Fig. 3). The results are displayed in Table 2.

No NMR signals of the enolate were observed with additive **5**, containing an aniline ligand, presumably owing to decomposition of the complex. Also, no monomer activation was observed with **5**. Complexes **7–12**, containing aromatic nitrogen substituents, formed an "ate" complex with the enolate and also uniformly appeared to coordinate the monomer **3**. By contrast, reagents **15** and **16**, with the adamantanamine ligand, did not complex with the enolate and no monomer activation was observed, presumably owing to steric and electronic factors.

The rationalisation of these results can be based on the possible dimeric nature of the aluminium catalyst in solution (Fig. 3).[19] If bridging by the ligand X in the dimer **17** is sufficiently weak, the enolate/monomer can complex to the aluminium. Clearly, the stronger this bridge is, the less favourable complexation will be. Bridges involving nitrogen atoms carrying alkyl substituents will be stronger than nitrogen atoms carrying an aromatic moiety and also than bridges to carbon atoms themselves. Thus, ligands based on alkylamines do not easily form complexes with the enolate and the monomer. Aromatic nitrogen bridges will be stronger than those based on bulky substituents. Complexation of the additive to both enolate and monomer reinforces the production of syndio-rich PMMA **4**.

In summary, we have shown that aluminium additives containing certain amine ligands afforded syndio-rich PMMA with high molecular weight and narrow polydispersity. The formation of an "ate" complex between either the enolate propagating species and/or the monomer with the aluminium additive is apparently required to control the polymerisation and also to achieve higher syndiotacticity. Intramolecular coordination of the lithium of the propagating species has previously been implicated in favouring the formation of isotactic PMMA, whereas syndiotactic polymer arises if this coordination is prevented,[23,24] as seems to be the case with the involvement of the "ate" complexes reported in this study. These design principles will enable further complexes to be used in refining the polymer microstructure in the anionic polymerisation of MMA.

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20 Typical procedure for the polymerisation of methyl methacrylate: MMA (25 mmol) was added dropwise over 1 min to a solution of enolate **2** (0.50 mmol) and the appropriate amount of aluminium catalyst (0.5 mmol or 1.50 mmol) in toluene (10 mL) at 0 °C. The reaction was stirred for 1 hour, and the polymerisation was terminated by the addition of a small quantity of methanol. The polymer was then precipitated in hexane, filtered and redissolved in CH_2Cl_2. This polymer was reprecipitated into MeOH and isolated by filtration. It was dried *in vacuo*. Triad tacticities were determined by the chemical shift of the quaternary methyl resonance in the ^1H NMR spectra. Molecular weights were determined by size exclusion chromatography in chloroform, using PMMA reference standards.

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