Ligand Effects in Organoaluminum Catalysts for the Tacticity Control in the Synthesis of Isotactic Poly(methyl methacrylate)

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Enormous differences in thermal and mechanical properties of poly(methyl methacrylate) (PMMA) arise as a result of polymer tacticity and stereoregularity.[1] For example, completely syndiotactic PMMA has a glass transition temperature above 130 °C, while that of the isotactic variant is much lower (~45 °C).[2] High tacticity and molecular weight control can often be realized by using low temperatures, as demonstrated by Hatada and co-workers in the synthesis of highly isotactic,[3] syndiotactic,[4] and heterotactic PMMA.[5] Organolanthanides have been employed to polymerize methyl methacrylate (MMA) in a highly living and syndiospecific manner, over a range of temperatures,[6] and also in chain transfer polymerizations.[7] Chiral metallocene complexes have been used by several groups to promote the isospecific polymerization of MMA.[8] More recently, Müller and co-workers completed an elegant series in which additives such as cesium[9] and tetraalkylammonium halides[10] and lithium salts[11] were used to modify kinetics and resulting polydispersity of the organoaluminum-mediated anionic polymerization of methacrylates.

Polymerization with a high degree of stereocontrol at near-ambient temperatures is a current strategic objective. Organoaluminum catalysts have previously been used to obtain syndiotactic rich PMMA (~60% *rr*) at ambient temperatures via the “screened” anionic polymerization route.[12] Schlaad and Müller[13] have reported that the Lewis acidity of the aluminum species strongly influences the tacticity of polymers produced in anionic polymerizations. A trialkylaluminum, for example, was found to give syndiotactic polymer with narrow polydispersity, while a trialkoxyaluminum gave highly isotactic polymer, but with little control of molecular weights. They concluded that at least one alkyl substituent was required to support the “screened” nature of the polymerization.

In this paper we have investigated the steric and electronic effects of oxygen-substituted ligands attached to aluminum on the tacticity of the polymers obtained, using a lithium enolate initiator **2** in the presence of organoaluminum catalysts (Figure 1) at near-ambient temperatures (~0 °C) in toluene. We demonstrate that the nature of the species $R_xAl(OR)_{3-x}$ determines the mode of interaction with the lithium enolate and the monomer, which in turn controls the final tacticity of the poly(methyl methacrylate). An important goal of this research was to develop practical conditions for the quasi-living controlled (including microstructure) anionic polymerization of methyl methacrylate by use of organoaluminum additives.

The catalysts were prepared by treating triisobutylaluminum with the stoichiometric quantity of the appropriate alcohol in toluene at 0 °C, followed by warming to ca. 25 °C. Molecular weight distributions and polymer tacticity are seen to be highly dependent on the nature of the organoaluminum species (**4a**−**g**) used (Table 1).

We note first that those systems with either one or two alkoxy ligands (**4f**−**4i**, entries 12−19) yield isotactic polymers. In a number of examples (entries 12−15, 18, and 19), the isotactic content of the polymers is higher than in the control experiment with no aluminum additive. However, the most dramatic effect is in the polydispersities of the polymers which are lower in all cases, the minimum being 1.5. We believe that it is of significance that both tacticity and polydispersity respond to the selected polymerization conditions. Furthermore, the systems with cyclohexanol ligands (**4f** and **4g**) gave lower polydispersities than those with menthol ligands (**4h** and **4i**), although yields are also lower.

Triisobutylaluminum[4] and the systems with 2,6-di-*tert*-butyl-4-methylphenoxy (BHT) ligands (**4d** and **4e**) gave syndiorich polymers with low polydispersity and in good yield. We observe that $BuAl(BHT)_2$ (**4e**) gives similar results to Ballard’s $Bu_2Al(BHT)$ (**4d**) system at 0 °C.[12] However, the system with phenoxy ligands (**4b,c**) either gave no polymer (entries 5−7) or isotactic polymer in low yield (entry 4).

By considering ethyl α-lithioisobutyrate **2** as a model for the enolate at the propagating chain end of the polymer, Schlaad and Müller have studied complexation of the living chain with aluminum alkyls by ^{13}C NMR and has provided valuable information on the nature of this propagating species.[14] We have carried out experiments using this model system with the aluminum compounds used in the polymerizations described above, using the ^{13}C NMR resonances of C_O and C_α in the enolate−aluminum complex to probe the formation of the complex (Figure 2). These data are summarized in Table 2. As reported in the literature, $AlBu^i_3$ causes a shift in the chemical shift of the ^{13}C NMR of the C_O and C_α atoms, indicating the formation of an “ate” complex. Complexation with the enolate **2** is also observed for the aryloxy aluminums **4b** and **4d**. We have used the lithium aluminate isolated by Snaith and co-workers as the basis for the structure of this “ate” complex suggested in Figure 2.[15]

There is little change in the chemical shift of the ^{13}C NMR signals for either C_O or C_α for the enolate complex with the menthoxyaluminum **4h**, indicating that for this compound no “ate” complex is formed. There is however a considerable broadening of these peaks, indicating that an interaction does occur. In the corresponding experiment involving complexation with **4f** neither C_O nor C_α was visible, possibly due to excessive broadening. In experiments with two oxygen ligands of any type (alkyl or aryl), no peaks for C_O and C_α were visible for the enolate in either complexed or uncomplexed form, possibly due to an intermediate rate of exchange of species on the NMR time scale.

As well as coordination to the enolate, aluminum alkyls can also complex with unreacted monomer, activating it toward nucleophilic attack. Such monomer activation by trialkyl aluminums has been investigated by ^{13}C NMR, using the chemical shifts of the C_O, C_α, $=CH_2$, and OCH_3 carbons relative to those for free MMA

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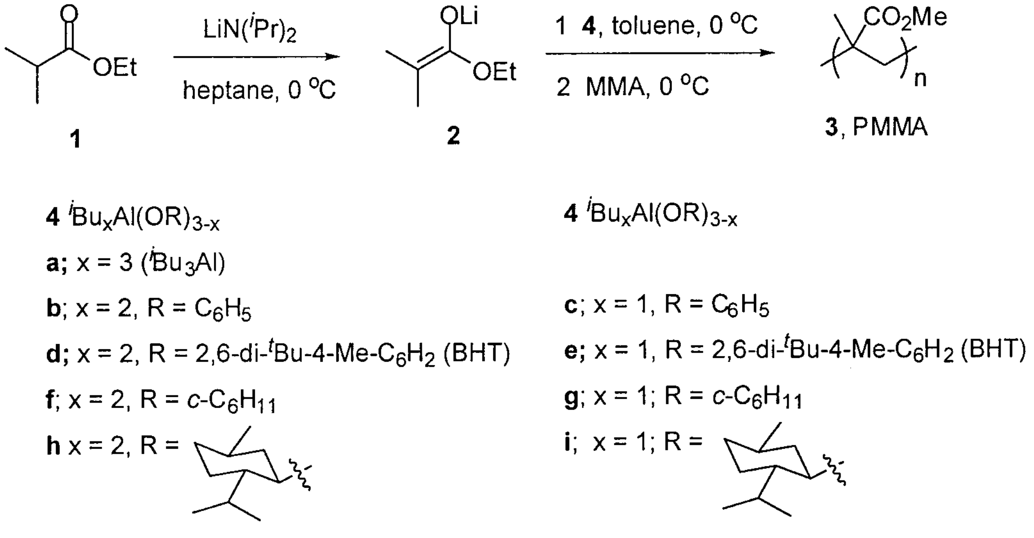

Figure 1. Range of organoaluminums (**4a**–**4i**), with chiral and nonchiral ligands, used in polymerization studies.

Table 1. Yields, Molecular Weight, and Tacticity Data for the Polymerization of Methyl Methacrylate Using Ethyl α-Lithioisobutyrate[a] in the Presence of Aluminum Alkyls[b]

entry	Al species	Al/Li[c]	triad tacticity[d] *mm*	*mr*	*rr*	M_n[e]	M_w/M_n[e]	yield[f]
1	none	n.a.	69	21	10	18 700	8.18	77
2	**4a**	1	6	34	60	10 600	1.15	83
3	**4a**	3	4	30	66	12 900	1.22	96
4	**4b**	1	72	21	7	7 900	1.98	28
5	**4b**	3		no polymer				0
6	**4c**	1		no polymer				0
7	**4c**	3		no polymer				0
8	**4d**	1	4	31	65	7 400	1.11	100
9	**4d**	3	4	35	61	7 300	1.47	100
10	**4e**	1	2	22	76	6 100	1.08	100
11	**4e**	3	3	22	75	12 400	1.10	100
12	**4f**	1	78	19	3	21 000	1.93	33
13	**4f**	3	69	25	6	14 100	1.47	49
14	**4g**	1	80	17	3	18 000	1.72	43
15	**4g**	3	78	18	4	28 900	2.57	45
16	**4h**	1	65	22	13	23 700	4.24	100
17	**4h**	3	51	29	20	26 500	2.02	87
18	**4i**	1	74	19	7	26 600	4.04	85
19	**4i**	3	79	16	5	30 000	6.28	86

[a] Prepared by the deprotonation of ethyl isobutyrate by LDA. [b] MMA (25 mmol) was added dropwise to a solution containing a mixture of ethyl α-lithioisobutyrate (0.50 mmol) and the appropriate aluminum alkyl (0.50 or 1.50 mmol) in toluene (10 cm^3) at 0 °C, and the polymerization was terminated after 1 h by the addition of a small quantity of methanol. [c] Molar ratio of aluminum alkyl to lithium enolate. [d] Determined by ^{1}H NMR (250 MHz, $CDCl_3$). [e] From size exclusion chromatography using $CHCl_3$ as eluent and poly(methyl methacrylate) standards. [f] Based on mass of MMA used.

to reveal complexation of the monomer to the aluminum center (Table 2). In certain cases assignment of some of the peaks is ambiguous, owing to the presence of other peaks in the same region. Those peaks which can be assigned reliably, however, are sufficient to allow conclusions to be drawn concerning the existence of complexation or not. A shift in the ^{13}C NMR chemical shift for these atoms shows that complexation occurs with **4d** and **4e**, but not **4b**, **4c**, **4h**, and **4i**. It has been shown that $AlBu_3$[14] and $MeAl(O\text{-}2,4\text{-}Bu^tPh)$[16] also activate MMA in this manner. The adduct of MMA with $AlMe_2$(BHT) has been isolated and the molecular structure determined by X-ray crystallography.[17] We have used this as a basis for our structural assignments.

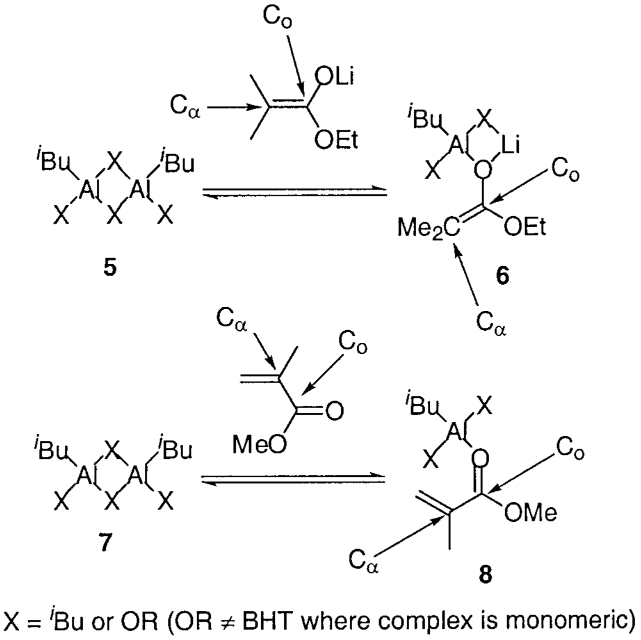

Figure 2. Coordination of ethyl α-lithioisobutyrate and MMA to dimeric aluminum species.

The complexation results described above can be rationalized by considering the possible involvement of dimeric aluminum compounds for most of the alkoxy ligands. $^iBu_2Al$(BHT) is predominantly monomeric in toluene solution.[18] For the less hindered alkoxy ligands to form a complex with either the enolate or monomer the bridge between the aluminum centers needs to be disrupted. Clearly the stronger this bridge is, the less favorable complexation will be. As alkoxy bridges (sp^3 donor oxygen) will be stronger than either unhindered aryloxy (sp^2 donor oxygen) or alkyl bridges (three-center, two-electron bond), it is understandable why the alkoxy aluminums tend not to form complexes with either enolate or monomer. The monomeric form of additives **4d** and **4e** may strongly favor the formation of an “ate” complex with either the monomer and/or the enolate, as in this case no disruption of the bridging bond will be required.

These complexation experiments can be used to rationalize the polymerization results. The formation of an “ate” complex has previously been associated with

Table 2. Selected ^{13}C NMR Data (100 MHz) for Aluminum Alkyls with Methyl α-Lithioisobutyrate or Methyl Methacrylate (in ppm)

	enolate[a]		MMA[b]			
Al compd	δ C$_O$	δ C$_\alpha$	δ C$_O$	δ C$_\alpha$	δ CH$_2$	δ OCH$_3$
none	159.0	77.0	167.3	136.7	125.0	51.3
4a[c]	150.2	91.6	173.0	134.1[d]	132.9[d]	55.3
4b	149.5	91.0	167.2	136.7	124.2	51.0
4c			167.0	136.5	124.7	51.0
4d	147.4	91.7	173.2	135.2[e]	133.9[e]	56.1
4e			172.6	NA[f]	NA[f]	55.5
4h	159.0	91.0	166.6	136.2	124.4	51.8
4i			166.9	136.4	124.7	51.9

[a] The solvent was a mixture (8:3 v/v) of toluene/toluene-d_8. [b] In benzene-d_6. [c] These data are taken from ref 14. [d,e] The assignment of these two peaks may be exchanged, but the argument regarding complexation remains unchanged. [f] Assignment of this peak is ambiguous owing to the presence of other peaks in the same region.

the formation of syndiotactic polymers. Both AlBu$_3$ and Bu$_2$Al(BHT) **4d** which favor syndiotactic polymers show complexation with both the enolate and the monomer. BuAl(BHT)$_2$ **4e** also gives syndiotactic polymers, and although the NMR complexation experiment provides no evidence for "ate" complex formation owing to the apparent absence of the C$_O$ and C$_\alpha$ peaks, it seems probable that this does occur. However, the additive **4e** does fulfill the other proposed prerequisite for syndiotactic polymer formation in the clear evidence of monomer activation (δ C$_O$ 172.6, see Table 2).

The lack of complexation between enolate **2** and **4h**, which suggests that alkoxy systems in general will not form "ate" complexes, is consistent with the formation of isotactic polymers. However, the broadening of the enolate peaks in the NMR experiments suggests that some form of interaction does take place, maybe with the oxygen atoms of the ligands acting as a Lewis base, and is probably responsible for the lower polydispersities in these systems than in the control experiment. These systems can be compared with those employing lithium alkoxides[19] in that the tacticity of the PMMA produced in toluene is affected little by the presence of the additive, but the polydispersity is significantly smaller.

The additive with one phenoxy ligand (**4b**) has been shown to form an "ate" complex but does not give syndiotactic polymers. This is possibly due to the greater stability, or different structure, of the "ate" complex arising from the lower steric bulk of phenoxy compared with the BHT ligand. However, no monomer activation was observed. Therefore, a better rationalization is that both monomer activation and "ate" complex formation with the enolate are required for production of syndiorich polymer.

In summary, we propose that the formation of an "ate" complex between enolate and organoaluminum as well as monomer activation is required to give controlled syndiotactic polymerization. Alkoxy aluminums do not form "ate" complexes and so give isotactic polymers. The polydispersity of these polymers is significantly lower than that of the control system, being as low as 1.5. It is both the electronic and steric nature of the ligands which controls this reactivity by influencing the bridge strength in dimeric aluminum compounds.[20]

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