Titanium mediated anionic polymerisation of methyl methacrylate

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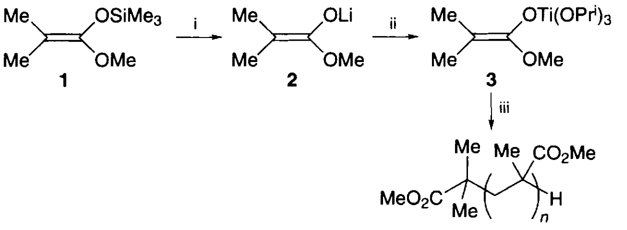
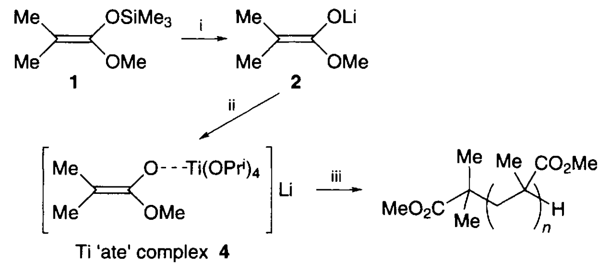
Polymerisation of methyl methacrylate using a tris(isopropoxy)titanium ester enolate and an analogous 'ate' complex is investigated; the latter affords poly(methyl methacrylate) in high yields with narrow polydispersity.

Recently, the polymerisation of methyl methacrylate using organolanthanides and zirconocene catalysts has afforded syndiotactic rich and highly isotactic poly(methyl methacrylate) (PMMA) in good yields.[1–4] Reetz's pioneering work with titanium enolates[5] and titanium 'ate' complexes[6,7] suggests that they should be effective initiators in the polymerisation of methyl methacrylate (MMA).[8] Here we report a more detailed study of the polymerisation of MMA using titanium ester enolates (Scheme 1) and preliminary results on the use of titanium 'ate' complexes as new initiators in MMA polymerisation (Scheme 2). Ti 'ate' complexes have also been used in conjugate additions to chiral α,β-unsaturated ketones or esters.[9]

Table 1 summarises results obtained from the polymerisation of methyl methacrylate in THF using the titanium enolate **3** as an initiator which was prepared by transmetallation [ClTi(OPr^i)$_3$] of methyl α-lithioisobutyrate **2**, itself obtained by butyllithium desilylation of the ketene acetal **1**. Different reaction temperatures and ratios of chlorotitanium triisopropoxide in relation to methyl α-lithioisobutyrate were used. At temperatures above 0 °C, almost no polymer was obtained, indicating rapid termination upon addition of monomer. Using an equimolar amount of methyl α-lithioisobutyrate and ClTi(OPr^i)$_3$, polymerisation of MMA was rapid at −20 to −30 °C (entries 1–4). Quantitative monomer conversion was not obtained but the GPC assay of the polymers revealed relatively narrow polydispersity, suggesting some degree of chain end control during the propagation steps.



Scheme 1 *Reagents and conditions*: i, BuLi, THF, 0 °C, 15 min.; ii, ClTi(OPr^i)$_3$, THF, −30 °C, 30 min.; iii, methyl methacrylate, THF, −30 °C, 1 h



Scheme 2 *Reagents and conditions*: i, BuLi, THF, 0 °C, 15 min.; ii, Ti(OPr^i)$_4$, THF, −30 °C, 30 min.; iii, methyl methacrylate, THF, −30 °C, 1 h

The use of excess ClTi(OPr^i)$_3$ relative to methyl α-lithioisobutyrate (Ti/Li > 1) unexpectedly produced no polymer (entries 5 and 6) although the deep orange–red colour of the titanium enolate was evident after adding ClTi(OPr^i)$_3$ to the lithium enolate. This suggests that the lithium and titanium enolates are in rapid exchange and that the lithium enolate may be the initiator and propagating species while the titanium enolate is 'dormant'. The titanium enolate may stabilise the chain end and minimise chain termination reactions to some extent as in the case of group transfer polymerisation.[10] However, this scenario remains to be confirmed at present. When the ratio of Ti/Li was ⩽1, polymerisation occurred rapidly giving the highest monomer conversions at ratios just below 1 (entry 4) at −30 °C.

In subsequent experiments, replacement of ClTi(OPr^i)$_3$ with titanium tetraisopropoxide led to the formation of an 'ate' complex instead (Scheme 2). The addition of Ti(OPr^i)$_4$ to the lithium enolate **2** produced a deep orange colour characteristic of such 'ate' species.[9] Addition of methyl methacrylate to the 'ate' complex at −30 °C unexpectedly produced rapid polymerisation and near quantitative monomer conversion. To our knowledge, this is the first reported polymerisation of acrylic monomers using such 'ate' complexes. Table 2 summarises the results obtained by varying reaction conditions such as temperature and the ratio of Ti(OPr^i)$_4$ to methyl α-lithioisobutyrate.

Polymerisation of MMA proceeded smoothly at −30 °C using the titanium 'ate' complex **4** as the initiating species, giving PMMA with narrow polydispersity. In the presence of excess Ti(OPr^i)$_4$, a slight increase in syndiotactic content was also observed (entries 2 and 4) along with slightly narrower polydispersity. Almost quantitative monomer conversion was

Table 1 Yields, molecular weight and tacticity data for the polymerisation of methyl methacrylate† as in Scheme 1, under different conditions

Entry	*T*/°C	Ti/Li[c]	Yield (%)	Tacticity[d] *mm*/*mr*/*rr*	M_n (M_w/M_n)[e]
1[a]	−20	1	52	4/34/62	17 000 (1.3)
2[a]	−30	1	61	2/29/69	15 000 (1.2)
3[b]	−30	0.5	38	5/36/59	7000 (1.2)
4[b]	−30	0.83	68	3/30/67	21 000 (1.4)
5[b]	−30	2	—	—	—
6[b]	−30	3	—	—	—

[a] MMA (2 ml, 1.872 g, 18.7 mmol); [MMA]/[BuLi] = 31; 10 ml THF; 1 h. [b] MMA (1 ml, 0.936 g, 9.35 mmol); [MMA]/[BuLi] = 16; 6 ml THF; 1 h. [c] [ClTi(OPr^i)$_3$]/[BuLi], mole ratio. [d] Tacticity determined from triad analysis [*mm* (isotactic), *mr* (atactic), *rr* (syndiotactic)] of ^{1}H NMR (500 MHz, CDCl$_3$) spectrum.[11] [e] From GPC assay using CHCl$_3$ as eluent and polystyrene standards.

obtained in some cases (entries 1–3). However, a large excess of $\mathrm{Ti(OPr^i)_4}$ (entry 8) seemed to inhibit polymerisation of the monomer and produced a yellow colour rather than the characteristic orange–red colour of the Ti 'ate' complex. We are still unclear why the formation of the 'ate' complex is inhibited by a large excess of $\mathrm{Ti(OPr^i)_4}$.

The polymerisation could also be carried out in a mixture of toluene and THF (1 : 1 *v*/*v*), resulting in a lower syndiotactic (*rr*) content (entry 3). However, no polymerisation occurred in pure toluene or dichloromethane. THF remained the preferred solvent, and the use of 2–3 equiv. of $\mathrm{Ti(OPr^i)_4}$ produced the highest syndiotactic content (entries 2 and 4). At 0 °C, almost no polymer was obtained, since an attempted precipitation of the polymer in excess MeOH produced a cloudy solution, indicating only oligomerisation had occurred. Polymerisation was very slow at −78 °C (entries 6 and 7); very little polymer was obtained even after 2 h although the polymerisation proceeded rapidly when the temperature was raised to −30 °C.‡

The role of the $\mathrm{Ti(OPr^i)_4}$ was to form 'ate' complexes which minimised chain termination side reactions, thus producing polymers of low polydispersity. There may be some similarities to the case of the 'screened' anionic polymerisation reported by Ballard *et al.*[12] Polymerisation of MMA using methyl α-lithioisobutyrate alone at −30 °C produced PMMA with much broader polydispersity.

Table 2 Yields, molecular weight and tacticity data for the polymerisation of methyl methacrylate† as in Scheme 2, under different conditions

Entry	*T*/°C	Ti/Li[f]	Yield (%)	Tacticity[g] *mm*/*mr*/*rr*	M_n (M_w/M_n)[h]
1[a]	−30	1	91	5/43/52	19 000 (1.4)
2[a]	−30	2	94	4/29/67	18 000 (1.3)
3[b]	−30	2	94	10/40/50	17 000 (1.1)
4[c]	−30	3	70	4/27/69	13 000 (1.1)
5[d]	−30	1	—	—	—
6[e]	−78	1	16	7/21/72	—[i]
7[e]	−78	2	18	4/26/70	—
8[c]	−30	5	—	—	—

[a] MMA (2 ml, 1.872 g, 18.7 mmol); [MMA]/[BuLi] = 31; 10 ml THF; 1 h. [b] MMA (1 ml, 0.936 g, 9.35 mmol); [MMA]/[BuLi] = 16; 1:1 THF:toluene *v*/*v*; 1 h. [c] MMA (1 ml, 0.936 g, 9.35 mmol); [MMA]/[BuLi] = 16; 6 ml THF; 1 h. [d] MMA (1 ml, 0.936 g, 9.35 mmol); [MMA]/[BuLi] = 16; 6 ml $\mathrm{CH_2Cl_2}$; 1 h. [e] MMA (1 ml, 0.936 g, 9.35 mmol); [MMA]/[BuLi] = 16; 6 ml THF; 2 h. [f] $[\mathrm{Ti(OPr^i)_4}]$/[BuLi], mole ratio. [g] Tacticity determined from triad analysis of ^{1}H NMR (500 MHz, $\mathrm{CDCl_3}$) spectrum.[11] [h] From GPC assay using $\mathrm{CHCl_3}$ as eluent and polystyrene standards. [i] Low molecular weight polymers.

Table 3 Attempted sequential monomer addition experiment using methyl methacrylate and the 'ate' complex **4** as initiator[a]

t/min	MMA added	M_n[c]	M_w/M_n[c]
0	2 ml (18.7 mmol)	21 600	1.3
30	3 ml (28.1 mmol)[b]	28 000	1.7
60	4 ml (37.4 mmol)[b]	29 000	1.7

[a] Conditions: BuLi 0.6 mmol; $[\mathrm{Ti(OPr^i)_4}]$/[BuLi] = 1; polymerisation at −30 °C; 3 ml THF used at start of reaction; 2 ml methyl methacrylate (1.87 g, 18.7 mmol) added initially; total reaction time was 90 min. [b] Additional 1 ml of methyl methacrylate (0.94 g, 9.35 mmol) added dropwise as a solution in 3 ml THF. [c] From GPC assay using a refractive index (RI) detector, $\mathrm{CHCl_3}$ as eluent and polystyrene standards.

In order to determine if the polymerisation was truly 'living', a monomer addition experiment was carried out. Fresh aliquots of MMA were added at three regular intervals. Table 3 shows the results obtained. The polymerisation appeared to have stopped sometime after the addition of the second aliquot of monomer, resulting in incomplete conversion of the second aliquot. This suggested that chain termination side reactions were indeed occurring at −30 °C and probably became dominant after the first batch of monomer has been consumed. Therefore, the polymerisation could probably be described as being 'quasi-living', showing 'living' characteristics only before the complete consumption of all the monomer.

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Footnotes

† All the polymers were characterised and analysed using IR, ^{1}H NMR and gel permeation chromatography (GPC) in chloroform against polystyrene reference standards.

‡ The increasing viscosity of the reaction mixture at −30 °C was taken as evidence of polymerisation.

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