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Polymerization of methyl methacrylate using organocalcium compounds

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Summary

We have studied the polymerization of methyl methacrylate (MMA) using biscyclopentadienylcalcium (Cp_2Ca) and bis(pentamethylcyclopentadienyl)calcium (Cp_2^*Ca) as initiators. Polymerizations initiated with CP_2Ca produced poly(methyl methacrylate), PMMA, with %rr = 80. This polymerization was conducted in 1,2-dimethoxyethane at 0°C; monomer conversion was 57% after 19 h. Lindsell and co-workers reported a much higher syndiotacticity for the same initiator. While 80%rr is higher than a free radical polymerization of MMA at the same temperature, the broad polydispersity and low conversions make this polymerization method unattractive. Use of the more soluble initiator Cp_2^*Ca significantly increases monomer conversion but produces PMMA with lower syndiotacticity.

Introduction

Syndiotactic PMMA

The control of tacticity is an important problem in polymer synthesis. Polymer tacticity can have a large impact on the physical properties. For example, estimates for the T_g of 100% syndiotactic poly(methyl methacrylate) (PMMA) range from 135-145 °C. A typical sample of PMMA produced by free radical polymerization (rr:rm:mm = 62:34:4) displays a T_g of 105°C.(1)

The literature contains numerous studies directed at controlling tacticity in PMMA. Early work has been reviewed.(2) Literature results of particular relevance to this report are given in Table 1. The success of Group IVB metallocene catalysts for the stereoregular polymerization of propylene has not been duplicated for methyl methacrylate (MMA). Some of the best work in this area has been that of Collins and co-workers;(3) entry 1 in Table 1 shows the conditions and initiating system used. The observed syndiotacticity is moderately higher than PMMA produced by free radical polymerization. Soga and co-workers(4) have also studied the polymerization of MMA with zirconocenes. Entry 2 in Table 1 shows the system of Hatada and co-workers(5) which produces highly syndiotactic: PMMA but only after long reaction times at low temperatures. Yashuda and co-workers(6) have used organolanthanides to produce highly syndiotactic PMMA (entry 3 in Table 1). The organolanthanides were active initiating species over a wide temperature range and produced PMMA with narrow polydispersity. Marks and co-workers(7) have studied the influence of catalyst structure on PMMA tacticity in the organolanthanide system. All of the polymerization methods in entries 1-3 in Table 1 control tacticity via a chain-end control mechanism.

The impetus for the research reported here was provided by the result shown in entry 4. Lindsell and co-workers(8) reported the preparation of PMMA with rr = 94% at 0°C using biscyclopentadienylcalcium (Cp_2Ca). To us, this provocative literature report was worth further investigation. Lindsell and co-workers studied other organocalcium compounds and examined the influence of temperature and solvent. Conversion was always less than 100% and often less than 50%. For the conditions

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in entry 4, only 8% conversion was obtained. Nonpolar solvents and higher temperatures reduced syndiotacticity. Initiator efficiencies were very low and the molecular weight distributions were broad (M_w/M_n = 3-12). The same research group also reported a study of MMA polymerization using triphenylmethylcalcium halide initiators.(9) In summary, organocalcium initiators produced highly syndiotactic PMMA but the polymerizations were not controlled and gave poor conversions.

Table 1. Literature Examples of Syndiotactic PMMA Preparations[a]

No.	Initiating System	Pzn. Conditions	% rr	Ref.
1	Cp_2ZrMe_2/ $[Cp_2ZrMe(THF)][BPh_4]$	0 °C, 60 min, CH_2Cl_2	(80)[a]	3
2	t-BuLi/R_3Al	-78 °C, toluene, 24 h	96	5
3	$[Cp_2{}^*SmH]_2$	-95 °C, toluene, 40 min	95	6
4	Cp_2Ca	0 °C, DME, 12 h	94	8

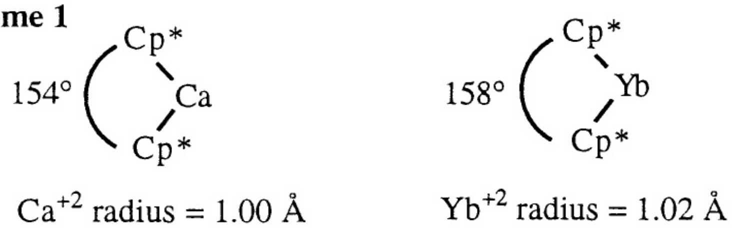
[a] Cp = cyclopentadienyl, Cp* = pentamethylcyclopentadienyl. [a] %r = 80.

Our research goal was to investigate Lindsell's work and potentially optimize organocalcium structure and polymerization conditions.

Organocalcium Chemistry

While the chemistry of Grignard compounds is well known, the organometallic compounds of Ca, Sr, and Ba are less familiar because they are more ionic and generally less soluble in organic solvents. Calcium and other alkaline-earth ions are similar to divalent lanthanide ions with regard to their electropositive nature and ionic radii.(10) For example, Cp_2^*Ca and Cp_2^*Yb are found to be bent sandwich structures with similar centroid angles (Scheme 1).(11) One major difference between organocalcium compounds and organolanthanide compounds is the number of available oxidation states.

Scheme 1



Results and discussion

Synthesis of Organocalcium Compounds

In this report, we have focused on the polymerization chemistry of two organocalcium compounds, Cp_2Ca and Cp_2^*Ca. In early work, we used the method of Lindsell and co-workers(12) to prepare Cp_2Ca. This method involved the reaction of cyclopentadiene with elemental calcium in THF at 45°C. The product is obtained as THF solvate with a Cp_2Ca:THF stoichiometry of 1:2. We were not able to purify this compound and found that samples from this synthesis produced variable results.

Our preferred method of synthesis for both Cp_2Ca and Cp_2^*Ca was the reaction of CaI_2 with the sodium salt of the corresponding cyclopentadienyl anion.(13) With considerable effort, we were able to recrystallize Cp_2Ca and compare the behavior of this purified sample with unrecrystallized Cp_2Ca. We synthesized Cp_2^*Ca to improve the solubility in THF and toluene.

We also synthesized bisfluorenylcalcium and attempted the polymerization of MMA but only obtained low conversions after 20 h; thus, we did not study this compound further.

Cp_2Ca initiated polymerization of MMA

Table 2 summarizes the MMA polymerization results when Cp_2Ca was used as the initiator. The data is for polymerization in DME because Cp_2Ca was sparingly soluble in THF. We did not perform molecular weight analysis for all samples since our principle figure of merit was conversion and %rr. In THF, we observed low conversions and lower syndiotacticity.

Table 2. Polymerization of MMA in DME.

No.	$[Cp_2Ca(THF)_2]_o$, mM	$[MMA]_o$, M	T,°C	t, h	% Conv.	% rr
1	2.7	0.85	0	22	17	76
2	4.4	1.51	0	19	10	76[a,b]
3	4.4[c]	1.51	0	19	57	80[d]
4	10.6	7.8	0	0.08	80	61
5	2.7	0.85	-10	22	4	80
6	4.4	1.51	-10	20	35	80
7	5.3	1.56	-10	22	35	80[e]

[a] T_g = 120°C. [b] M_n(exp)=24.5k g/mol, M_w/M_n =1.47, initiator efficiency = 14%.(14) [c] Recrystallized $Cp_2Ca(THF)_2$. [d] M_n(exp)=25.8k g/mol, M_w/M_n =1.73, initiator efficiency = 76%. [e] T_g = 125°C.

We observed good conversions in short times only for high monomer concentrations (entry 4); however, syndiotacticity was lower. Purified Cp_2Ca (entry 3) afforded a higher initiator efficiency. The effect of temperature was negligible for the small range studied (0 vs. -10°C). The best result in Table 2 is entry 3 where polymer with 80% rr was obtained. Collins and co-workers (3) observed similar tacticity at the same temperature but they obtained complete conversion of monomer in 1 h.

The most important conclusion from Table 2 is that we did not reproduce the results of Lindsell. Lindsell reported PMMA with 94% rr after 19h at 0°C using $[Cp_2Ca]_o$ = 1.9 mM and $[MMA]_o$ = 1.87 M. Entry 2 in Table 2 represents the best duplication of Lindsell's experimental conditions; similar conversions were observed but the polymer syndiotacticity was significantly lower. We repeated many of the experiments in Table 2 and never observed %rr greater than 80. We can not account for the difference in our results compared to Lindsell's report.

Cp_2^*Ca initiated polymerization of MMA

Table 3 summarizes the results for the polymerization of MMA using Cp_2^*Ca. Cp_2^*Ca was soluble in a greater range of solvents including THF and toluene. The greater solubility was accompanied by improvements in conversions (for polymerizations at 0°C). Low conversions were observed at temperatures below 0°C.

Table 3. Polymerization of MMA by $Cp_2{*}Ca(THF)_2$[a]

No.	Solvent	T,°C	t, h	% Conv.	M_n(exp)[b]	%Init. Eff.	% rr
1	DME	0	1	82	38k	51	57
2	DME	-30	9	0	-	-	-
3	THF	0	2	81	34k	57	37
4	THF	-20	4	11	28k	9	43
5	THF	-30	9	0	-	-	-
6	Toluene	20	8	23	38k	14	23

[a] $[MMA]_o$ = 0.92M, $[Cp_2Ca(THF)_2]_o$ = 3.85 mM. [b] M_w/M_n = 3-5; distributions were generally multimodal.

Organolanthanide catalysts with the Cp^* auxiliary ligand produced syndiotactic PMMA (80% rr at 0 °C). However, lanthanides bearing the less bulky Cp ligand produced polymer with high syndiotacticity only at low temperatures.[6] Unlike lanthanide compounds, Cp_2^*Ca did not produce syndiotactic PMMA at 0 °C. For polymerization in DME at 0°C, %rr = 57. This result is similar to free radical polymerization. In the less polar solvent THF, the syndiotacticity of PMMA decreased further, %rr = 37.

We briefly studied the polymerization of *t*-butyl methacrylate using Cp_2^*Ca. We obtained 100% conversion in 1 h for polymerization in THF at 0°C. However, the initiator efficiency was only 4% and rr = 66%.

Conclusions

Cp_2Ca and Cp_2^*Ca polymerize MMA with low conversions at 0°C. We obtained PMMA with 80% rr using purified Cp_2Ca. This result contrasts the report of Lindsell and co-workers where they reported a much higher syndiotacticity using the same catalyst. Lower syndiotacticity was obtained with Cp_2^*Ca. Even though the 80% rr observed with Cp_2Ca is higher than a free radical process at the same temperature, the poor conversions and broad molecular weight distributions observed with organocalcium compounds makes them unattractive. We are currently studying the mechanism of the polymerization.

Experimental section

Materials 1,2-Dimethoxyethane, THF and toluene were dried and deoxygenated by distillation from sodium benzophenone ketyl. Anhydrous CaI_2, cyclopentadienyl sodium, and pentamethylcyclopentadienyl sodium were purchased from Aldrich and used as received. Methyl methacrylate was purchased from Aldrich and purified by the method of Allen, Long and McGrath.(15) All reactions were performed under dry argon using standard Schlenk techniques.

Synthesis of Cp_2Ca and Cp_2^*Ca. Cp_2Ca and Cp_2^*Ca were prepared according to the literature.[13] Anhydrous CaI_2 (4.67 g, 15.9 mmol) and cyclopentadienyl sodium (17.6 mL of a 2M THF solution, 35.2 mmol) were added to a 250 mL flask containing 75 mL THF. The cloudy reaction mixture was stirred overnight and was then filtered. The precipitate was washed twice with 30 mL THF. Removal of the solvent afforded crude $Cp_2Ca(THF)_2$. The crude product was recrystallized from DME.

An analogous procedure was used for Cp_2^*Ca.

Polymerization of MMA. MMA polymerization was carried out in a 50 mL round-bottomed flash equipped with a magnetic stir bar. A typical polymerization procedure is as follows. 2 mL MMA was added to 10 mL DME. The polymerization was started by injection of 2 mL of a 30 mM Cp_2Ca DME solution. The reaction was quenched with methanol and the polymer precipitated into methanol followed by drying in a vacuum oven.

Characterization. Syndiotacticity was determined by analysis of ^1H NMR spectrum which was recorded on a Varian Gemini 200 MHz spectrometer. Molecular weight analysis was determined by gel permeation chromatography which was performed with a Waters 501 pump, 2 PLgel (Polymer Laboratories) mixed-D columns (5 micron), and a Waters 410 differential refractometer. The eluent was THF and the flow rate = 1 mL/min. Molecular weights were calibrated by comparison to narrow molecular weight PMMA standards (Polymer Laboratories).

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