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Syndiotactic polymerization of styrene with $CpTiCl_2(OPr^i)$/methylaluminoxane

Jianfei Liu [1], Jiling Huang [1], Yanglong Qian [1,*], Fan Wang [1], Albert S. C. Chan [2]

[1] Laboratory of Organometallic Chemistry, East China University of Science and Technology, Shanghai 200237, People's Republic of China
[2] Department of Applied Biology and Chemical Technology, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

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Summary

$CpTiCl_2(OPr^i)$ was a very active catalyst for syndiotactic polymerization of styrene when activated with methyl aluminoxane(MAO). The catalyst activity and syndiospecificity of $CpTiCl_2(OPr^i)$/MAO were about 10^7 g PS / mol Ti·mol S·h and about 95% respectively, both higher than those of $CpTiCl_3$ / MAO.

Introduction

In 1986, a breakthrough concerning the stereospecific polymerization of styrene was made by Ishihara(1), who found that $CpTiCl_3$ activated with MAO (methyl aluminoxane) could initiate syndiotactic polymerization of styrene . Since then the syndiotactic polymerization of styrene attracts much attention(2-8). It was reported that the performances of syndiotactic polystyrene was comparable to that of resins like nylon 66 and polyphenyl sulfide in some aspects(9). Thus syndiotactic polystyrene may be a promising engineering polymer. Recent years, a lot of half-sandwich titanocene compounds, including $CpTi(OR)_3$(8), $RCpTi(OR)_3$(10), and $IndTiCl_3$(11), have been used to polymerize styrene, among which $IndTiCl_3$ was reported to be a superior one due to its high activity, high syndiospecificity and relative insensitive to polymerization conditions.

Now we reported here that $CpTiCl_2(OPr^i)$ was also a catalyst with both high activity and high syndispecificity towards the polymerization of styrene.

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[*] Corresponding author

Experimental

$CpTiCl_3$, $CpTiCl_2(OPr^i)$(12) and MAO(13) were prepared according to litreature procedures. Styrene was purified by washing with dilute NaOH solution, dried over anhydrous $CaCl_2$, vacuum distillation from CaH_2 and stored at-20°C in darkness. Toluene is distilled from sodium and diphenyl ketone under argon just before use.

Polymerization was conducted in 50 ml Schlenk flask containing magnetic bar under Ar. Thus, an appropriate amount of MAO, styrene (2 ml), toluene (10 ml) were introduced into a flask and stirred under Ar. $CpTiCl_2(OPr^i)$ in toluene was then injected. The polymerization mixture was stirred for a certain time at a given temperature and then quenched by addition of 100 ml 10% HCl in EtOH.

Results and Discussion

Several $CpTi(OR)_3$ have been previously used for the syndiotactic polymerization of styrene(8,10). But their syntheses and purification were tedious due to their liquid properties. Pure $CpTi(OPr^i)_3$ could not, according to the literature(10), be purified by vacuum distillation though it could be obtained by passing several times through Bio-Bead columns. However, $CpTiCl_2(OPr^i)$(12), a solid compound, could be very easily prepared in high yield by $CpTiCl_3$ and $HOPr^i$ in the presence of NEt_3,and conveniently purified by recrystallization.

Table 1. Styrene polymerization catalyzed by $CpTiCl_2X$ / MAO

run	[Ti] mM	[Al] M	Time min.	Temp °C	X	yield PS(g)	A^a (10^7)	S^b %
1	0.05	1.25	30	53	OPr^i	0.362	6.9	93.7
2	0.10	1.25	30	53	OPr^i	0.404	3.9	93.6
3	0.21	1.25	30	53	OPr^i	0.861	3.9	96.6
4	0.28	1.25	30	53	OPr^i	0.860	3.0	97.7
5	0.42	1.72	30	53	OPr^i	1.04	2.4	97.7
6	0.42	1.55	30	53	OPr^i	0.918	2.1	96.8
7	0.42	1.18	30	53	OPr^i	0.649	1.5	95.8
8	0.42	0.88	60	53	OPr^i	0.513	0.59	95.0
9	0.70	3.2	5	53	OPr^i	1.68	23.1	99.5
10	0.42	0.83	60	30	OPr^i	0.413	0.47	91.4
11	0.42	0.83	60	50	OPr^i	0.520	0.59	93.6
12	0.42	0.83	60	70	OPr^i	0.374	0.42	90.1
13	0.42	0.83	60	90	OPr^i	0.280	0.32	75.4
14	0.05	1.25	50	53	Cl	0.242	2.8	85.4
15	0.10	1.25	30	53	Cl	0.289	2.7	89.7
16	0.42	1.73	30	53	Cl	1.14	2.6	98.4

a: g PS / (mol Ti .mol S.h)

b: g of 2-butanone insoluble polymer / g of bulk polymer

The results showed that at a constant [Al], the decrease of [Ti] increased activity (runs 1, 2, 3, 4). When [Al]=1.25M, the decrease of [Ti] from 0.28 mM to 0.05 mM increased the activity from 3.0 $\times 10^7$ to 6.9 $\times 10^7$ g PS /mol Ti·mol·S·h, while syndiotacticity of polystyrene tended to decrease slightly (from 97.7% to 93.7%). At low [Ti] (0.05 mM) the activity and syndiospecificity of $CpTiCl_2(OPr^i)$ / MAO were evidently highter than those of $CpTiCl_3$/ MAO (runs 1, 2, 14, 15). It should be noticed that little polymer was formed in run 14 when polymerization proceeded for 30 minutes (as it was in run 1), indicating propagation rate in $CpTiCl_2(OPr^i)$ / MAO was also faster than that in $CpTiCl_3$ / MAO. In comparison with $CpTiCl_3$ / MAO, the syndiospecificity of $CpTiCl_2(OPr^i)$ was less sensitive to polymerization conditions (run 1, 2, 14, 15).In case of [Ti] = 0.42 mM, the activity was enhanced by increasing [Al], while syndiotacticity of polymer were not much affected (5, 6, 7, 8). At higher[Ti] (0.70mM) and [Al] (3.2M), the highest activity (2.31$\times 10^8$ g PS / mol Ti·mol·S·h and the highest syndiotacticity (99.5%) were obtained.

It appeared that the activity and syndiotacticity of polystyrene were not much affected by polymerization temperature in the range of 30-70°C (runs 10, 11, 12,). However, higher temperature (90°C) leads to much loss of syndiotacticity of polystyrene (run 13).

In conclusion, $CpTiCl_2(OPr^i)$ / MAO was a more active, more syndiospecific and comparatively less sensitive to polymerization conditions catalyst for styrene polymerization than $CpTiCl_3$ / MAO. A serial study on monocycloopentadienyl titanium derivatives / MAO towards styrene polymerization is now in progress.

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