

NOTES

A Catalyst for Syndiotactic Polymerization of Styrene

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Since Ishihara and co-workers discovered that titanium compounds, when activated with methylaluminoxane (MAO), formed very active catalysts for the syndiotactic polymerization of styrene,^{1,2} syndiotactic polymerization of styrene has been the focus of polymer synthesis,^{3–10} due to good performance of syndiotactic polystyrene (s-PS) claimed to be comparable to that of resins like nylon 66 and poly(phenylene sulfide).¹¹ Recent years a lot of half-sandwich titanocene compounds, including CpTi(OR)₃,¹² and IndTiCl₃,¹³ have been synthesized and used to polymerize styrene.

To search for high active and high syndiospecific catalysts, we prepared a series of monocyclopentadienyl titanium dichloroalkoxides CpTiCl₂(OR) (R = Me, Et, Prⁱ)¹⁴ and used these compounds with MAO to polymerize styrene.

EXPERIMENTAL

CpTiCl₃,¹⁴ CpTiCl₂(OMe),¹⁵ CpTiCl₂(OEt),¹⁴ CpTiCl₂(OPrⁱ),¹⁴ and MAO¹⁶ were prepared according to the literatures.^{14–17} Styrene was purified by washing several times with dilute NaOH solution, dried over anhydrous CaCl₂, vacuum distillation from CaH₂, and stored at –20°C in darkness. Toluene was distilled from sodium and diphenyl ketone under argon just before use.

Polymerization was conducted in small ampules baked under vacuum and flushed with Ar for several times. Styrene (2 ml), an appropriate amount of MAO in toluene (0.1 g ml⁻¹), and titanium compounds in toluene were sequentially injected. The mixtures were kept at 50°C for a certain time, then terminated with 100 ml 10% HCl in EtOH, and dried under vacuum at 50°C to constant weight.

RESULTS AND DISCUSSION

CpTi(OR)₃ is used to polymerize styrene. But pure CpTi(OPrⁱ)₃, not attainable by vacuum distillation according to the literature, has only been obtained by tedious procedures.¹² However, solid compounds, CpTiCl₂(OR), were easily prepared by reaction of CpTiCl₃ with HOR in the presence of NEt₃ in high yield.¹⁴ Pure CpTiCl₂(OR) was conveniently obtained by recrystal-

lization. A literature survey indicates no such compounds have been previously used for styrene polymerization. We thus present here our results of syndiotactic polymerization of styrene with CpTiCl₂(OR)/MAO.

The experimental results are shown in Table I. Apparently, the catalyst activity and syndiospecificity of CpTiCl₂(OR)/MAO were higher than those of CpTiCl₃/MAO. When R = Me, Et, Prⁱ, the catalytic activity of CpTiCl₂(OR)/MAO was about 2 fold higher than that of CpTiCl₃/MAO. However, activity of catalysts was not much affected by change of alkyl groups. But the syndiospecificity of CpTiCl₂(OR)/MAO was 10 percent higher than that of CpTiCl₃/MAO except CpTiCl₂(OMe)/MAO, which was slightly higher than CpTiCl₃/MAO, demonstrating the steric effect of ligands to play an important role in determining the syndiospecificity of catalysts. Evidently, more sterically hindered ligands yield more syndiospecific catalysts. We attempted to synthesize CpTiCl₂(OBu^t) and failed to get a pure product. An impure sample was about 5 fold more active than CpTiCl₃ at a syndiospecificity of 97.5% when used to catalyze the syndiotactic polymerization of styrene with MAO.

Figure 1 shows the carbon-13 NMR spectrum of the phenyl C-1 of polystyrene measured in 1,2,4-trichlorobenzene at 50°C with a Gemini-300 MHz spectrometer. This spectrum is in accordance with Ishihara's report though the solubility of our sample is poor at 50°C. Apparently, our sample (2-butanone insoluble) is syndiotactic polystyrene.

James C. W. Chien found that hydrotitanium(III) is the syndiospecific species in styrene polymerization catalyzed by CpTi(OBu)₃/MAO.⁸ We believe that in our catalytic system CpTi(OR)H may be the precursor of active site.¹⁸ Thus the R groups may have considerable influence on syndiospecificity. As for the activity dif-

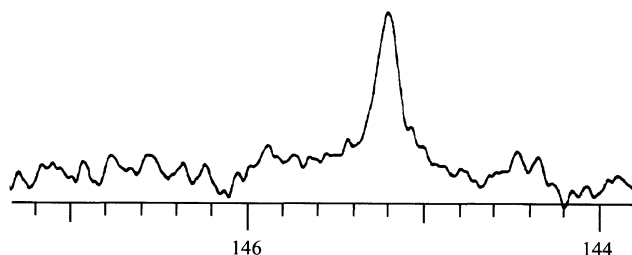


Figure 1. Carbon-13 NMR spectrum of polystyrene.

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ferences between CpTiCl₂(OR) and CpTiCl₃, we believe that reduction of CpTiCl₂(OR) by MAO to Ti(III) may be faster and easier than the reduction of CpTiCl₃ by MAO. In fact, we found that the polymerization reaction catalyzed by CpTiCl₂(OR) was completed sooner than the polymerization reaction catalyzed by CpTiCl₃ (see Table I).

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Table I. Styrene polymerization by CpTiCl₂ X/MAO at 50°C

X	Cl	OMe	OEt	OPr ⁱ
[Ti]/m mol L ⁻¹	0.54	0.54	0.54	0.54
[Al]/mol L ⁻¹	0.96	0.96	0.96	0.96
[St]/mol L ⁻¹	2.5	2.5	2.5	2.5
Al/Ti (molar ratio)	1750	1750	1750	1750
Time/h	2	1	1	1
Yield/g	0.390	0.455	0.430	0.385
A ^a (10 ⁶)	2.18	5.21	4.47	4.41
Syndio ^b /%	86.5	90.5	96.1	95.4

^a g PS/mol Ti · mol St · h. ^b g of 2-butanone insoluble polymer/g of bulk polymer.

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