Communications to the Editor

Homo- and Copolymerization of Ethylene and Styrene Using $TiCl_3$ (AA)/Methylaluminoxane

Introduction. The combination of titanocene or zirconocene compounds with methylaluminoxane (MAO), the hydrolysis product of trimethylaluminum, to form highly efficient homogeneous Ziegler–Natta catalysts for various α-olefin polymerizations is well documented in the literature.[1-3] The cocatalyst MAO has been recently used in combination with other titanium or zirconium complexes to produce stereospecific polystyrene.[4-10] During our recent investigations on the use of homogeneous catalytic systems for ethylene/vinylcyclohexane copolymerization,[11] we found $TiCl_3$ (AA, aluminum activated)/MAO, hitherto not reported to our knowledge, to be active for ethylene and styrene. Highly isotactic polystyrene (95%) was obtained. It is of interest to note that, while $TiCl_3$ (AA)/MAO produced isotactic polystyrene in our studies, (η-C_5H_5)$TiCl_3$/MAO has been reported to produce highly syndiotactic polystyrene.[7] The copolymerization of ethylene and styrene was also studied by using the above catalytic system. We present in this paper the results of our preliminary investigations.

Experimental Section. $TiCl_3$ (AA) was purchased from Akzo Chemicals. Trimethylaluminum, styrene, and toluene were obtained from Aldrich Chemical Co. Toluene was refluxed over calcium hydride for 24 h followed by distillation. Styrene was purified by the conventional method. High-purity ethylene (Linde) was passed through a column of 4A molecular sieves before using it for the reaction. MAO was prepared by reacting Me_3Al with $Al_2(SO_4)_3 \cdot 16H_2O$ ($Al/H_2O = 1$) as reported by Tsutsui et al.[12] The reaction mixture was filtered and stored under nitrogen as a 1.25 M Al stock solution containing MAO and unreacted Me_3Al.

Polymerization reactions were carried out in a 200-mL four-neck reaction flask. A typical procedure is described as follows: Toluene (75 mL), styrene (25 mL), and the Al solution (4 mL) were charged into the flask under an argon atmosphere at room temperature. The contents were degassed by bubbling with argon for 1 h. The polymerization was started by the addition of $TiCl_3$ with vigorous stirring. After 20 h the reaction was quenched by addition of a small amount of acidified methanol. The polymer was isolated by pouring the reaction mixture into an excess methanol/HCl mixture, filtered, washed repeatedly with methanol, and dried in vacuo at 60 °C.

DSC analysis was carried out on a Perkin-Elmer DSC-4 instrument equipped with a thermal analysis data station (TADS-101). ^{13}C NMR spectra of the samples were recorded on a Brüker AM-250 instrument operating at 62.9-MHz frequency. ^1H NMR spectra of the polystyrene samples were recorded in $CDCl_3$ at room temperature on a Brüker AC-300 instrument. The molecular weights and polydispersity ratios were determined in 1,2,4-trichlorobenzene using a Waters 150C GPC instrument at 120 °C with a Jordi mixed-bed column. The polymer samples were fractionated by extracting with boiling methyl ethyl ketone for 5 h.

Results and Discussion. Preliminary experimental results of the polymerization reactions using $TiCl_3$ (AA)/MAO are given in Table I. Although the catalytic activity in general is not very high, its reactivity toward styrene polymerization was better than had been reported recently[13] using a supported $Ti(OBu)_4$/MAO system. Highly isotactic (95%) polystyrene was obtained. The ^{13}C NMR spectrum of a typical sample is shown in Figure 1. The single peak due to the phenyl C_1 resonance of polystyrene at δ 146.4 clearly identifies the *mmmm* pentad configuration of isotactic polystyrene. The methylene and methine proton signals in the ^1H NMR spectrum of the sample are shown in Figure 2. The multiplicity of the methine proton signal and the difference in the chemical shift between methylene and methine protons of polystyrene are known to vary for isotactic, syndiotactic, and atactic forms.[4] The ^1H NMR spectrum of the sample in the present study is consistent with that observed for isotactic polystyrene. The observed glass transition temperature (96 °C) and crystalline melting point (221 °C) of the polystyrene sample are in agreement with the values reported[7] for isotactic polystyrene. The number-average molecular weight and polydispersity ratio of the polystyrene were found to be 67 700 and 7.38, respectively. A thorough characterization of the polystyrene obtained was necessary in order to confirm unambiguously the interesting difference in the stereospecificity observed between

Table I
Results of Polymerization Reactions[a]

[Ti] × 10^3, mol/L	[Al],[b] mol/L	ethylene	[styrene], mol/L	reaction time, h	yield, g
1.62	0.05	1 atm		1	1.5
3.17	0.05	1 atm	2.18	1	1.4
1.87	0.05		2.18	20	1.3
1.04	0.05		4.36	20	1.2

[a] Total reaction volume was 100 mL for all reactions. [b] MAO/Me_3Al.

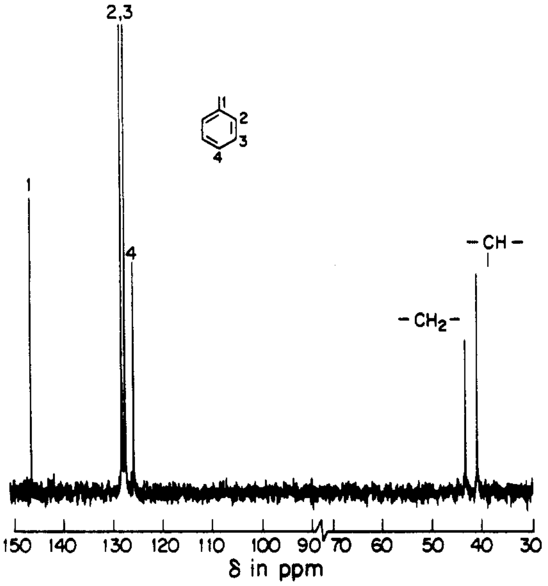

Figure 1. ^{13}C NMR spectrum of polystyrene in $CDCl_3$ at room temperature.

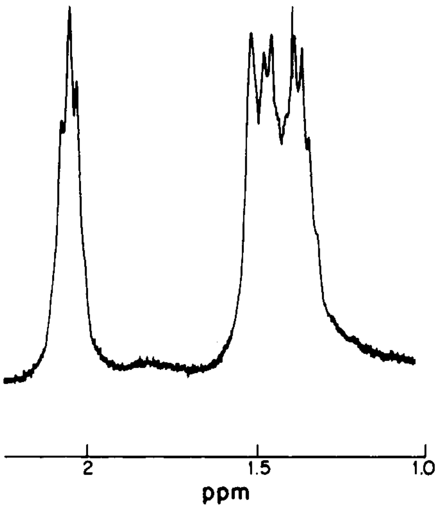

Figure 2. ^{1}H NMR spectrum of the methylene and methine protons of polystyrene.

the (η-C_5H_5)$TiCl_3$/MAO and the $TiCl_3$ (AA)/MAO catalytic systems.

Comparison of the results for pure styrene (Table I) indicates that lowering the catalyst concentration and increasing the monomer concentration enhances the conversion of the reaction. However, the portion of polystyrene insoluble in boiling methyl ethyl ketone was 95% at the higher catalyst concentration, whereas it was 60% at the lower catalyst concentration. The insoluble and soluble portions were clearly identified by ^{1}H and ^{13}C NMR analyses as isotactic and atactic polystyrenes, respectively.

The yield per gram of Ti is lower for the copolymerization than for the homopolymerization of polyethylene (Table I). The ^{13}C NMR spectrum of the copolymer in 1,2,4-trichlorobenzene at 120 °C is shown in Figure 3. Although weak, the presence of signals at δ 145–146 assigned to phenyl C_1 in short sequences of styrene units and other signals shown in Figure 3 confirms that copolymer has been formed. The complex signal composed of several peaks at δ 145–146 has the same features as the phenyl C_1 signal of atactic polystyrene. Because of the large signal/noise ratio, the copolymer composition was not determined for this sample. The melting point (T_m) and the heat of fusion (ΔH_f) of the copolymer ($T_m = 129.8$ °C; $\Delta H_f = 23.3$ cal/g) are lower than those of homopolyethylene ($T_m = 133$ °C; $\Delta H_f = 28.8$ cal/g). These results are similar to those reported by Soga et al.[14] for ethylene/styrene copolymerization. The number-average molecular weight and polydispersity ratio were determined to be 94 900 and 5.9 for the polyethylene homopolymer and 78 700 and 5.6 for the copolymer, respectively. The similar polydispersity ratios indicate that the active species may be the same for the homopolymerization and copolymerization reactions.

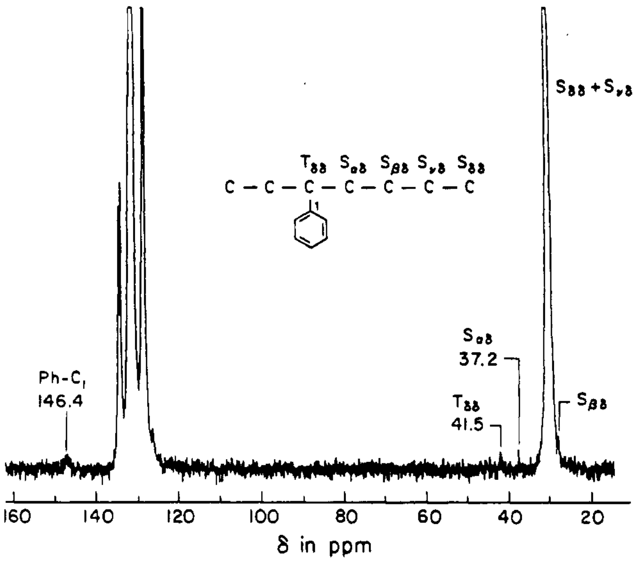

Figure 3. ^{13}C NMR spectrum of the copolymer in 1,2,4-trichlorobenzene at 120 °C.

In conclusion, $TiCl_3$ (AA)/MAO was found to be active for the polymerization of ethylene and styrene and their copolymerization. Highly isotactic polystyrene was obtained. More detailed studies on the catalytic system and the kinetics of styrene polymerization are in progress.

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