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Preparation of syndiotactic polystyrene having bimodal molecular weight distribution with dinuclear titanocenes

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Using a mixture of dinuclear hexamethyltrisiloxanediylbis(cyclopentadienyltitanium trichloride), $Cl_3Ti-CpSi(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_2Cp-TiCl_3$ and mononuclear cyclopentadienyltitanium trichloride ($CpTiCl_3$), pentamethylcyclopentadienyltitanium trichloride (Cp^*TiCl_3) with the modified methylaluminoxane cocatalyst in styrene polymerization, the syndiotactic polystyrene having bimodal molecular weight distribution was obtained. The polydispersity index of the obtained polystyrene could be controlled by the relative concentrations of the two or three titanocenes. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: dinuclear titanocene; mixture of titanocenes; syndiotactic polystyrene)

Introduction

The molecular weight distribution (MWD) of polymer obtained with metallocene catalyst is usually narrow due to the single site of metallocene[1]. To improve the processability and broaden the MWDs of metallocene polyolefins, many trials such as using a mixture of different metallocenes[2,3] or a hybrid catalyst of Ziegler–Natta and metallocene catalysts[4,5] have been carried out.

The mononuclear titanocenes such as $CpTiCl_3$[6] and Cp^*TiCl_3[7] can initiate styrene polymerization and the obtained syndiotactic polystyrene (sPS) also has a narrow MWD.

Recently it was found that the siloxane-bridged dinuclear titanocene[8] such as hexamethyltrisiloxanediylbis(cyclopentadienyltitanium trichloride), $Cl_3Ti-CpSi(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_2Cp-TiCl_3$ can polymerize styrene as well as ethylene. Until now few studies have been reported for the MWD broadening of sPS obtained with titanocenes.

In this communication, a mixed catalyst of dinuclear and mononuclear titanocenes was used in styrene polymerization with modified methylaluminoxane cocatalyst to prepare sPS having a wide and bimodal MWD. The weight-average molecular weight (M_w) and polydispersity index, M_w/M_n of the prepared sPS have been examined for various compositions of the mixed catalysts.

Experimental

Materials. The mononuclear titanocenes, $CpTiCl_3$ and Cp^*TiCl_3 were purchased from Strem Chemicals, USA and used without further purification. The dinuclear titanocene, $Cl_3Ti-CpSi(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_2Cp-TiCl_3$ was prepared according to the literature[8]. The modified methylaluminoxane (MMAO-4, 12.2 wt% Al, Akzo, USA) cocatalyst was used as received. The styrene (Junsei Chemical Co., Japan) was purified by distillation under reduced pressure after refluxing with CaH_2. The toluene was purified after refluxing with sodium-benzophenone complex.

Polymerization and polymer chacterization. All operations were carried out under a nitrogen atmosphere. The proper amounts of toluene, MMAO solution and styrene were introduced sequentially in a 400 ml glass reactor, and the polymerization was initiated by injecting the required amount of mixed solution of titanocene catalysts. The melting temperature of the obtained syndiotactic poly-styrene (sPS) was measured by means of differential scanning calorimetry (d.s.c., Dupont TA 2000) at 20°C min^{-1}. The syndiotactic index of sPS was obtained by extraction with boiling methylethylketone[6,8]. The molecular weight of sPS was measured by means of gel permeation chromatography (g.p.c., Waters 150C) with 1,2,4-trichlorobenzene at 135°C.

Results and discussion

The styrene polymerizations initiated with dinuclear titanocene, $Cl_3Ti-CpSi(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_2 Cp-TiCl_3$ (**1**), mononuclear titanocenes, $CpTiCl_3$ (**2**) or Cp^*TiCl_3 (**3**) and modified methylaluminoxane (MMAO) cocatalyst were carried out and the results are shown in *Table 1*.

Being used as a catalyst alone, the dinuclear **1** exhibited lower catalyst activity than the mononuclear

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Table 1 Polymerization of styrene initiated with **1**, **2** or **3** and MMAO cocatalyst

Catalyst^a	Activity^b	M_w ($\times 10^{-3}$)	M_w/M_n	SI (wt%)	T_m (°C)
1 (3,1)	7.7	35	2.5	84.2	250
2 (3,3)	32.6	12	1.9	73.7	245
3 (3,2)	945.0	175	2.4	93.5	271

^{a} Concentration in mol l^{-1}($\times 10^6$)
^{b} Activity in kg sPS mol Ti^{-1} h^{-1}
Polymerization conditions: [Al]/[Ti] = 1000, [Styrene] = 1.04 mol l^{-1}, 70°C, 2 h

Table 2 Polymerizations of styrene initiated with binary or ternary mixed catalyst of **1**, **2** and **3** and MMAO cocatalyst

Catalyst **1**/**2**/**3**^{a}	Activity^b	M_w ($\times 10^{-3}$)	M_w/M_n	SI (wt%)	T_m (°C)
3.6/1.8/none	19.2	19	3.1	75.2	246
3.6/none/1.7	30.7	149	6.4	89.3	268
1.3/1.3/1.9	92.5	129	7.9	90.3	267
none/1.9/1.3	112.5	98	5.8	86.6	265
none/1.3/1.9	128.7	112	7.2	87.2	267
none/0.6/2.6	152.0	136	5.6	89.6	268

^{a} Concentration in mol l^{-1}($\times 10^6$)/mol l^{-1}($\times 10^6$)/mol l^{-1}($\times 10^6$)
^{b} Activity in kg sPS mol Ti^{-1} h^{-1}
Polymerization conditions: [Al]/[Ti] = 1000, [Styrene] = 1.04 mol l^{-1}, 70°C, 2 h

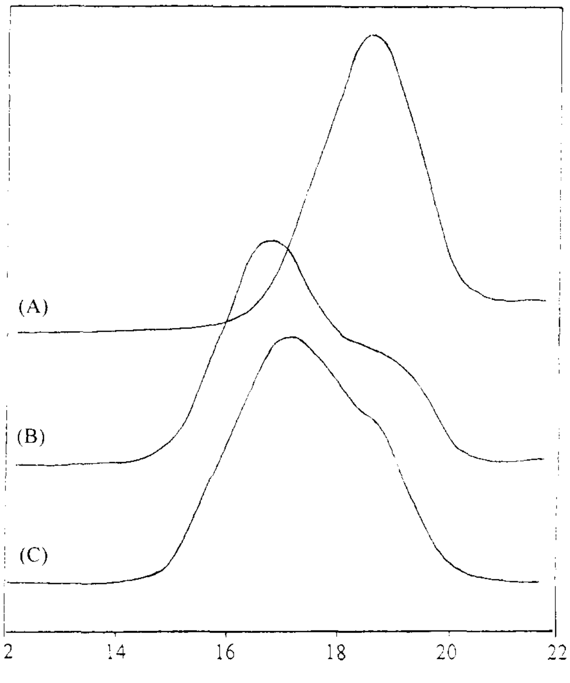

Figure 1 Gel permeation chromatograms of sPS prepared with binary or ternary mixed catalyst of $Cl_3Ti-CpSi(CH_3)_2-O-Si(CH_3)_2-O-Si(CH_3)_2Cp-TiCl_3$ (**1**), $CpTiCl_3$ (**2**) and/or Cp^*TiCl_3 (**3**) and MM AO cocatalyst: concentrations ($\times 10^6$)(mol l^{-1}/mol l^{-1}) of **1**/**2** = 3.6/1.8 (**A**), **1**/**3** = 3.6/1.7 (**B**), **1**/**2**/**3** = 1.3/1.9/1.3 (**C**)

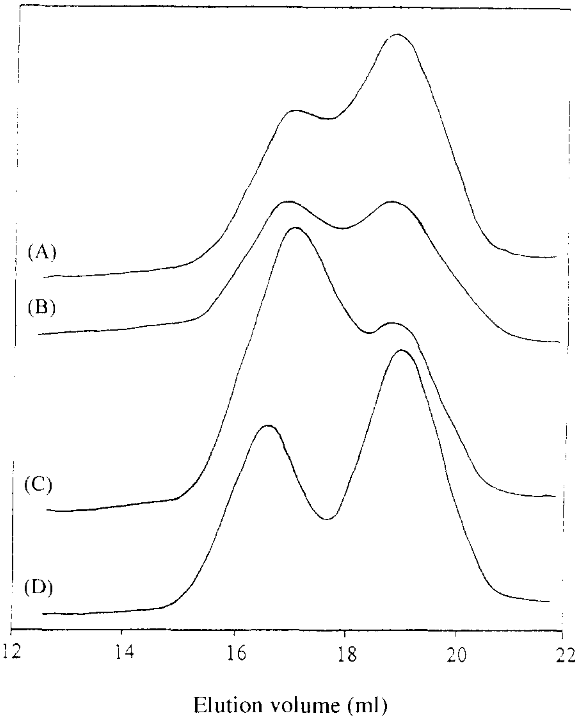

Figure 2 Gel permeation chromotograms of sPS prepared with binary mixed catalyst of $CpTiCl_3$ (**2**)/Cp^*TiCl_3 (**3**) and MMAO cocatalyst: concentrations($\times 10^6$)(mol l^{-1}/mol l^{-1}) of **2**/**3** = 1.9/1.3 (**A**), 1.3/1.9 (**B**), 0.6/2.6 (**C**): mixture of sPS (weight ratio = 1/1) prepared with **2** or **3** alone (**D**)

2 or **3**. The M_W of syndiotactic polystyrene (sPS) obtained with **3** was higher than that of sPS with **1** or **2**. Syndiotactic index (SI) and melting temperature (T_m) of sPS obtained with **1** and **2** were lower than those of sPS with **3**. On the other hand, the dinuclear titanocene **1** gave a higher M_w, M_w/M_n, SI and T_m of sPS than the corresponding mononuclear titanocene **2**, although the catalyst activity of **1** was less than that of **2**. The M_w/M_n of sPS obtained with **1**, **2** or **3** alone was *ca* 2, showing that molecular weight distribution (MWD) of sPS is as narrow as that of polyolefin obtained with metallocene catalyst[1].

To broaden the MWD of sPS, the polymerizations of styrene initiated with the binary or ternary mixed catalyst of **1**, **2** and/or **3** were carried out and the results are given in *Table 2*.

For the binary mixed catalyst of **1**/**2**, the catalyst activity decreased while the M_w and M_w/M_n as well as the SI increased slightly compared to those for **2**. With the addition of **1** to **3**, the MWD of sPS became broader and M_w/M_n increased from 2,4 to 6,4. For the ternary mixed catalysts of **1**/**2**/**3**, the M_w/M_n increased to 8 and sPS of a broader MWD was prepared.

The g.p.c. curves of sPS prepared with the binary and ternary mixed catalysts including **1** were obtained and are shown in *Figure 1*.

For the binary mixed catalyst, the MWD curve (curve A) of sPS obtained with **1**/**2** was almost unimodal, while a bimodal MWD curve (curve B) appeared for sPS prepared with **1**/**3**. With the ternary mixed catalyst of **1**/**2**/**3**, a pseudo-bimodal MWD curve was obtained (curve C). In other words, sPS having a bimodal MWD could be prepared with appropriate arrangement of not only compositions but components of the mixed catalysts.

For the binary mixed catalyst of **2**/**3**, the catalyst activity and M_w as well as SI increased steadily with the added amount of **3**. The T_m of sPS prepared with mixed catalyst also increased with the amount of **3** due to the improving syndiotacticity. The physical properties of sPS after extraction with methylethylketone was almost unchanged (i.e. after extraction of sPS obtained with **2**/**3** (1.3/1.9): M_w, 122 × 10^3; M_w/M_n 7.0; T_m, 268°C).

By adjusting the relative concentration of **3** in the mixed catalyst of **2**/**3**, the M_w/M_n could increase up to 7 and sPS of a broader MWD was prepared. In addition, simple adjustment of the relative concentrations of each component in the mixed catalyst permitted the tailoring of M_w between 98 000 and 136 000.

To check the bimodality in MWD, the g.p.c. curves of sPS prepared with the binary mixed catalysts of **2**/**3** for various compositions were obtained and are shown in *Figure 2*.

For the mixed catalyst of two titanocenes, the MWD curves of sPS had a shoulder (curves A and C). Especially, the clear bimodal MWD (curve B) appeared and M_w/M_n increased to 7 with the appropriate compositions of **2**/**3**. The two maximum peaks of MWD curves were corresponding to those (curve D) of mixture of sPSs which were obtained with each titanocene separately. In addition, the height of two peaks in g.p.c. curves could be controlled by adjusting the relative concentrations of two titanocenes.

Acknowledgement

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