APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2002; **16**: 575–579

DOI:10.1002/aoc.344

Styrene polymerization in the presence of the $CpTiCl_3/Al_2O_3–SiO_2$/MAO catalytic system

Dariusz Jamanek, Anna Woyda and Wincenty Skupiński*

Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warsaw, Poland

Received 28 March 2002; Accepted 15 May 2002

Syndiotactic polymerization of styrene in the presence of heterogenized hemititanocene catalysts $CpTiCl_3/Al_2O_3–SiO_2$/MAO (Cp = cyclopentadienyl; MAO = methylaluminoxane) showed that the yield and selectivity of this reaction depend on the support composition, i.e. on the Al_2O_3 content in the support. The most active catalysts contained Al_2O_3 in a quantity of 50 to 70 wt%. Despite a relatively lower selectivity of 75–59%, the amount of syndiotactic polystyrene in the presence of those catalysts was the greatest. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: polymerization; styrene; titanium; aluminoxane; cyclopentadienyl syndiotactic

INTRODUCTION

Catalysts of syndiotactic styrene polymerization most commonly covered in the literature contain hemicene titanium complexes modified with methylaluminoxane (MAO) or tris-perfluorophenylborane compounds. They act in homogeneous systems in forms dissolved in the monomer or in a suitable solvent.[1–4]

A separate group of procedures to produce syndiotactic polystyrene (s-PS) are heterogenized titanium complexes, also activated with MAO. The titanium complexes here are titanium halides and cyclopentadienyl compounds. The supports for these complexes, according to the literature, are syndiotactic polystyrene itself, natural polycarbohydrates, and magnesia, alumina, or silica gels.[5–9] Use of these catalysts allows one to run the s-PS preparation process in a solventless, fluidized phase.[5] Owing to this approach, the manufacturing costs for this polymer can be lowered significantly. The supports used in this catalyst group may perform as fillers that enhance the mechanical strength of s-PS. The polymer produced in the presence of homogeneous catalysts requires such fillers to be used.[2]

As we mentioned above, the heterogenized catalysts under discussion thus far described used $Mg(OH)_2$, Al_2O_3, or SiO_2 as inorganic supports; in the case of our studies, Al_2O_3–SiO_2 gels were used as catalyst supports. The gels differ from the silica or alumina gels in both their structure and their acid–base properties.[10,11] The aim of our study was to verify whether the different properties allow us to obtain more efficient and selective catalysts for s-PS production.

EXPERIMENTAL

Alumina–silica gels were obtained by precipitation from Na_2SiO_3 (pure-POChem) and $Al(NO_3)_3$ (pure-POChem) water solutions with ammonium nitrate and additional ammonia to reach a pH 8 at 80 °C. The gels thus obtained were separated, washed free of sodium cations, dried at 150 °C for 16 h, calcined at 600 °C, also for 16 h, and crushed into 0.5–1 mm grains. The silica and alumina sources were taken in such a quantity so as to obtain the desired gel compositions. These compositions are abbreviated herein as Al_2O_3 wt%.

The specific surface area, the overall volume of the grain pores, and the average pore diameter of the alumina–silica gels obtained after calcination at 600 °C were measured using a Gemini 2370 ID 529 instrument. The overall acidity of the gels was evaluated by titration with *n*-butylamine.[10] The hydroxyl group content was estimated by titration using naphthalene sodium.[12] The results of these determinations are presented in Table 1.

The IR spectra of the gels calcined at 873 K (wafer technique; Perkin–Elmer System, 2000 FT-IR) demonstrated bands typical of surface hydroxyl groups bonded to the:

- silica phase for SiO_2 (3748–3700 cm^{-1} – isolated vicinal and geminal partly hydrated);
- aluminosilicate phase for 10–70 wt% of Al_2O_3 (a sharp 3748 cm^{-1} – isolated);

---

*Correspondence to: W. Skupiński, Industrial Chemistry Research Institute, Rydygiera 8, 01-793 Warszawa, Poland.
E-mail: wincenty.skupinski@ichp.pl

Table 1. Physico-chemical properties of alumina-silicas

Al_2O_3 (%)	Specific surface (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore diameter (Å)	OH group content (mmol OH g^{-1})	Acidity (mmol g^{-1})	OH surface area (nm^2)
0	388.4	0.73	37.6	0.22	0.5	3.00
10	223.8	0.68	60.4	0.21	0.4	1.74
30	248.7	0.30	24.4	0.10	1.0	4.64
50	184.9	0.23	25.1	0.16	0.6	1.92
70	198.5	0.29	28.9	0.21	1.3	1.58
90	229.8	0.25	21.9	0.21	1.4	1.85
100	67.9	0.25	73.9	0.19	0.5	0.61

- alumina phase for 50–100 wt% of Al_2O_3 (broad 3800–3650 cm^{-1}).[13,14]

All operations in the catalyst preparation procedures and in styrene polymerization were conducted in moistureless and oxygen-free conditions with the use of an argon–vacuum system and the Schlenk technique. The toluene solvent was distilled from Na–K alloy directly prior to use. Styrene (FC DWORY, pure) was distilled from CaH_2. MAO as a 10% toluene solution (WITCO) was used directly. $CpTiCl_3$ was obtained as described previously.[15]

The weighed samples of grains of the alumina–silica gels obtained were placed in a quartz tube and annealed at 600 °C for 16 h under an air flow, then for 1 h in an argon flow, and subsequently cooled to room temperature under argon. The gel grains thus prepared were transferred into Schlenk vessels and a $CpTiCl_3$ solution in toluene was added of a known titre (0.01 M) in a sufficient amount to secure a Ti/OH ratio of 1:2. A similar titanium content in each of the catalyst samples was used in the polymerization reaction. The reaction of the titanium complexes with the surface OH groups proceeded for 16 h at room temperature. Upon completion of the reaction, the toluene was removed from above the grains using a syringe, and the grains were dried under reduced pressure (rotary oil pump vacuum) until the residual toluene was driven off. The catalysts obtained were of different colours, depending on the support, from lemon-yellow for SiO_2 to orange for Al_2O_3.

Into the catalysts thus obtained were added: a 10% MAO toluene solution in a quantity to secure an Al/Ti ratio of 300, then styrene in a quantity of styrene/Ti = 2600. The polymerization reaction was allowed to proceed at 60 °C for 3 h. The reaction was stopped by adding 5 cm^3 of methanol and then 5 cm^3 2% HCl in methanol into the reaction mixture. The polymer obtained was filtered off and dried to a constant weight under vacuum (rotary oil pump) at 90 °C.

The syndiotactic index of the polystyrenes obtained was established as a percentage weight of the polymer fraction insoluble in boiling acetone (6 h under reflux[1]). Polymer melting points were measured by means of the differential thermal analysis method using Perkin–Elmer DSC7 apparatus.

The average molecular weights and their distribution coefficients were determined using Waters-GPC-150 CV apparatus.

RESULTS

The synthesis of the catalysts under investigation proceeded in two stages. In the first stage, $CpTiCl_3$ reacted with the surface OH groups of the alumina–silica gels according to Eqn. (1):

$$CpTiCl_3 + nHO\cdots\square \rightarrow \underset{\textbf{I}}{CpTiCl_{3-n}(\text{--}O\cdots\square)_n} + nHCl \qquad (1)$$

where $n = 1, 2, 3$; $\square$: alumina–silica gel surface.

In this reaction, surface titanium complexes (**I**) are formed; these are permanently bonded to the support surface through an oxygen atom. The measurements of the non-bonded $CpTiCl_3$, evolved HCl, and the quantity of the surface OH groups indicate that every other OH group participates in the reaction in Eqn. (1) and $n = 1$.

In the second stage of the catalyst synthesis, MAO becomes added to the surface titanium complexes in an amount that secures an Al/Ti ratio of 300:1; see Eqn. (2). The ratio is assumed as standard in our studies carried out to date:[16]

$$\begin{aligned} &CpTiCl_2\text{--}O\cdots\square + MAO \\ &\qquad \rightarrow \text{active catalytic centres} + MAO'(\cdots\square) \end{aligned} \qquad (2)$$

As a result of the reaction in Eqn. (2), some active catalytic centres of the catalysts studied are produced along with new MAO′, which contains chloride ligands and O···□ previously bonded to titanium in the surface complex **I**.

The catalyst amounts and compositions, the polymerization reaction yields (styrene conversion), the syndiotactic index of the products (IS), and the composition of the products: (sPS content in the crude products (SsPS), glass transition temperature T_g, melting point T_m, the polymer

Table 2. Composition of the s-PSs and their properties[a]

Catalyst			Conversion	IS_o	SsPS	T_{go}	T_{mo}	$T_{g\ ac}$	$T_{m\ ac}$	$IS_{ac\text{-}II}$		
Al_2O_3 content (%)	(g)	(mmol Ti)	(%)	(%)	(%)	(°C)	(°C)	(°C)	(°C)	(%)	M_w ($\times 10^{-4}$)	M_w/M_n
0	0.212	0.022	46	82	37	97.3	246.3	114.3	259.1	94	5.2	2.11
10	0.274	0.020	55	83	46	99.4	247.4	113.9	255.6	99	9.4	3.04
30	0.452	0.021	54	79	45	105.0	245.8	112.1	255.8	99	14.7	3.94
50	0.318	0.024	88	79	70	114.2	243.8	109.1	256.2	99	9.8	2.99
70	0.360	0.036	81	75	61	108.3	242.4	103.9	255.2	98	10.7	3.84
90	0.300	0.031	60	81	49	98.6	244.0	109.9	257.2	96	13.1	2.98
100	0.328	0.030	16	81	12	96.8	243.6	110.6	256.1	91	4.9	2.39

[a] IS_o, T_{go}, T_{mo}—for crude s-PS; $T_{g\ ac}$, $T_{m\ ac}$—for purifed s-PS (acetone extraction 6 h); $IS_{ac\text{-}II}$—for the second acetone extraction (6 h).

weight-averaged molecular weight M_w, and the molecular weight distribution coefficients M_w/M_n, where M_n is the average molar molecular number), are presented in Table 2. The molecular weight parameters and the distribution coefficients were measured for samples from which low-molecular-weight syndiotactic and atactic polystyrene fractions were removed by extraction with boiling acetone.

The results obtained indicate that the activity of the catalysts studied in terms of styrene conversion increased with the alumina content in the supports over the range from zero to 50 wt%. The styrene conversion for these catalysts increased from 46 to 88%. A further rise in Al_2O_3 content in the catalysts leads to a gradual decrease in their activity, which is due to a drop in substrate conversion to 16% for the catalyst containing neat alumina gel as a support.

The high-activity catalysts exhibit a slightly lower selectivity in s-PS preparation, equal to 75–77%. Considering both the yield and selectivity of the synthesis of this polymer, the most effective catalyst contains 50% Al_2O_3.

The polystyrenes isolated directly from the reaction products showed vitrification points ranging between 96 and 114 °C, whereas the melting points are in the range 242–247 °C.

Extraction with boiling acetone of the polymers obtained made their vitrification point rise to a range of 109–119 °C, whereas the melting points rose to 256–259 °C.

No clear correlation could be noted for the characteristic temperatures of the crude and purified products and the catalyst properties.

Re-extraction with boiling acetone of the polymers obtained showed 99% syndiotacticity coefficients (IS) for the polystyrenes produced in the presence of catalysts containing from 10 to 50% Al_2O_3. For the other polymers the values of this coefficient were smaller, and the values gradually decreased from 99 to 91% for the polymers obtained in the presence of catalysts for which the Al_2O_3 content was raised from 50 to 100%.

The lowest weight-averaged molecular weights of the polystyrenes thus purified, of the order of 5×10^4, were measured for the polymers obtained in the presence of the Al_2O_3- and SiO_2-containing catalysts. The weights for the other polymers are twice as high, and the highest weight of 14.7×10^4 was found in the polymer obtained in the presence of a catalyst containing 30% Al_2O_3.

Scatter coefficients close to two were evaluated for polymers obtained in the presence of the Al_2O_3- and SiO_2-containing catalysts. The coefficients for the other polymers were higher and ranged from 2.98 to 3.94.

DISCUSSION

The heterogeneous catalysts made up of grains of porous inorganic gels have active centres located on both the pore outer surface and the pore wall surface inside the grains. The area of the pore walls commonly exceeds the outer surface area by a few hundred times. The accessibility of the reagents of a given size to the active centres on the inner pore surface should be controlled by pore diameter. If the reaction in the presence of the catalysts studied does occur inside the pores, it would be expected that the reaction yield should depend on pore volume.[11]

A high concentration of the centres on the catalyst surface may, due to steric hindrance, render their full use impossible; e.g. the building up of the polymer chain may make access of monomers to the adjacent and too close by situated catalytic centre difficult. Hence, on the assumption of a uniform distribution of these centres in the catalysts under investigation, proper use should depend on the surface area per one surface hydroxyl group.[17]

The electron-accepting interaction of the surface, which is determined by the amount of *n*-butylamine adsorbed, i.e. overall acidity (the total of the Brönsted and Lewis acid centres), may, by the inductive effect, affect the catalytic activity of the surface complexes.[18]

To find which of these factors is the controlling factor with regard to the yield and selectivity of the heterogeneous titanium catalysts under examination in the reaction of syndiotactic styrene polymerization, some of the suitable properties of the alumina–silica gels used were measured.

A comparison of these properties with the yields and selectivities of the reaction under study failed to provide unambiguous conclusions. This is evidence that none of the parameter measures is critical with regard to the performance of the catalysts used.

The results obtained, however, indicate that the catalysts whose supports are made up of mixed gels, i.e. alumina–silica gels, which are made up of aluminosilicate phases, are more active than those catalysts containing a silica gel or alumina gel only. Examination of the structure of the amorphous alumina–silica gels showed that the amount of aluminosilicate phase increased with the Al_2O_3 content up to a value of 50% by weight. A further rise in alumina content results in the formation of a separate Al_2O_3 phase, which gradually dilutes the aluminosilicate phase.[19] The IR investigation of the gels used showed that their similar composition, in terms of the Al_2O_3 content in the support from 0 to 50%, could be ascribed to a rise in the aluminosilicate phase in the catalysts. The decline in activity observed in the catalysts containing more than 50% Al_2O_3 in the supports is the result of dilution of the aluminosilicate phase with the alumina phase.

The mechanism of syndiotactic styrene polymerization in the presence of hemititanocene catalysts assumed previously admits the following occurrence of the formation of active catalyst forms: (Eqns (3)–(5))

$$\mathrm{CpTiX_3 + MAO \rightarrow CpTiMe_3 + MAO(X_3)} \qquad (3)$$

$$\mathrm{CpTiMe_3 \rightarrow CpTiMe_2 + Me^{\cdot}} \qquad (4)$$

$$\mathrm{CpTiMe_2 + MAO(X_3) \rightarrow CpTiMe^+ + MAO(Me)^-} \qquad (5)$$

where Me = methyl(CH_3).

In these reactions, MAO, which is an oligomer made up of an $-(-O-Al(Me)-)_n-$ skeleton from which up to 30 wt% Me_3Al can be isolated by distillation, is a titanium-ion alkylating agent (cf. reaction (3)) and at the same time a 'soft' Lewis acid that is capable of complexing the CH_3^-.[20] This makes the occurrence of reactions (4) and (5) feasible.[21] As a result of reaction (3), new MAO* = $MAO(X_3)$ is formed; this contains X ligands that can modify the properties of the newly formed catalytic system.[16]

Cation $CpTiMe^+$ is an active form of the catalysts; in addition to this cation, the other titanium complexes occurring in reactions (3) and (4) may also be active in styrene polymerization. Owing to three coordination sites being used in styrene polymerization, cationic $CpTiMe^+$ affords s-PS as the reaction product. The other complexes do not have such a property and can be the centres only of atactic styrene polymerization.[22]

What is most significant in the mechanism of the catalytic centre formation is the fact that the active form of the catalyst does not have the initial X ligands, which are removed in the alkylation reaction (3).

This signifies that if, in the catalysts studied, the formation of active centres follows the same pattern, the $Ti-O-$ support surface bond must become cleaved. The same $Ti-O$ bond cleavage must be considered, say, in the syndiotactic styrene polymerization catalytic system $CpTi(OMe)_3/MAO$, where, likewise, the formation of active centres must proceed through $Ti-O$ bond cleavage.[3]

In the case under study, $MAO(X_3)$ molecules are now linked to the support grain surface, as X is also an $-O\cdots\square$ group, and the active centres, $CpTiMe^+$, go into solution or are adsorbed on the surface of the oligomeric $MAO(X_3)$ molecules bonded to the surface. It is expected that MAO used in excess can also react with the surface OH groups that did not participate in reaction (1) to form an $Al-O-\square$ bond. It can therefore be assumed that the grain surface in the system studied is covered with MAO and $MAO(X_3)$ oligomers bonded to the catalyst surface.

This system is analogous to the ansa zirconocene system deposited on silica gels, where the active form in olefin polymerization is obtained first by a reaction of MAO with the surface OH groups of the inorganic gel, then by depositing zirconium complex.[23]

If this is actually the active form of the catalysts under study, the activating role of the aluminosilicate phase can be seen in an effect of this phase on $CpTiMe^+$ transmitted through the chemisorbed MAO oligomer layer, e.g. through an increased strength or number of the Lewis acid centres in that layer, with a resultant higher yield of reactions (4) and (5).

It is possible that the surface complexes **I** bonded to the aluminosilicate phase may more easily undergo alkylation of the $Ti-O-$ surface of the phase (reaction (3)), compared with the SiO_2 or Al_2O_3 phases. As a result, a larger number of the $CpTiMe^+$ active centres can finally be obtained.

An 80% selectivity of the syndiotactic styrene polymerization in the presence of the catalyst used is indicative of atactic styrene polymerization occurring in the systems under investigation. The process may be initiated by methyl radicals formed in reaction (4) or by titanium complexes that contain two coordination sites only.[22]

The polymers obtained with the use of metallocene catalysts should have similar chain lengths; hence, their distribution coefficient should be close to two.[24]

The higher molecular weights, as well as the relatively greater coefficients of dispersion of molecular weights of the polystyrenes obtained in the presence of the more active catalysts, suggest, on their surfaces, the presence of a relatively greater diversity of the syndiotactic styrene polymerization centers with regard to their high activity, which results in the formation of polymers of different chain lengths.

REFERENCES

1. Ishihara N, Seimiya T, Kuramoto M and Uoi M. *Macromolecules* 1986; **19**: 2464.

2. Kuramoto M, Polystyrene, syndiotactic. In *Polymer Materials Encyclopedia*, Salomon JC (ed.). CRC Press: New York, 1996; 6828.
3. Po R and Cardi N. *Prog. Polym. Sci.* 1996; **21**: 47.
4. Tomotosu N, Ishihara N, Newman TH and Malanga MT. *J. Mol. Catal. A. Chem.* 1998; **128**: 167.
5. European patent, EP 0 535 582 A1, 1992.
6. Lee D, Yoon K, Lee E and Noh S. *Polym. (Korea)* 1995; **19**: 700.
7. Ishihara N and Kuramoto M. *Stud. Surf. Sci. Catal.* 1994; **89**: 339.
8. Soga K, Uozumi T, Yanagihara H and Shiono T. *Macromol. Chem. Rapid. Commun.* 1990; **11**: 229.
9. Soga K and Nakatani H. *Macromolecules* 1990; **23**: 1558.
10. Tanabe K. *Solid Acids and Bases*. Academic Press: London, 1969.
11. Anderson JR. *Structure of Metallic Catalysts*. Academic Press: London, 1975.
12. Kijeñski J, Hombek R and Malinowski S. *J. Catal.* 1976; **50**: 186.
13. Snyder LR and Ward JW. *J. Phys. Chem.* 1966; **70**: 3941.
14. Knoezinger H and Ratnasamy P. *Catal. Rev. Sci. Eng.* 1978; **17**: 31.
15. Gorisch RD. *J. Am. Chem. Soc.* 1960; **82**: 3211.
16. Skupiński W, Wasilewski A, Woźniewski T, Bazarnik A and Jodłowski M. *ICRI Annual Report* 1998; 26.
17. Yermakov YuI. *Catal. Rev. Sci. Eng.* 1976; **13**: 77.
18. Skupiński W and Malinowski S. *J. Mol. Catal.* 1978; **4**: 95.
19. Rouxhet PG, Scokart DO and Damon JP. *J. Colloid Inter. Sci.* 1976; **VIII**: 81.
20. Togni A, Halterman RL (eds). *Metallocenes*. Wiley–VCH: New York, 1998.
21. Grassi A, Zambelli A and Laschi F. *Organometallics* 1996; **15**: 480.
22. Green MLH and Ishihara N. *J. Chem. Soc. Dalton Trans.* 1994; 657.
23. Kaminsky W and Arndt M. *Adv. Polym. Sci.* 1997; **127**: 143.
24. Brintzinger HH, Fischer D, Mülhaupt R, Rieger B and Waymouth RM. *Angew. Chem. Int. Ed. Engl.* 1995; **107**: 1255.