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Syndiotactic Polymerization of Styrene with Supported Kaminsky-Sinn Catalysts

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ABSTRACT: Two kinds of supported catalysts, $Ti(OBu)_4/SiO_2$ (A) and $Ti(OBu)_4/MAO/SiO_2$ (B), were prepared and styrene polymerization was conducted by using the catalyst systems of A with methylaluminoxane (MAO) and B alone. In the case of A with MAO, the rate of polymerization rapidly increased to reach a nearly constant value at a MAO/Ti ratio near 1 (Al/Ti = 20) with a slow increase as the molar ratio MAO/Ti is increased. On the other hand, very high activity was obtained when bulk polymerization was carried out using B. All the polymers obtained with these catalysts were highly syndiotactic (approximately 100%) with narrow molecular mass distributions.

Introduction

Idemitsu Kosan Co. Ltd.[1] has recently succeeded in preparing syndiotactic polystyrene by using Kaminsky-Sinn catalysts composed of some titanium compounds and methylaluminoxane (MAO).[2-4] Zambelli et al.[5,6] reported that some zirconium compounds are also effective for the polymerization when MAO is used as cocatalyst.

More recently, we have succeeded in preparing supported Kaminsky-Sinn catalysts that effectively catalyze syndiotactic polymerization of styrene at a low molar ratio of MAO/Ti. The catalyst systems seem to be useful not only for the production of syndiotactic polystyrene but also for the investigation of the active species in the Kaminsky-Sinn catalyst.

This paper reports the preparation of the catalysts as well as brief results of styrene polymerization with these supported catalysts.

Experimental Section

Materials. Toluene (from Kanto Chemicals Co. Ltd.) was purified by refluxing over calcium hydride for 24 h, followed by fractional distillation. Styrene (from the same company) was washed with an aqueous solution of sodium hydroxide, dried over calcium hydride for 12 h, and distilled under reduced pressure. SiO_2 (350 m^2/g, from Fuji-Davison Chemicals Ltd., grade 952) and γ-Al_2O_3 (150 m^2/g, from Nishio Industry Co.) were heated under reduced pressure at 300 °C for 4 h. $AlMe_3$, $CuSO_4{\cdot}5H_2O$, and $Ti(OBu)_4$ were commercially obtained and used without further purification. Nitrogen (99.9989%, from Toyo Oxygen Co.) was used after passing through a 3A molecular sieve column. Methylaluminoxane (MAO) was prepared from $AlMe_3$ and $CuSO_4{\cdot}5H_2O$ according to literature.[2] It is said that an appreciable amount of the unreacted $AlMe_3$ remains in the MAO.[7] Since $AlMe_3$ is considered to be more reactive than MAO, it is recommended to remove the unreacted $AlMe_3$. From such a viewpoint, 22 mmol of MAO (referred to $AlMe_3$) was brought into contact with 1.2 g of γ-Al_2O_3 for 24 h at room temperature. The MAO thus treated was reserved as a stock solution in toluene (0.40 mmol/dm^3). Sinn et al.[7] measured the CH_3/Al ratio of their MAO by complete hydrolysis and obtained $CH_3/Al = 1.59$. The CH_3/Al ratios of untreated and γ-Al_2O_3-treated MAO were analyzed by a similar method (HCl/H_2O) by using approximately 4-mL samples. The results obtained were as follows: untreated MAO, Al = 2.0 mmol, CH_4 evolved = 3.42 mmol, $CH_3/Al = 1.71$; treated MAO, Al = 2.0 mmol, CH_4 evolved = 3.12 mmol, $CH_3/Al = 1.56$. Thus, the treatment of MAO with γ-Al_2O_3 caused a slight decrease in the CH_3/Al ratio, suggesting that $AlMe_3$ contained in MAO is partly removed. However, the CH_3/Al ratio is still much higher than unity, which indicates that the structure of MAO is very complicated.

Preparation of Supported Catalysts. $Ti(OBu)_4/SiO_2$ catalyst (catalyst A): To a solution of $Ti(OBu)_4$ in toluene (51.4 cm^3, 0.747 mol/dm^3) at room temperature was added 2.3 g of SiO_2. After raising the temperature to the boiling point, the mixture was kept standing for 8 h with vigorous stirring. Then the precipitate was filtered under nitrogen, washed five times with plenty of toluene, and dried under reduced pressure at 40 °C for 4 h. $MAO/Ti(OBu)_4/SiO_2$ catalyst (catalyst B): 9.76 mmol of the MAO (referred to $AlMe_3$) was added dropwise at −20 °C to the slurry containing 10 cm^3 of toluene and 0.30 g of the $Ti(OBu)_4/SiO_2$ catalyst, which had been prepared from 1.5 g of SiO_2 and 37.6 cm^3 of $Ti(OBu)_4$ solution in toluene (0.747 mol/dm^3). Then the mixture was kept standing at room temperature for 1 h. The precipitate was filtered, washed with toluene, and dried under reduced pressure at 40 °C for 4 h.

Polymerization and Analytical Procedures. Polymerization of styrene was carried out in a 0.1 dm^3 glass reactor equipped with a magnetic stirrer. Measured amounts of catalyst A and MAO or catalyst B were placed in the reactor containing styrene or styrene and toluene at room temperature. Polymerization was stopped by adding a mixture of hydrochloric acid and methanol; the mixture was filtered and dried under reduced pressure at 60 °C.

The ^{13}C NMR spectra of the polymers were measured at 25.1 Hz in chloroform-*d* at 60 °C with a JEOL JNH FX-100 spectrometer. The amounts of titanium and aluminum contained in the supported catalysts were determined by atomic absorp-

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Table I
Results of Styrene Polymerization with Various Catalysts[a]

		supported on the cat., mmol/g of SiO_2					polymer yield, mg/mmol of Ti	
run	catalyst, g	Ti	Al	Ti, mmol	MAO,[b] mmol	Al/Ti[b]	syndio[c]	ata[c]
1	$Ti(OBu)_4$, 0.0340			0.10	1.0	10	30	271
2	$Ti(OBu)_4$, 0.0340			0.10	2.0	20	860	0
3	$Ti(OBu)_4$, 0.0340			0.10	3.0	30	716	56
4	$Ti(OBu)_4$, 0.0340			0.10	4.0	40	406	57
5	$Ti(OBu)_4/SiO_2$, 0.100	1.00		0.10	0.5	5	47	0
6	$Ti(OBu)_4/SiO_2$, 0.100	1.00		0.10	1.0	10	595	0
7	$Ti(OBu)_4/SiO_2$, 0.100	1.00		0.10	2.0	20	1800[e]	0
8	$Ti(OBu)_4/SiO_2$, 0.100	1.00		0.10	3.0	30	2190	0
9	$Ti(OBu)_4/SiO_2$, 0.100	1.00		0.10	4.0	40	2100	0
10	$Ti(OBu)_4/MAO/SiO_2$,[d] 0.360	0.616	16.1	0.22	5.8	26	3450	0
11	$Ti(OBu)_4/MAO/SiO_2$,[d] 0.270	0.616	11.0	0.17	3.0	18	10222	0
12	$Ti(OBu)_4/MAO/SiO_2$,[d] 0.140	0.616	14.2	0.088	2.0	23	27028	0

[a] Polymerization was conducted at 20 °C (runs 1–4) or at 40 °C (runs 5–9) for 3 h by using 30 cm^3 of toluene and 10 cm^3 (86.6 mmol) of styrene. [b] Referred to $AlMe_3$. [c] Separated by extraction with boiling MEK. [d] Polymerization was conducted at 40 °C (run 10), 60 °C (run 11), and 90 °C (run 12) for 1 h by using 20 cm^3 (173 mmol) of styrene without solvent. [e] $M_w = 3.3 \times 10^6$, $M_w/M_n = 1.7$.

tion spectrophotometry. The molecular mass distribution of the polymer was measured at 140 °C by GPC (Shodex LC HT3) using *o*-dichlorobenzene as solvent.

Results and Discussion

The contents of Ti and Al in the supported catalysts were obtained from the analysis of the catalysts. Catalyst A contained 1.04 mmol of Ti/g of SiO_2. We previously analyzed the concentration of surface hydroxyl groups of SiO_2, which had been heated under similar conditions, to obtain approximately 1 mmol of OH/g of SiO_2.[8] Therefore, the following reaction might proceed almost quantitatively in the case of catalyst A.

$$>SiOH + Ti(OBu)_4 \rightarrow >SiOTi(OBu)_3 + BuOH$$

On the other hand, the precursor ($Ti(OBu)_4/SiO_2$) of catalyst B was prepared by using a little less $Ti(OBu)_4$ to leave unreacted OH on the SiO_2 surface, which is necessary to fix MAO. The precursor was then reacted with MAO to obtain catalyst B. As shown in Table I, the reproducibility of the contents of Ti and Al in the catalyst was not complete but did not scatter so much. Since MAO is said to be composed of about 20 units of $AlMe_3$,[7] the total contents of $Ti(OBu)_4$ and MAO in these catalysts can be approximately estimated as follows: (mmol of Ti, Al/g of SiO_2) = (0.616, 16.1), (0.616, 11.0), (0.616, 14.2); (mmol of Ti, MAO/g of SiO_2) = (0.616, 0.805), (0.616, 0.550), (0.616, 0.710); total contents of Ti and MAO/g of SiO_2 = 1.42, 1.17, 1.33. Thus, the total contents of Ti and MAO supported on these catalysts agree fairly well with the amount of OH groups on the SiO_2 surface (ca. 1 mmol/g of SiO_2). Although we have to do much more experimentation to clarify the surface compositions on the supported catalysts, the present results may suggest the following scheme that one mole of MAO can be fixed by using only one OH group.

$$>SiOH + MAO \rightarrow >SiO\text{-}MAO + CH_4$$

Polymerization of styrene was conducted by using the catalyst systems of catalyst A with MAO or catalyst B alone. For reference, polymerization was also carried out with the usual homogeneous catalyst composed of $Ti(OBu)_4$ and MAO. The results obtained are summarized in Table I.

When the homogeneous $Ti(OBu)_4$–MAO system was used (runs 1–4), both the polymer yield and syndiotacticity of polystyrene increased remarkably, reached maximum values, and then decreased gradually with an increase in the molar ratio of Al/Ti. The color of the catalyst system changed from yellow at low Al/Ti, to brown at around Al/Ti = 20, and finally to dark brown at high Al/Ti. The crude polymers were separated by extracting with boiling methyl ethyl ketone (MEK) for 8 h. From the ^{13}C NMR analysis, the MEK-insoluble and -soluble polymers were confirmed to be highly syndiotactic (approximately 100%) and atactic, respectively. Thus, the polymers obtained at very low and high molar ratios of Al/Ti are mixtures of syndiotactic and atactic polystyrene. The highly syndiotactic polystyrene is considered to be produced via a coordination mechanism catalyzed by the active species formed between $Ti(OBu)_4$ and MAO. Atactic polystyrene might be produced via cationic or radical species. However, the precise mechanism is not clear at present. When polymerization was conducted by using catalyst A combined with MAO (runs 5–9), the polymer yield increased to reach a saturated value at around MAO/Ti = 1 (Al/Ti = 20) and then it did not change much in the range 20 < Al/Ti < 40 with increasing the molar ratio of Al/Ti. The syndiotacticity of polystyrene, on the other hand, was approximately 100%, independent of the Al/Ti ratio. It may be said, therefore, that the active species formed on SiO_2 are more stable against reduction as compared with those formed in the homogeneous $Ti(OBu)_4$ and MAO system.

As mentioned above, MAO is said to be composed of about 20 units of $AlMe_3$, indicating that Al/Ti = 20 is equivalent to MAO/Ti = 1. Thus, these results strongly suggest that the active species in these catalyst systems include equimolar amounts (1:1) of MAO and $Ti(OBu)_4$.

Polymerization of styrene was finally carried out by using catalyst B ($Ti(OBu)_4/MAO/SiO_2$) alone. Since the catalyst is solid and requires no additives, both gas-phase and bulk polymerizations (without solvent) could be conducted by using this catalyst. Typical results obtained in bulk polymerization are shown in Table I (runs 10–12). The catalyst was thus found to be highly effective for the production of syndiotactic polystyrene. In addition the polymerization activity increased remarkably on raising the polymerization temperature from 40 to 90 °C, which may be due to the stability of the active species formed on the surface.

It is not clear at present whether the real active species is a simple 1:1 complex formed between MAO and a transition-metal compound or some complicated reaction product between them. However, it may be said that this catalyst system is very different from the usual Kaminsky-Sinn catalysts composed of MAO and Cp_2TiCl_2 etc., which effectively catalyze olefin polymerization.

As is well-known, heterogeneous catalyst systems usually give polymers having molecular mass distributions with a broad polydispersity.[9] However, the polydispersity of syndiotactic polystyrene obtained with the present heterogeneous catalysts was very narrow, indicating that these catalysts contain not multiple but single, equivalent active species.

In conclusion, we have prepared a new supported Kaminsky-Sinn catalyst useful for the syndiotactic polymerization of styrene.

A more detailed study is now being carried out, mainly to clarify the nature of active species in the present catalyst system, and the precise results will be published in another paper.

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Intramolecular O-H Bond Length and Quadrupole Coupling Constants of Water in Polyelectrolyte Solutions. A Nuclear Magnetic Relaxation Study

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ABSTRACT: The relaxation rates of D and ^{17}O and the rate of H due to dipolar coupling to ^{17}O were obtained in a series of poly(acrylic acid) solutions completely neutralized with lithium and cesium hydroxide. From these data the intramolecular O-H bond distance and quadrupole coupling constants have been derived. It is found that the changes in O-H bond distance and quadrupolar coupling constants induced by the charged polymer and its counterions are moderate.

Introduction

A D and ^{17}O quadrupolar relaxation study on water dynamics in linear polyelectrolyte solutions was reported recently.[1] It was found that the solvent dynamical perturbation is confined to the vicinity of the macromolecular surface. The water reorientational mobility near the chain decreases and is sensitive to the specific short-range polyion-counterion interaction. In a small-angle neutron-scattering and X-ray scattering study, a monomolecular hydration layer between the poly(methacrylic acid) (PMA) polyion and the accumulated counterions was observed.[2] The structure around lithium counterions in completely neutralized poly(acrylic acid) (PAA) solutions has been investigated by the first-order-difference neutron diffraction method.[3] It was shown that counterions remain hydrated when they accumulate about a highly charged linear macromolecule. From these high-resolution neutron diffraction experiments it was concluded that these hydration water molecules are still oriented with their oxygen atoms toward the small ions.

The D and ^{17}O relaxation rates are completely intramolecularly determined by the quadrupolar relaxation mechanism. The corresponding correlation times refer to reorientation of the intramolecular coupling tensor; the coupling constants may depend on intermolecular interactions. In the previous investigation on water dynamics in completely neutralized PAA and poly(styrenesulfonic acid) (PSS) solutions, a possible deviation of the coupling constants from the pure water values was not considered. However, if water molecules are hydrogen bonded to polymeric charged sites, the coupling constants may be affected considerably. Therefore, to investigate a possible change in coupling constants, the ^{17}O-induced H relaxation in ^{17}O-enriched solutions is explored and compared to D relaxation.

From this comparison, values of the intramolecular O-H bond distance and D coupling constant can be derived.[4] The O-H bond distance provides an indication about specific interaction of a water molecule with a charged site. For instance, stretching of the O-H bond distance is observed when a water molecule coordinates to an ion such as F^-, Li^+, Mg^{2+}, Zn^{2+}, and Al^{3+}.[4,5] In water-dimethyl sulfoxide (DMSO) mixtures, a variation of the D coupling constant over the water fraction has been observed too.[6] This has been attributed to specific water-DMSO interaction and/or disruption of the H bond network.

Theory

In PAA solutions the water reorientational motion occurs on the picosecond time scale.[1] As a consequence, the

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