Note

Synthesis of Ultra-high Molecular Weight Polystyrene with a Catalyst System Based on Calixarene-yttrium Complex

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Polymerization of styrene (St) with a new catalyst system composed of calixarene-yttrium complex, magnesium-aluminium alkyls and hexamethyl phosphoramide was studied. The catalyst system shows extremely high activity (> 7 × 10⁶ g PSt/mol Y · h) and gives polystyrene with very high viscosity-average molecular weight (> 5 × 10⁵).

Keywords polystyrene, polymerization, rare earth catalyst, calixarene

Introduction

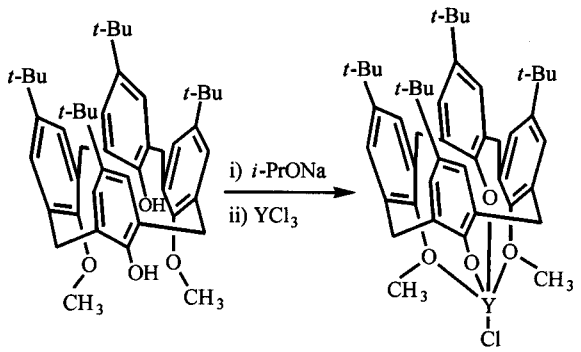
In order to exploit new applications of rare-earth catalysts in polymer synthesis, polymerization of styrene with rare earth catalyst has been carried out in our lab recently.[1-6] In this paper the new catalytic system of calixarene-yttrium for the preparation of ultra-high molecular weight polystyrene ($M_w > 4 \times 10^5$) is reported, because of its excellent mechanical and thermal characteristics compared with the general purpose polystyrene.

Experimental

Materials

Styrene (chemical reagent grade) was dried over calcium hydride for several days, then distilled under reduced pressure. Toluene was refluxed over sodium benzophenone and distilled under dry nitrogen atmosphere. HMPA (hexamethyl phosphoramide) was refluxed over calcium hydride and distilled through a Vigreux column under reduced pressure. Triethylaluminium ($AlEt_3$) was purchased from the Roth Chemical Co.. 1,3-Methyl ether calix[4]arene and 1,3-methyl ether calix[4]arene-neodynium (C_4Nd) were prepared according to the reported method.[6] 1,3-Methyl ether calix[4]-arene-yttrium (C_4Y) was synthesized following a procedure for the preparation of 1,3-methyl ether calix[4]arene-neodynium (C_4Nd) (Scheme 1).[6] A toluene solution of magnesium-aluminium alkyls [$Mg(n\text{-}Bu)_2\text{-}AlEt_3$] was prepared according to the reference.[4] Magnesium and aluminium concentrations of the $Mg(n\text{-}Bu)_2\text{-}AlEt_3$ solution were determined by EDTA titration of the aqueous portion of hydrolyzed sample at pH 10 and 4.5, respectively.

Scheme 1



Polymerization

All the procedures were carried out under dry nitrogen atmosphere. A certain amount of rare-earth complex solution, the $Mg(n\text{-}Bu)_2\text{-}AlEt_3$ solution and HMPA were added to a bottle to produce a catalyst system and then styrene was injected via syringe. The polymerization was performed at 70 ℃. After a certain time, the reaction was terminated by addition of ethanol with 10% hydrochloric acid. The resultant polymer was purified by the dissolution-sedimentation method, and finally dried *in vacuo* at 50 ℃.

Measurements

The intrinsic viscosity of the polymer was measured with an Ubbelohde-type viscometer at 30 ℃ in toluene. The viscosity-average molecular weight (M_η) was calculated according to the equation:[7]

$$[\eta] = 9.2 \times 10^{-5} M_\eta^{0.72}$$

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Results and discussion

The polymerization results of styrene with Mg(n-Bu)$_2$-AlEt$_3$/HMPA, C_4Nd/Mg(n-Bu)$_2$-AlEt$_3$/HMPA and C_4Y/Mg(n-Bu)$_2$-AlEt$_3$/HMPA catalyst systems are listed in Table 1. The C_4Y/Mg(n-Bu)$_2$-AlEt$_3$/HMPA catalyst system shows the highest activity and gives the highest molecular weight polystyrene in the three catalytic systems. It is more interesting that the polystyrene obtained with C_4Y as a main catalyst has very high viscosity-average molecular weight as high as 56.9×10^4.

Table 1 Polymerization of styrene with various catalyst systems

Catalyst system	Mg/HMPA	C_4Nd/Mg/HMPA	C_4Y/Mg/HMPA
Conv. (%)	32	53	97
M_η (10^4)	6.5	11.4	56.9

Polymerization conditions: St/Ln (mol/mol) = 4.0×10^4, Mg/Ln (mol/mol) = 40, Mg: Mg(n-Bu)$_2$-AlEt$_3$[Mg/Al (mol/mol) = 6.69], HMPA/Mg (mol/mol) = 1, T = 70 ℃, t = 1.5 h.

The molar ratio of styrene to C_4Y (St/Y) has great influence on the polymerization (Fig. 1). The monomer conversion increases with the decreasing of St/Y molar ratio, which is due to the increasing of the concentration of active species. The molecular weight increases with the decreasing of St/Y molar ratio and reaches the maximum value at St/Y molar ratio of about 4.0×10^4. The catalytic activity of 7.4 $\times 10^6$ g PSt/mol Y · h was obtained. Further decreasing of St/Y molar ratio causes the molecular weight of PSt to decrease as observed in polymerization of styrene with [Nd(P_{204})$_3$]/Mg(n-Bu)$_2$-AlEt$_3$/HMPA catalyst system.[5]

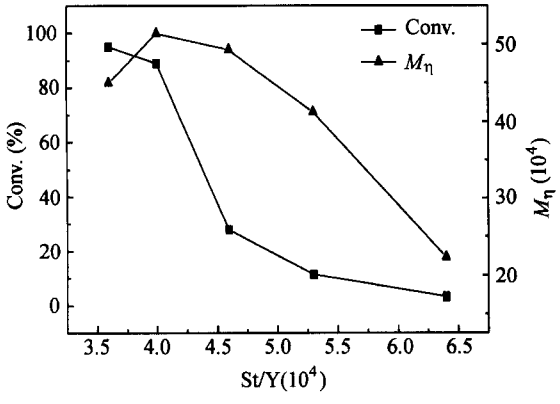

Fig. 1 Effect of St/Y molar ratio on the polymerization. Conditions: Mg/Y (mol/mol) = 40, Mg/Al (mol/mol) = 6.69, HMPA/Mg (mol/mol) = 1, T = 70 ℃, t = 0.5 h.

The effect of the molar ratio of Mg(n-Bu)$_2$-AlEt$_3$ to C_4Y (Mg/Y molar ratio) on the polymerization was also investigated. As shown in Fig. 2, the monomer conversion increases with the increasing of Mg/Y molar ratio. The increase of the catalytic activity can be ascribed to the more active species produced from the alkylation of the C_4Y under higher Mg/Y molar ratio.

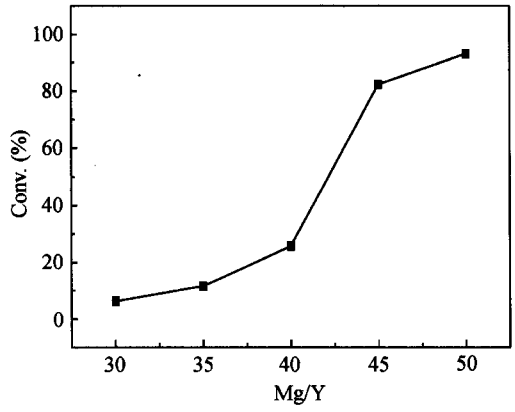

Fig. 2 Effect of Mg/Y molar ratio on the polymerization. Conditions: St/Y (mol/mol) = 5.3×10^4, Mg/Al (mol/mol) = 6.69, HMPA/Mg = 1, T = 70 ℃, t = 0.5 h.

References

1 Zhao, J.; Yang, M.-J.; Zheng, Y.; Shen, Z.-Q. *Makromol. Chem.* **1991**, *192*, 309.

2 Yang, M.-J.; Cha, C.-X.; Shen, Z.-Q. *Chin. J. Polym. Sci.* **1992**, *10*, 106 (in Chinese).

3 Zhao, J.; Yang, M.-J.; Zheng, Y.; Shen, Z.-Q. *Chin. J. Polym. Sci.* **1991**, *9*, 65 (in Chinese).

4 Jiang, L.-M.; Shen, Z.-Q.; Zhang, Y.-F.; Zhang, F.-R. *J. Polym. Sci., Polym. Chem.* **1996**, *34*, 3519.

5 Jiang, L.-M.; Shen, Z.-Q.; Yang, Y.-H.; Zhang, Y.-F. *Polym. Int.* **2001**, *50*, 63.

6 Zheng, Y.-S.; Shen, Z.-Q. *Eur. Polym. J.* **1999**, *6*, 1037.

7 Brandrup, J.; Immergut, E. H. *Polymer Handbook*, Interscience Publishers, **1975**, IV-18.

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