Polymer 42 (2001) 4087–4090

polymer

www.elsevier.nl/locate/polymer

Isospecific polymerization of styrene with modified ziegler-type catalysts

Qi Sun[a], Yinheng Fan[a], Shijian Liao[b,c,*], Jing Liu[b], Fudong Wan[b], Jie Xu[b]

[a]*Department of Chemistry, Liaoning Normal University, Dalian 116029, People's Republic of China*
[b]*Dalian Institute of Chemical Physics, The Chinese Academy of Sciences, P.O. Box 110, Dalian 116023, People's Republic of China*
[c]*Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences, Shanghai 200032, People's Republic of China*

Received 21 March 2000; received in revised form 21 June 2000; accepted 17 July 2000

Abstract

Effects of various kinds of additives as well as aging of the catalyst on the polymerization of styrene catalyzed by $TiCl_4/MgCl_2–AlEt_3$ system have been studied. Experiments show that in toluene the isotacticity of polystyrene can be up to 83% for aged catalyst, whereas when the catalyst is not aged, non-stereospecific polymer is the main product. When PCl_3 is used as an additive, the catalyst system gives high activity and isotacticity. The use of a mixture of $AlEt_3/H_2O$ (1:1 mole ratio) as a cocatalyst is also efficient. The catalyst $[TiCl_4–PCl_3/MgCl_2–AlEt_3/H_2O]$ displays high activity and product isotacticity (94%) with an average molecular weight up to 2×10^{-6}. When $Co(acac)_3$ is added to $[TiCl_4/MgCl_2–AlEt_3]$ catalyst after it was aged, the isotacticity can be up to 97%.

Keywords: Polymerization of styrene; Supported titanium catalyst; Stereospecificity

1. Introduction

It has been reported in the literature that syndiotactic, isotactic and atactic polystyrene can be obtained by using different catalyst systems [1–13]. Isotactic polystyrene was obtained using $TiCl_4/MgCl_2–AlEt_3$ catalyst, in which the isotacticity could be up to 84% [2]. In the recent years, much effort has been made to enhance the catalyst activity and stereospecificity for the polymerization of styrene. Kashiwa et al. [3] found that the catalyst stereospecificity for the polymerization of styrene could be improved using a $TiCl_4$/ethyl benzoate(EB)/$MgCl_2–AlEt_3$ catalyst in combination with EB as an external donor. The isotacticity can be increased up to 90% [3]. Lin et al. [10] reported that high catalytic specificity was obtained by the addition of a rare-earth compound to the titanium catalyst ($TiCl_4–NdCl_3/MgCl_2–AlR_3$). In this paper, we report the polymerization of styrene using modified Ziegler-type catalysts. These catalysts show both high specificity and activity in the isospecific polymerization of styrene. At the same time, isotactic polystyrene with high molecular weight was achieved. Moreover, a synergic effect has been observed using multimetallic catalyst system.

2. Experimental

2.1. Materials and catalysts

Argon was dried and deoxygenated by 5A molecular sieve and activated Cu at 180°C. Toluene (A.R) was distilled from sodium benzophenone under argon before use. $120^{\#}$-Petrol (a kind of petrol with a boiling point range between 80 and 120°C which is mainly composed of saturated aliphatic hydrocarbons) was dried with 5A molecular sieve under argon. Styrene was distilled from calcium hydride and stored in a refrigerator under argon in darkness. $AlEt_3$ was commercially available and used without further purification. Various additives were commercial products and purified according to the usual procedures. The anhydrous $MgCl_2$ (15.6 g) was firstly heated at 550°C for 4 h under evacuation, and then milled with $TiCl_4$ (1 ml) (or together with PCl_3 etc.) in a vibration mill at a high frequency ($100\ s^{-1}$) without solvent for 8 h. The prepared catalyst was stored in a Schlenk tube under dry Ar. This supported catalyst was used as prepared without washing. The catalyst $[TiCl_4/MgCl_2–AlEt_3(aged)]–Co(acac)_3$ was made by mixing $TiCl_4/MgCl_2$ and $AlEt_3$ together, stirred (aged) for 20 min, then $Co(acac)_3$ ($Fe(acac)_3$, or $NiCl_2$) was added and the catalyst was used immediately. The catalyst $[TiCl_4/MgCl_2–Co(acac)_3]–AlEt_3$ was made by mixing the $TiCl_4/MgCl_2$ and $Co(acac)_3$

---

* Corresponding author. Tel.: +86-411-469-1570; fax: +86-411-4691-570.

PII: S0032-3861(00)00607-8

Table 1
Effect of various additives and solvents on the polymerization of styrene catalyzed by $TiCl_4/MgCl_2-AlEt_3$ system (polymerization conditions: 50°C; 2 h; 5 ml styrene; 10 ml solvent; $Ti = 1.6 \times 10^{-5}$ mol; $Al/Ti = 20$; $TiCl_4/AlCl_3 = 1$; $TiCl_4/PCl_3 = 1$, $TiCl_4$/aconitic acid = 1)

Catalyst	Solvent	Activity(gPS/gTi)	Acetone-insoluble part (wt%)	$M_\eta \times 10^{-5}$	T_m (°C)
$TiCl_4/MgCl_2-AlEt_3$	$120^{\#}$-Petrol	731	25	6.3^{a}	236
$TiCl_4/MgCl_2-AlEt_3$(aged)^{b}	$120^{\#}$-Petrol	101	80	7.2^{a}	228
$TiCl_4/MgCl_2-AlEt_3$	Toluene	1100	trace	0.35^{c}	88
$TiCl_4/MgCl_2-AlEt_3$(aged)^{b}	Toluene	160	83	9.2^{a}	231
$(TiCl_4-AlCl_3)/MgCl_2-AlEt_3$	Toluene	1008	0	0.42^{c}	89
$(TiCl_4-AlCl_3)/MgCl_2-AlEt_3$(aged)^{b}	Toluene	171	81	8.9^{a}	228
$(TiCl_4-PCl_3)/MgCl_2-AlEt_3$	Toluene	2510	83	5.7^{a}	235
$(TiCl_4-PCl_3)/MgCl_2-AlEt_3$(aged)^{b}	Toluene	1320	94	8.2^{a}	232
($TiCl_4$–aconitic acid)/ $MgCl_2-AlEt_3$	Toluene	307	0	0.40^{c}	88

[a] Referred to acetone-insoluble part.
[b] Aged for 20 min.
[c] Referred to acetone-soluble part.

together, stirred for 20 min, then $AlEt_3$ was added. This catalyst was used immediately.

2.2. Polymerization of styrene

The polymerization of styrene was carried out in a 50 ml three necked jacketed flask closed with self-sealing silicon rubber septum, and connected to the vacuum, argon lines. The temperature of the water circulating through the jacket was maintained by a thermostat. Agitation was provided by a magnetic stirrer. The temperature of the reaction flask was raised to 50°C (reaction temperature). It was alternately evacuated and flushed with argon three times. In the case of catalyst without aging, we added the supported Ti catalyst, solvent (10 ml), styrene (5 ml) successively under stirring (15 min), then $AlEt_3$ was added and the reaction started immediately. In the case of catalyst aging, the supported Ti catalyst, solvent and $AlEt_3$ were added into the reactor successively. It was stirred under Ar for 20 min (aging). After which the styrene was added and the reaction started immediately. The so-called time of aging was the time for the reaction between $TiCl_4/MgCl_2$ and $AlEt_3$ before the catalyst was used. Polymerization mixture was stirred for 2 h, and then quenched by the addition of 2 ml alcohol. The whole product was then poured into 50 ml of alcohol. The resulting precipitate was collected by filtration and vacuum dried at 80°C for 8 h.

2.3. Polymers characterization

The polystyrene sample was extracted by boiling acetone with a Soxhlet extractor for 5 h. The isotacticity (wt%) of polystyrene was defined as the weight fraction of acetone-insoluble part. The acetone-insoluble part (isotactic polystyrene) was examined by ^{13}C-NMR using a Bruker DPX300 NMR spectrometer at 27°C in *o*-dichlorobenzene containing 10% C_6D_6. Only a single peak was found at 146.56 ppm. The viscosity-average molecular weight was determined by the viscosity method [15] using toluene as a solvent.

3. Results and discussion

In order to improve the catalytic activity and stereospecificity, various kinds of additives, such as PCl_3, $AlCl_3$, aconitic acid, ethylene diamine, triphenyl phosphine, and benzoic acid, were milled with $TiCl_4$ supported on $MgCl_2$ using a vibration mill at a high frequency. The experimental results are listed in Table 1. Experiments show that the sequence of adding various catalyst components and substrate as well as aging of the catalyst are very important. For the aged catalyst in toluene the amount of acetone-insoluble part which is isotactic polystyrene as shown by ^{13}C-NMR can be up to 83%, whereas, when the catalyst is not aged, i.e. $TiCl_4/MgCl_2$ and $AlEt_3$ are added to the reaction system and polymerization starts immediately, non-stereospecific polymer is the main product. Only a trace amount of isotactic polystyrene is produced. One of the functions of catalyst aging is to reduce titanium (IV) to its lower valence state. Therefore, the isotactic active site of this catalyst system ($TiCl_4/MgCl_2-AlEt_3$) might be the Ti species of low valence state and the non-stereospecific site might be the Ti species of high valence state. The choice of solvent is also crucial for the $TiCl_4/MgCl_2-AlEt_3$ system. In $120^{\#}$-petrol when the catalyst is not aged, the isotacticity of polystyrene is 25%, whereas in toluene, no isotactic polystyrene can be obtained. The catalytic activity is higher in toluene than that in $120^{\#}$-petrol. Among the various modified catalysts, $(TiCl_4-PCl_3)/MgCl_2-AlEt_3$ system gives both high activity and stereospecificity even if it is not aged before use. The isotacticity can be up to 83%. If the corresponding catalyst is aged, the isotacticity can reach 94%, although the catalyst activity somewhat decreases. Aconitic acid markedly inhibits the catalytic activity. For other additives, either

Table 2
Effect of PCl_3 content on the styrene polymerization catalyzed by $(TiCl_4–PCl_3)/MgCl_2–AlEt_3$ (polymerization conditions are the same as in Table 1, solvent: toluene)

P/Ti ratio	Polymerization temperature (°C)	Activity (g PS/g Ti)	Acetone-insoluble part (wt%)	$M^{a}_{\eta} \times 10^{-5}$	T_m (°C)
0.5	50	1687	22	4.8	219
0.7	50	1958	45	5.1	225
1	50	2510	83	5.7	235
1	25	1650	73	6.0	226

[a] Referred to acetone-insoluble part.

the catalyst system displays no activity at all (ethylene diamine, triphenyl phosphine, benzoic acid etc.) or only a slight effect can be observed on the catalyst behavior, e.g. when $AlCl_3$ is used as an additive. The molecular weight of the isotactic fraction is much higher than that of the acetone-soluble fraction. In addition, the molecular weight of the isotactic fraction obtained by aged catalyst increases somewhat in comparison with that obtained by catalyst without aging. Table 2 shows the influence of PCl_3 content on the styrene polymerization catalyzed by $[(TiCl_4–PCl_3)/MgCl_2–AlEt_3]$. The addition of PCl_3 to the catalyst markedly enhances both the catalyst activity and selectivity. Furthermore, when the amount of PCl_3 is increased, the catalysts exhibit a higher activity and stereospecificity for the polymerization of styrene, meanwhile there is only a slight increase in the molecular weight of isotactic polystyrene. In addition, when the polymerization temperature decreases from 50 to 25°C, the catalyst activity decreases significantly and the isotacticity also decreases. $MgCl_2$ is not an inert carrier for the catalyst. The nature of $TiCl_4$ is changed partially by milling $MgCl_2$ with it. The situation becomes more complicated by adding additives to $TiCl_4$ supported on $MgCl_2$. Among which, the PCl_3 can be strongly bonded to the $MgCl_2$ crystal lattice according to a report by Coutinho et al. [14]. PCl_3 in relation to $TiCl_4/MgCl_2$ may function as a Lewis base acting as an internal electron donor. A mixture of $AlEt_3/H_2O$ (1: 1 mole ratio) as cocatalyst is also effective (Table 3). Both the activity and stereospecificity are increased by using the catalyst activated with $AlEt_3/H_2O$ instead of $AlEt_3$. Catalyst composed of $[(TiCl_4–PCl_3)/MgCl_2–AlEt_3/H_2O]$ displays high stereospecificity (93%) and activity. In this case, the viscosity-average molecular weight of isotactic part increases remarkably up to 2×10^6. The increase of molecular weight can be attributed to the decrease of chain transfer reactions with $AlEt_3/H_2O$. In a previous paper we have reported the synergic effect of multimetallic catalysts in the cyclotrimerization of butadiene [16]. In the polymerization of styrene the effect of adding a second transition metal compound, such as $Fe(acac)_3$,$Co(acac)_3$, and $NiCl_2$ etc. to the $TiCl_4/MgCl_2–AlEt_3$ system has been studied (Table 4). Experimental results indicate that both activity and stereospecificity are slightly affected by the addition of $Fe(acac)_3$ to the catalyst and decreased by the addition of $NiCl_2$. The isotacticity of polystyrene can be increased up to 97% by the addition of $Co(acac)_3$ to the Ti–Al system. The second metal compound must be added to the Ti–Al system after $[TiCl_4/MgCl_2–AlEt_3]$ catalyst was aged, otherwise the catalyst would lose its entire activity. The second metal compound itself (Fe, Co, Ni) combined with $AlEt_3$ shows no catalytic activity in the polymerization of styrene under these reaction conditions.

4. Conclusion

Modified catalysts were prepared by milling the anhydrous $MgCl_2$ with $TiCl_4$ and various kinds of additives, among which, PCl_3 was an effective additive in enhancing both the catalyst activity and stereospecificity. The nature of the catalyst was strongly affected by aging the catalyst system, since the valence state of titanium (IV) species

Table 3
Polymerization of styrene catalyzed by $(TiCl_4–PCl_3)/MgCl_2$ or $TiCl_4/MgCl_2$ using $AlEt_3/H_2O$ as a cocatalyst (Ti: P = 1; $AlEt_3/H_2O$ = 1, other polymerization conditions are the same as in Table 1)

Catalyst	Al/Ti (mole ratio)	Ti (Ti × 10^{-5})	Activity (gPS/gTi)	Acetone-insoluble part (wt%)	$M^{a}_{\eta} \times 10^{-5}$	T_m (°C)
$TiCl_4/MgCl_2–AlEt_3/H_2O$	20	1.6	1720	87	11.9	228
$TiCl_4/MgCl_2–AlEt_3/H_2O$(aged)	20	1.6	630	94	12.1	238
$(TiCl_4–PCl_3)/MgCl_2–AlEt_3/H_2O$	45	1	2540	93	21.4	230
$(TiCl_4–PCl_3)/MgCl_2–AlEt_3/H_2O$(aged)	45	1	1240	94	20.2	232

[a] Referred to acetone-insoluble part.

Table 4
Activity and isotacticity of styrene polymerization catalyzed by [$TiCl_4/MgCl_2$–$AlEt_3$(aged)] + MX_n system ($Ti/MX_n = 1$, other polymerization conditions are the same as in Table 1)

Catalyst	Activity (gPS/gTi)	Acetone-insoluble part (wt%)	$M^a_\eta \times 10^{-5}$	T_m (°C)
$TiCl_4/MgCl_2$–$AlEt_3$(aged)	160	83	9.2	231
[$TiCl_4/MgCl_2$–$AlEt_3$(aged)]–$NiCl_2$	101	80	8.7	228
[$TiCl_4/MgCl_2$–$AlEt_3$(aged)]–Fe(acac)$_3$	160	86	9.0	230
[$TiCl_4/MgCl_2$–$AlEt_3$(aged)]–Co(acac)$_3$	600	97	10.2	233
[$TiCl_4/MgCl_2$ + Co(acac)$_3$]–$AlEt_3$	0	–	–	–

[a] Referred to acetone-insoluble part.

would be reduced by the cocatalyst (triethylaluminum). As a cocatalyst, $AlEt_3/H_2O$ was more effective than $AlEt_3$ for the preparation of isotactic polystyrene with high molecular weight. Multimetallic catalyst was prepared in order to improve the catalytic activity and stereospecificity further. A remarkable synergic effect was found in the [$TiCl_4$/$MgCl_2$–AlEt (aged)]–Co(acac)$_3$ catalyst system. The isotacticity of the polymer generated could be up to 97%.

Acknowledgements

This project was supported by the Educational Committee of Liaoning Province, People's Republic of China.

References

[1] Soga K, Monoi T. Macromolecules 1990;23:1558.
[2] Kashiwa N. Polym Prepr 1985;26:370.
[3] Kashiwa N, Yoshitake J, Tsutsui T. Polym Commum 1987;28:292.
[4] Kaminsky W, Lenk S. Macromol Chem Phys 1994;195:2093.
[5] Crossetti GL, Bormioli C, Ripa A, Giamsso A, Porri L. Macromol Chem Rapid Commun 1997;18:801.
[6] Boucher DG, Parsons IW. Polymer 1981;22(2):255.
[7] Dias ML, Crossetti GL, Bormioli C, Giarusso A, Maria LCS, Coutinho FMB, Porri L. Polym Bull 1998;40:689.
[8] Xu XX, Xie GH. Acta Polym Sinica 1997;2:253.
[9] Porri L, Giarusso A, Crossetti GL, Ripa A, Ricci G. Polym Prepr 1996;37(2):470.
[10] Zhou XH, Zhao ZH, Lu Y, Lin SA. Acta Polym Sinica 1987;4:265.
[11] Kucht A, Kucht H, Barry S, Chien JCW, Rausch MD. Organometallics 1993;12:3075.
[12] Thomas ER, Roberta OD, James CWC, Marvin DR. Macromolecules 1993;26:5822.
[13] Longo P, Grassi A, Oliva L, Ammendol P. Makromol Chem 1990;191:237.
[14] Coutinho FMB, Xavier JLL. Eur Polym J 1997;33(6):897.
[15] Danusso F, Moraglio G. J Polym Sci 1957;24:161.
[16] Sun Q, Liao SJ, Xu Y, Yu DR. Chem J Chin Univ 1997;6:951.