Syntheses and Characterizations of Polypropene, Polystyrene and Their Block Copolymers with Titanocene Catalysts

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Summary: Pentamethylcyclopentadienyltitanium tribenzyloxide, $Cp^*Ti(OBz)_3$, was used as the catalyst precursor for polymerizations of propene and styrene. The titanocene catalyst affords atactic polypropene and syndiotactic polystyrene with high activities in the presence of methylalumimoxane (MAO). Block copolymerization of propene and styrene was carried out in the presence of $Cp^*Ti(OBz)_3$/MAO catalyst system by the means of external addition of triisobutylaluminum (TIBA) and sequential monomer feed. The copolymerization product is mainly a mixture of atactic polypropene(aPP) and syndiotactic polystyrene(sPS) homopolymers and aPP-b-sPS block copolymers, which can be separated into fractions with successive extraction with boiling methylethyl ketone(MEK), heptane, tetrahydrofuran(THF), and chloroform. Studies on thermal properties showed that rubbery phases and crystalline regions both appear in the block copolymer at the room temperature and that aPP-b-sPS block copolymer has better toughness than sPS.

Keywords: block copolymer; metallocene catalysts; polymerization; polypropene; syndiotactic polystyrene

Introduction

Ishihara et. al. firstly used a monotitanocene $CpTiCl_3$ and MAO to prepare sPS.[1] Up to now, plenty of investigations have been made in relation to catalyst systems and catalytic activity for syndiotactic styrene polymerization.[2-4] With regard to Group 4 metal coordination compounds, it was shown that titanium complexes are much more effective than those of zirconium and hafnium. Also, it was revealed that catalytic activity and molecular weight of the product could be improved by designing more electron-donating catalysts.[5-7] Syndiotactic polystyrene has held a great interests because of its high performances as thermoplastic engineering material, e.g. outstandingly high melting point of 270 °C, high modulus of elasticity, low viscosity, low specific gravity as well as excellent resistance to chemicals and moisture.

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Copolymerizations of styrene with ethylene or dienes have been done with some metallocene catalyst systems.[8-12] The products were mainly alternating copolymers and random or pseudorandom copolymers with isolated styrene units and low styrene content. The complexity of styrene and olefins copolymerization is attributed to the findings that different active species are required by styrene and olefin polymerizations in monotitanocene catalyst systems. It has been known that the MAO-activated monotitanocene catalysts are multi-site systems containing tetravalence $Ti^{(IV)}$, trivalence $Ti^{(III)}$, and divalence $Ti^{(II)}$ species.[13,14] The distribution of these species can be adjusted by the Al/Ti ratio, $Ti^{(IV)}$ is predominant in a lower ratio whereas $Ti^{(III)}$ is in majority with higher Al/Ti ratio. Some investigations for monotitanocene catalyst systems suggested $Ti^{(III)}$ species are favorable for styrene syndiospecific polymerization. And some studies indicated that $Ti^{(IV)}$ species promote ethylene and α-olefin polymerization.[15, 16] Considering aPP elastomeric segments attached on sPS will possibly improve the toughness of sPS, herein, we synthesize atactic polypropene-b-syndiotactic polystyrene (aPP-b-sPS) block copolymer with $Cp^*Ti(OBz)_3/MAO$ by sequential feeding propene and styrene and external addition of TIBA. The effects of reaction conditions on propene/styrene block copolymerization will be investigated in details.

Results and Discussion

Data for the syndiospecific polymerization of styrene in different temperatures are presented in Table 1. In most cases, the catalytic activity was higher at high temperatures than at low ones, while the highest activity was displayed at 90°. However, consequent elevation of temperature will cause to catalyst deactivation and enhancement in the acceleration of chain transferring reaction, therefore the activity and molecular weight decrease at 100° or 110°.

External additions of triisobutylaluminurn (TIBA) to the $Cp^*Ti(OBz)_3/MAO$ catalyst cause an increase of the mol% of Ti(III) active species, and promote the styrene syndiospecific polymerization with higher catalytic activity as shown in Table 2. The external additions of TIBA into the catalyst system may also reduce the dosage of MAO to get good results of styrene syndiospecific polymerization. However, the activity for the polymerization at Al_{TIBA}/Ti= 100(mol/mol) is lower than that at Al_{TIBA}/Ti=50(mol/mol), owing to the overdose of TIBA added which causes the drastic decrease in mol% of Ti(III) species and the obvious chain transferring effect of TIBA.

Table 1. Effect of Temperature on styrene syndiopolymerization with $Cp^{*}Ti(OBz)_3$/MAO catalyst.[a)]

T_p (°)	Yield (g)	Activity×10^{-5} (gPS/molTi.h)	S. I[b)]. (wt%)	M_w ×10^5	T_m (°)
70	8.12	3.8	93.8	–	–
80	11.63	5.5	95.7	3.0	271.9
90	13.17	6.2	96.1	2.6	272.3
100	10.89	5.1	95.1	2.1	269.5
110	9.27	4.4	88.6	–	–

[a)] Polymerization conditions: $[Ti]=5.0\times10^{-4}$mol/L, $Al_{MAO}/Ti=200$(mol/mol), $Al_{TIBA}/Ti=50$(mol/mol), Styrene=20mL, Toluene=20mL, t_p=1h.

[b)] S.I.=syndiotactic index: insoluble weight in boiling 2-butanone (g)/total weight (g).

Table 2. Styrene polymerization with $Cp^{*}Ti(OBz)_3$/MAO catalyst in the presence of TIBA.[a)]

Al_{TIBA}/Ti (mol/mol)	Ti^{III} (%)	Activity×10^{-6} (gPS/molTi.h)	S.I. (wt%)	T_m (°)	M_w ×10^5
0	19.3	trace	–	–	–
25	47.6	3.9	92.8	271.2	2.8
50	71.2	6.2	96.1	272.3	2.6
100	68.7	4.7	94.3	266.1	1.8

[a)] Polymerization conditions: $[Ti]=1.04\times10^{-4}$mol/L, Al/Ti=800(mol/mol), T_p=90° t_p=1h.

As shown in Table 3, with MAO as cocatalyst to promote $Cp^{*}Ti(OBz)_3$, the polymerizations of propene were performed in different Al/Ti molar ratios. The catalyst exhibited the best Al/Ti molar ratio to assure the highest activity was around 300. At lower ratios, sharp drop of activity were observed, and a minimum value of Al/Ti (about 150 mol/mol) was required because the MAO is necessary for the reaction of MAO with $Cp^{*}Ti(OBz)_3$ to produce alkylated active species for propene polymerization and used to scavenge impurities. However, when the Al/Ti molar ratio increases, the amount of Ti(IV) active species in the polymerization systems decreases. The activity of the catalyst was increased with increasing the content of Ti(IV). It can be understood that Ti(IV) active species is more favorable for propene polymerization. The polypropene obtained was extracted with boiling ether for 12h, and the soluble fraction with more than 98wt% by weight was isolated and characterized. ^{13}C NMR analysis confirmed that the soluble fraction was atactic polypropene (aPP). The pentad configuration of methyl group carbon exhibits a statistically random distribution, and rrrr=32%. The aPP molecular chain involves primarily head-to-tail sequences (72.3 %), and the proportion of head-to-tail or tail-to-tail sequences (27.7%).

Table 3. Effect of Al/Ti molar ratios on propene polymerization with $Cp^{*}Ti(OBz)_3$/MAO catalyst.[a)]

Al/Ti (mol/mol)	Ti^{IV} (%)	Ti^{III} (%)	Ti^{II} (%)	Activity×10^{-4} (gPP/molTi.h)	Soluble fraction in ether (wt%)	M_w ×10^5
160	81.9	17.5	0.6	8.9	98.9	3.3
240	–	–	–	10.4	98.6	2.9
330	79.8	19.5	0.7	14.9	98.2	3.6
430	–	–	–	5.0	98.1	3.0
550	60.5	33.0	6.5	3.3	98.2	2.5

[a)] Polymerization conditions: [Ti]=1.04×10^{-3}mol/L, P=140KPa, Toluene=20mL, T_p=40°, t_p=1h.

The results of homopolymerizations of styrene and propene using $Cp^{*}Ti(OBz)_3$ activated by different MAO indicated that the oxidation states of titanium depended on the polymerization conditions, and Ti(III) active species produces sPS and Ti(IV) active species does aPP. It was also that the external addition of TIBA can promoted styrene syndiospecific polymerization with high activity. All these gave us a way to design the copolymerization of styrene and propene.

When styrene and propene were copolymerized with $Cp^{*}Ti(OBz)_3$ in the presence of MAO by the addition of the monomers in the same time, the products mainly were polystyrene (content of sPS>97wt%) with negligible amount of polypropene and copolymer. These results suggest that the styrene decreases largely the activity of propene polymerization.

When the propene was prepolymerization in a period with $Cp^{*}Ti(OBz)_3$/MAO catslyst, and then the styrene and TIBA were added in the same time, styrene could be copolymerized with propene. Propene proportions in the copolymerization products could be adjusted by controlling its prepolymerization time. Table 4 lists the comparison of the successive solvents extraction of the homopolymerization and styrene/propene copolmerization products with boiling butanone, heptane, tetrahydrofuran (THF) and chloroform. The copolymerization products could be separated into homopolymers and block copolymers, and each fractions were characterized by ^{13}C NMR and DSC.

With above analyses and compared to the result of the successive solvents extraction of homopolymers of styrene and propene, it was concluded that the copolymerization products were a mixture of sPS existing mainly in chloroform insoluble fraction, aPP existing mainly in heptane soluble fraction and block copolymers (sPS-b-aPP) composed of longer segments of syndiotactic polystyrene and shorter atactic polypropene existing chiefly in THF and chloroform soluble fraction. The result may be explained that TIBA added externally changes Ti(IV) active species with a growing chain of polypropene to Ti(III) active species, which is in favour of styrene syndiospecific polymerization and lead to the formation of the block copolymmer of styrene and propene.

Table 4. Results of successive extraction for styrene/proprene copolymerization products.

Comonomers feed ratio(mol/mol)	Activity×10^{-5} (gPP/molTi.h)	Successive extraction fractions (wt%) with boiling				
		2-Butone soluble	Heptane soluble	THF soluble	Chloroform soluble	Chloroform insoluble
S/P[a](80:20)[b]	4.5	5.2	2.5	17.2	48.8	26.4
S/P[a](80:10)[b]	8.6	4.0	4.0	8.0	30.6	53.4
S/P[a](100:0)[c]	8.8	2.6	0	0	3.3	94.2
S/P[a](0:100)[d]	1.7	0	100	0	0	0

[a] The S/P was the value of molar feed ratio of two monomers styrene/propene (mol/mol).

[b] Styrene and propene block copolymerziation conditions: [Ti]=1.0×10^{-3}mol/L, Al_{MAO}/T=260(mol/mol), Al_{TIBA}/Ti= 50(mol/mol), Toluene=20mL, T_p=90°, $t_{Propene}$=30 min, $t_{Styrene}$=30 min.

[c] Styrene homopolymerization conditions: [Ti]=1.0×10^{-3}mol/L, Al_{MAO}/T=260(mol/mol), Al_{TIBA}/Ti=50(mol/mol), [Styrene]= 4.2 mol/L , Toluene=20mL, T_p=90°, t_p=60 min.

[d] Propene homopolymerization conditions: [Ti]=1.0×10^{-3}mol/L, Al_{MAO}/T=260(mol/mol), P(C_3H_6)=0.13MPa, Toluene= 20mL, T_p=40°, t_p=30min.

Figure 1 displays the ^{13}C NMR of sPS-b-aPP copolymer prepared by the feeded ratio of propene to styrene of 20/80 (mol/mol) as shown in Table 4. The chemical shift of the phenyl C-1 carbon in the copolymer was observed at 145.6ppm, and the peak was single and sharp, corresponding to the rrrr pentad configuration of syndiotactic polystyrene segment. The chemical shift of the methyl carbon in the copolymer was observed in the range 19.0-20.0 ppm corresponding to the configurational sequences of atactic polypropene segment. The content of the propene unit in the copolymer was 20.0mol% in THF-soluble fraction and 9.0mol% in chloroform-soluble fraction.

The DSC curves of the block copolymers obtained from THF-soluble fraction or chloroform-soluble fraction appeared two glass transition temperatures (T_g) at –7.8° and 83.0° or –8.3° and 89.1° respectively, and the melt temperature(T_m) appear at 265.0° or 266.7°. The facts that the T_g and T_m of sPS are 104.3° and 272.3°, and the aPP has only a T_g of –12.7°. Accordingly, the glass transition temperatures of the resulting block copolymer were between those of each homopolymers, and the melt temperature is low to sPS, so it is supposed to be a block copolymer with a long syndiotactic polystyrene segment which is crystallizable and a short atactic polypropene segment.

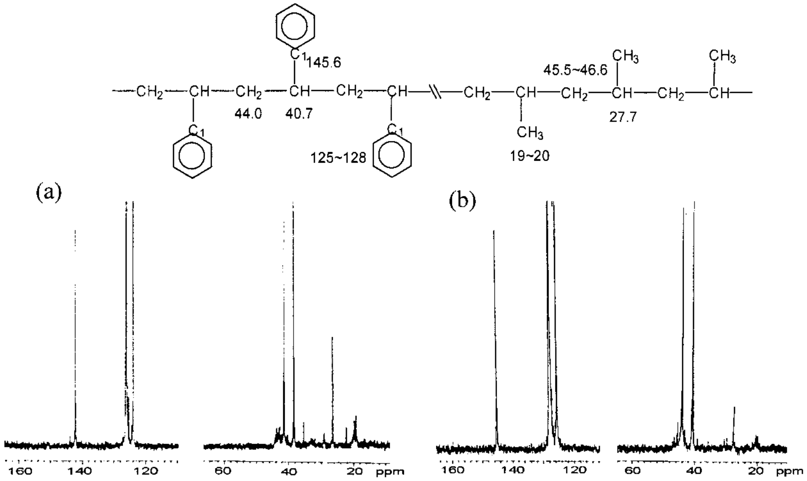

Figure 1. ^{13}C NMR spectra of (a) THF-soluble fraction, (b) chloroform-soluble fraction.

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