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Chain transfer reactions in metallocene catalyzed polymerization of allylbenzene

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Summary

Allylbenzene was polymerized in the presence of two types of homogeneous zirconocene catalysts (co-catalyst methylaluiminoxane). Selective chain termination through ß-hydride elimination or chain transfer to aluminum was observed depending upon the catalysts employed. The rac-Et(Ind)$_2$ZrCl$_2$, and rac-Me$_2$Si(Ind)$_2$ZrCl$_2$, catalysts gave the polyallylbenzenes with saturated end groups due to chain transfer to aluminum, while the Cp$_2$ZrCl$_2$ catalyst gave the polyallylbenzenes with vinylidene end groups due to ß-hydride elimination.

Introduction

Research activities of homogeneous metallocene catalysts have created new opportunities for the molecular design of controlled polymer structures. The versatile electronic and steric control of the catalysts through ligand structure allows the design of catalyst precursors that direct the polyinsertion reaction to form regioregular and stereoregular polyolefins with high selectivity. An understanding of the process that governs chain transfer is critical for the control of polymer molecular weight and chain end structures. Chain transfer is believed to occur via facile ß-hydride (ß-H) elimination in metallocene catalyzed olefin polymerization, which is the main reason for the lower molecular weight of the polymers obtained with metallocene catalysts than the polymers obtained with heterogeneous catalysts.[1,2] Chain transfer to aluminum (Al-t) has been considered as a minor chain transfer reaction in metallocene catalyzed polymerizations.[1~5]

In this paper, we report the allylbenzene polymerization where chain transfer reactions are unprecedentedly selective, depending upon type of metallocene/MAO catalysts, between two chain transfer reactions: ß-hydride elimination and chain transfer to aluminum.

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Experimental

Materials & Instruments

Zirconocene dichlioride was used as received from Strem. Methylaluminoxane (MAO) was obtained from Akzo as a toluene solution (6.4 wt.% aluminum). Toluene was distilled over calcium hydride in a dry nitrogen atmosphere. Allylbenzene was obtained from Aldrich, and was vacuum distilled over calcium hydride.

Molecular weights of the polyallylbenzenes were measured by Waters 150C gel permeation chromatography (GPC) equipped with a refractive index detector, using three polystyrene gel column (5E-4E-2E) and 1,2,4-trichlorobenzene as a solvent at 135°C. The weight average molecular weight and polydispersity (M_w and M_w/M_n, respectively) of the polyallylbenzenes were calculated on the basis of a polystyrene standard. ^1H and ^{13}C NMR spectra of polymers were recorded at 110°C on a Bruker AMX-500 spectrometer. Samples of 20 ~ 50mg polymers were dissolved in 0.5ml of tetrachloroethane-d_2 in a 5mm (o.d.) tube.

Polymerization

All reactions and manipulation were carried out in an atmosphere of dry argon or nitrogen using Schlenk technique, except for the purification of the polymers. Polymerizations were carried out in a 100ml jacketed glass reactor at 50°C. The glass reactor was charged with toluene and the catalyst solution consisting of prescribed amount of MAO and 2.5×10^{-6} mol of the zirconocene dichloride. Immediately after 10ml of allylbenzene was injected into the reactor, the polymerization started. After certain time of polymerization, the reaction mixture was precipitated in a mixture of methanol and small amount of concentrated hydrochloric acid, and filtered. The filtered polymer was then washed with methanol several times and dried in a vacuo.

Results and discussion

Table 1 compiles the polymerization results of allylbenzene by various catalysts with different amount of MAO. Most of the polymerization showed low activities that may be attributed to slow insertion (propagation) rate caused by the steric hindrance of the bulky benzyl group of the monomer. The relatively higher activities of run 2 and run 3 may be correlated with steric effect of the ligand structure. Among the catalysts employed, Cp_2ZrCl_2 has less steric hindrance than any other catalysts. Activity of Cp_2ZrCl_2 catalyst was significantly increased with high MAO concentration, but the molecular weight of the polymers was not affected. It seems that the low activity of run 1 is caused by the low concentration of active species for allylbenzene polymerization. In all cases the allybenzene oligomers with narrow molecular weight distribution were obtained.[5]

The end groups analysis of the oligomers obtained with Cp2ZrCl2 showed the presence of a vinylidene group ($R_1R_2C{=}C\mathit{H}_2$) based on ^1H (δ = 4.8~4.9ppm, broad peak) and ^{13}C NMR [δ = 113.2($C{=}\mathit{C}H_2$) and 147.5ppm($\mathit{C}{=}CH_2$)] spectra. It should be noted that Zr-CH_3 species produce methyl and vinylidene end groups with allylbenzene, which occur only for the first oligomeric molecule (structure **<u>1</u>** in Figure 1). For all other subsequent catalytic cycles, Zr-H species formed by ß-hydride elimination give benzyl and vinylidene end groups, if ß-hydride elimination is the only chain transfer reaction (structure 2 in Figure 1). Chain transfer to aluminum regenerates the Zr-CH_3 species and gives oligomers with saturated end groups (structure 3 in Figure 1).

Table 1. Results of allylbenzene polymerization at various Al/Zr ratio[a]

run	catalyst	Al/Zr	yield (g)	activity[b]	M_w[c] (g/mol)	M_w/M_n
1	Cp_2ZrCl_2	2,000	1.23	6.8	1,400	1.2
2	Cp_2ZrCl_2	4,000	3.69	20.5	1,600	1.2
3	Cp_2ZrCl_2	8,000	4.29	23.8	1,400	1.2
4	$Et(Ind)_2ZrCl_2$	2,000	0.95	5.3	9,200	2.2
5	$Et(Ind)_2ZrCl_2$	4,000	0.86	4.8	5,000	1.9
6	$Et(Ind)_2ZrCl_2$	8,000	0.39	2.2	2,400	1.3
7	$Me_2Si(Ind)_2ZrCl_2$	2,000	2.84	15.8	7,800	2.0
8	$Me_2Si(Ind)_2ZrCl_2$	4,000	3.61	20.1	5,300	1.8
9	$Me_2Si(Ind)_2ZrCl_2$	8,000	2.46	13.7	3,200	1.5

[a] Polymerization conditions: amount of catalyst = 2.5×10^{-6} mol, amount of allylbenzene = 7.5×10^{-2} mol (10 ml), volume of toluene = 20 ml, temperature = 50 ℃, polymerization time = 72 h. [b] Activity = kg polymer per mol Zr per h, [c] Weight average molecular weight determined by GPC

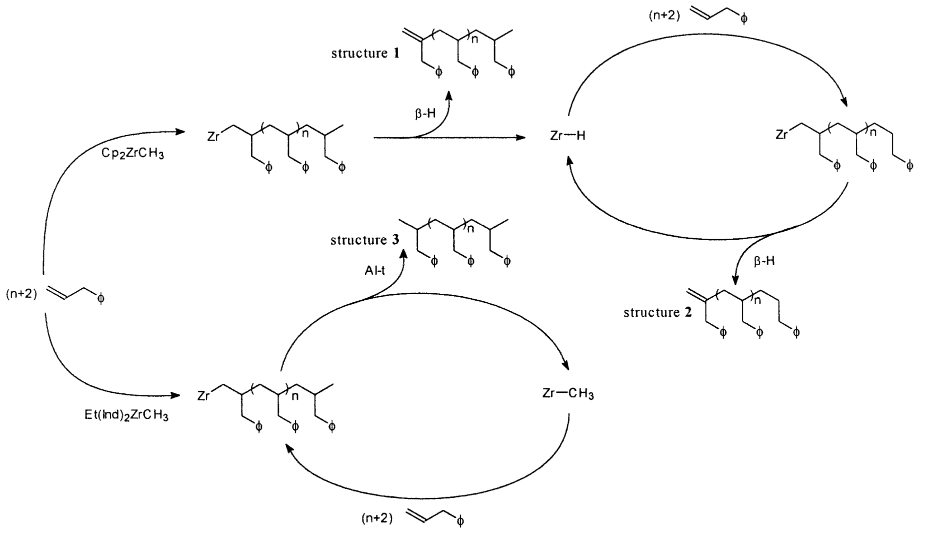


Figure 1. Catalytic cycles for allylbenzene polymerization with zirconocene catalysts

NMR spectrum of the allylbenzene oligomer obtained with Cp_2ZrCl_2/MAO catalyst (Figure 2 and 3) showed that the peak (0.7ppm) of methyl end groups is very weak compared to the peak (4.9ppm) of vinylidene end groups generated by ß-hydride elimination. The above NMR data indicate that ß-hydride elimination is a dominant chain transfer reaction in the Cp_2ZrCl_2/MAO catalyzed allylbenzene polymerization.

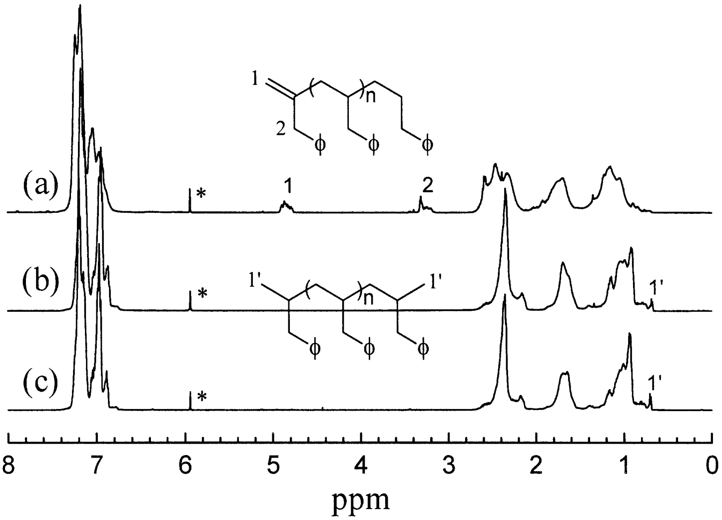


Figure 2. ^{1}H-NMR spectra of poly(allylbenzene)s obtained with (a): Cp_2ZrCl_2/MAO (run 1) (b): $Et(Ind)_2ZrCl_2$/MAO (run 4) (c): $Me_2Si(Ind)_2ZrCl_2$/MAO (run 7). The asterisk denotes a solvent peak.

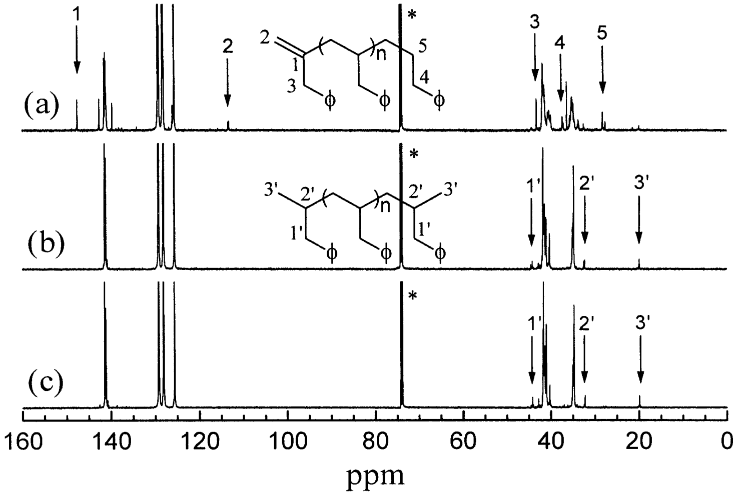
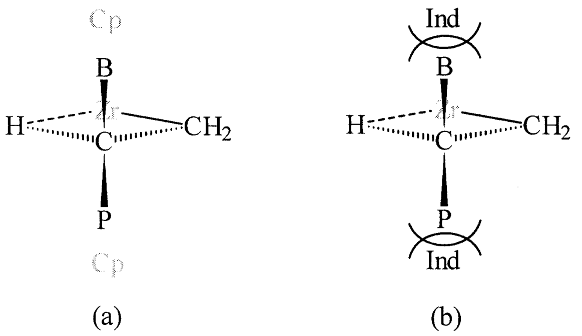


Figure 3. ^{13}C NMR spectra of poly(allylbenzene)s obtained with (a): Cp_2ZrCl_2/MAO (run 1) (b): $Et(Ind)_2ZrCl_2$/MAO (run 4) (c): $Me_2Si(Ind)_2ZrCl_2$/MAO (run 7). The asterisk denotes a solvent peak.

However, the ansa metallocene catalysts with indenyl ligand exhibit a different chain transfer route in the allylbenzene polymerization.

As shown in Figure 2 and 3, the NMR spectra of the poly(allylbenzene)s obtained with $Et(Ind)_2ZrCl_2$/MAO and $Me_2Si(Ind)_2ZrCl_2$/MAO did not have any vinyl or vinylidene peaks, but showed the peaks corresponding to the methyl end group (^1H: 0.7ppm, ^{13}C: 19.9ppm). The above NMR data clearly indicate that almost all the chain transfer reaction occurred through chain transfer to aluminum under the polymerization condition investigated. It is somewhat unusual that at 50°C the polymer with saturated end groups was produced in homopolymerization of mono-substituted olefin which usually undergoes chain termination via ß-hydride elimination,[5~9] but it can be rationalized in terms of transition state conformation required for ß-hydride elimination (or ß-agostic interaction).



Scheme 1. Schematic representation of chain conformation for transition states of β-agostic interaction at Cp_2ZrR centers (a), and $Et(Ind)_2ZrR$ centers showing nonbonded interaction (b). B = benzyl group, P = polymer chain.

The transition state for ß-hydride elimination requires the overlapping of a $\sigma_{C\text{-}H}$ orbital with an empty d orbital of the metal,[3,10~13] and the two carbon adjacent to the metal and ß-hydrogen must be on the same plane containing the metal in between the two Cp rings of the zirconocene. Therefore, the energy of the conformation needed for ß-hydride elimination increases with increase of steric hindrance around the metal (cf. Scheme 1).[14]

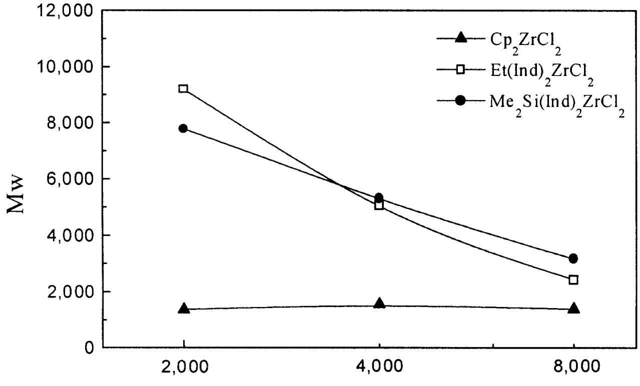


Figure 4. Molecular weight vs Al/Zr ratio in allylbenzene polymerization.

It seems that ß-carbon of polymer chain is not easily accommodated in the plane because of the steric interaction between indenyl ligands of catalyst and benzyl group of propagating chain end. Thus the metal center without ß-agostic conformation becomes more reactive and undergoes chain transfer reaction to aluminum. Also, the energy of the conformation needed for ß-hydride transfer to the coordinated allylbenzene monomer increases with a bulky ligand. Since substituents in the Cp ring cause a strong suppression of the both ß-hydride elimination and ß-hydride transfer to monomer,[11,15] the steric effect of the indenyl ligand is likely to block the both chain transfer processes. A similar effect has been observed in Cp^*_2Sc-Et and Cp^*_2Sc-nPr complex,[12] where steric interaction between a Cp* ligand and the propyl CH_3 is responsible for the absence of ß-agostic interaction.[3,16,17] Free trimethylaluminum included in MAO solution becomes an effective chain transfer agent in this case.[2,18~21]

The above mentioned chain transfer mechanism with two types of metallocene catalysts was further supported by the change of molecular weight depending on the amount of MAO used (Figure 4). The rate of the termination reactions via chain transfer to aluminum will increase as aluminum concentration increases, that causes a decrease in molecular weight (M_w). The molecular weight of the allylbenzene oligomers obtained with Cp_2ZrCl_2 catalyst is independent of MAO concentration indicating that chain transfer to aluminum is not a dominant termination reaction in this case. However, the molecular weights of the polyallylbenzenes obtained with the two ansa metallocene catalysts decrease with increasing MAO concentration. The decrease of molecular weight with increasing MAO concentration is consistent with the above explanation that chain transfer to aluminum is a dominant chain transfer mode with the two ansa metallocene catalysts.

Conclusions

Metallocene catalyzed polymerization of allybenzene produced low molecular weight polyallylbenzene with different chain end groups depending on the type of catalyst employed. Ansa metallocene catalysts gave polyallylbenzene with saturated end groups due to chain transfer to aluminum, while the Cp_2ZrCl_2 catalyst gave polyallylbenzene with vinylidene end groups due to ß-hydride elimination. The preference for ß-hydride elimination vs chain transfer to aluminum may be attributed to the steric interaction between the ligand of the catalyst and the growing polymer chain, which affects the ß-agostic interaction resulting in selective chain transfer reaction depending on the type of catalysts used.

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