Polymer Bulletin 42, 265–272 (1999)

Polymer Bulletin

Polymerization of allylbenzene with metallocene catalysts

Doo-Jin Byun[1], Dong-Keun Shin[2], Juwhan Liu[3], Sang Youl Kim[1,*]

[1] Center for Advanced Functional Polymers, Department of Chemistry, Korea Advanced Institute of Science and Technology, Yusung, Taejon 305-701, Korea
[2] Materials Testing Laboratory, Korea Research Institute of Chemical Technology, P.O. Box 107, Yusung, Taejon 305-600, Korea
[3] Department of Polymer Science and Engineering, Chungnam National University, Yusung, Taejon 305-764, Korea

Received: 7 December 1998/Revised version: 29 January 1999/Accepted: 9 February 1999

Summary

Homopolymerization of allylbenzene was carried out with various metallocene/ methylaluminoxane (MAO) catalysts. Different polymerization behavior was observed depending upon the catalysts empolyed. rac-Et(Ind)$_2$ZrCl$_2$ and rac-Me$_2$Si(Ind)$_2$ZrCl$_2$ gave semicrystalline polyallylbenzenes while i-Pr(CpFlu)ZrCl$_2$ and CpTiCl$_3$ did not give any polymeric product. The Cp$_2$ZrCl$_2$ gave amorphous polyallylbenzene with low molecular weight. The effect of temperature on the polymerization was investigated with a constant Al/Zr ratio. The temperature showing maximum catalyst activity is higher for the ansa metallocene catalysts than Cp$_2$ZrCl$_2$ catalyst. The IR and NMR spectra indicated that the polyallylbenzene consisted of allylbenzene repeating unit and no isomerization occurred.

Introduction

Recent discoveries of metallocene catalysts have provided exciting opportunities for the molecular design of new polymers. New types of polyolefins that have not been accessible can be synthesized. Allylbenzene has been considered as a non-polymerizable monomer because of degradative chain transfer behavior of allyl group.[1,2] High molecular weight polyallylbenzene can not be obtained with conventional polymerization methods such as free radical, cationic and anionic polymerization. D'alelio and Boiteux reported that Zieglar-Natta polymerization of allylbenzene gave the better results than any other types of polymerization investigated,[2,3] but in some cases isomerization of allylbenzene was occurred during the polymerization. To our knowledge, there aren't any reports on allylbenzene polymerization with metallocene catalysts, although allylbenzene belongs to a family of α-olefin compounds.

---

* Corresponding author

The present study describes the polymerization of allylbenzene in the presence of various metallocene catalysts.

Experimental

Materials & Instruments

Toluene was distilled over calcium hydride in a dry nitrogen atmosphere. Allylbenzene purchased from Aldrich was vacuum distilled over calcium hydride. Metallocene compounds (Strem) and MAO (MMAO-4, Al 6.4wt-% in toluene, Akzo) were used as received.

Melting temperature and recrystallization temperature were recorded with Dupont DSC 910 differential scanning calorimeter at heating rate of 10°C/min. The molecular weight of polyallylbenzenes was 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) were calculated on the basis of a polystyrene standard. Crystalline structure of the polymers was measured with a Rigaku D/MAX-IIIB wide angle X-ray differactometer (WAXD). The scan range was 5 ~ 50° and the scan speed was 2°/min. Infrared (IR) spectra were taken on a Digilab FTS-165 FT-IR spectrometer using KBr pellet technique. ^1H and ^{13}C NMR spectra of polymers were recorded at 110°C on a Bruker AMX FT500 spectrometer operated at 500MHz and 125MHz, respectively.

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 performed in a 100ml jacketed glass reactor. Toluene was charged under an argon atmosphere into the reactor, and then the temperature was raised to the desired polymerization temperature. A prescribed amount of MAO and a metallocene catalyst dissolved in toluene were injected into the reactor by a syringe. Immediately after allylbenzene was injected into the reactor, the polymerization was started. After the certain time of polymerization, the reaction mixture was precipitated in a mixture of methanol and a small amount of concentrated hydrochloric acid, and filtered. The filtered polymer was then washed with methanol and water several times and dried *in vacuo*.

Results and discussion

Table 1 compiles the polymerization results of allylbenzene with various metallocene catalysts. Among the catalysts investigated, three catalysts, Cp_2ZrCl_2, $Et(Ind)_2ZrCl_2$ and $Me_2Si(Ind)_2ZrCl_2$ produced the polymers which have relatively low molecular weight and narrow molecular weight distribution.

Table 1. Results of allylbenzene polymerization with various metallocene catalysts[a]

run	catalyst	Al/Zr(Ti)	yield (g)	activity[b]	M_w[c] (g/mol)	M_w/M_n
1	Cp_2ZrCl_2	1,000	0.00	-	-	-
2	Cp_2ZrCl_2	8,000	4.29	23.8	1,400	1.2
3	$(2\text{-MeInd})_2ZrCl_2$	1,000	0.00	-	-	-
4	$(2\text{-MeInd})_2ZrCl_2$	8,000	0.00	-	-	-
5	$Et(Ind)_2ZrCl_2$	1,000	0.35	1.9	8,600	2.4
6	$Et(Ind)_2ZrCl_2$	8,000	0.39	2.2	2,400	1.5
7	$Me_2Si(Ind)_2ZrCl_2$	1,000	0.57	3.2	7,500	1.9
8	$Me_2Si(Ind)_2ZrCl_2$	8,000	2.46	13.7	3,200	1.5
9	$CpTiCl_3$	1,000	0.00	-	-	-
10	$CpTiCl_3$	8,000	0.00	-	-	-
11	$i\text{-Pr(CpFlu)}ZrCl_2$	1,000	0.00	-	-	-
12	$i\text{-Pr(CpFlu)}ZrCl_2$	8,000	0.00	-	-	-

[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] M_w: weight average molecular weight

$(2\text{-MeInd})_2ZrCl_2$ catalyst did not give any polymeric products (Table 1, runs 3~4), while Cp_2ZrCl_2 catalyst gave a oligomeric product with relatively high activity at high MAO concentration (Table 1, run 2). The difference between the two catalysts may stem from the different spatial circumstances for allylbenzene coordination that is affected by the ligand structure of the catalysts. A similar effect has been observed in the ethylene polymerization by metallocene catalysts with alkyl-substituted Cp ligands, where the activity difference between the most and the least active catalyst amounts to a factor of about 100.4 $Et(Ind)_2ZrCl_2$ and $Me_2Si(Ind)_2ZrCl_2$ catalyst show recognizable activities (Table 1, runs 5~8) compared to $(2\text{-MeInd})_2ZrCl_2$ catalyst. It seems that rigid ligand structure of the bridged metallocene catalysts allows the coordination of bulky allylbenzene monomer to the metal.[5]

The attempt for the preparation of polyallylbenzene was failed with $CpTiCl_3$ catalyst which was used to polymerize styrene (Table 1, runs 9~10). It implies that allylbenzene could not be polymerized via 2,1-insertion mode involving η^3-coordination of the growing chain end to the catalytic site. In the case of $i\text{-Pr(CpFlu)}ZrCl_2$ catalyst which is known as a syndiospecific catalyst, the polymerization of allylbenzene was also unsuccessful. This result may stem from the steric interaction between the ligand of the catalyst and bulky benzyl group of the monomer.

The effect of temperature on allylbenzene polymerization was investigated with a constant Al/Zr. The polyallylbenzene obtained with different reaction temperature (-10°C ~ 110°C) were analyzed with GPC. The results represented in Table 2 and Figure 1 showed a difference between bridged and non-bridged metallocene catalysts. In the case of bridged metallocene catalysts, the maximum activities occurred at 80°C. Further increase to 110°C caused deactivation of the active sites. This behavior is similar to that of the metallocene catalyzed ethylene polymerization.[6~8]

Table 2. Temperature effect on allylbenzene polymerization with zirconocene /MAO catalysts[a]

run	catalyst	temperature (℃)	yield (g)	Activity[b]	M_w[c] (g/mol)	M_w/M_n
13	Cp_2ZrCl_2	-10	0.04	0.2	3,400	1.4
14	Cp_2ZrCl_2	20	0.57	3.2	2,200	1.5
15	Cp_2ZrCl_2	50	1.23	6.8	1,400	1.2
16	Cp_2ZrCl_2	80	0.10	0.6	1,500	1.2
17	Cp_2ZrCl_2	110	0.00	-	-	-
18	$Et(Ind)_2ZrCl_2$	-10	0.00	-	-	-
19	$Et(Ind)_2ZrCl_2$	20	0.07	0.4	12,100	2.4
20	$Et(Ind)_2ZrCl_2$	50	0.98	5.4	9,200	2.2
21	$Et(Ind)_2ZrCl_2$	80	2.67	14.8	6,000	2.1
22	$Et(Ind)_2ZrCl_2$	110	1.15	6.4	2,800	1.6
23	$Me_2Si(Ind)_2ZrCl_2$	-10	0.12	0.7	-	-
24	$Me_2Si(Ind)_2ZrCl_2$	20	0.17	0.9	10,100	2.0
25	$Me_2Si(Ind)_2ZrCl_2$	50	2.84	15.8	7,800	2.0
26	$Me_2Si(Ind)_2ZrCl_2$	80	7.12	39.6	5,500	1.9
27	$Me_2Si(Ind)_2ZrCl_2$	110	3.97	22.1	2,900	1.6

[a]Polymerization conditions: amount of catalyst = 2.5×10^{-6} mol, Al/Zr = 2000, allylbenzene = 7.5×10^{-2} mol (10 ml), volume of toluene = 20 ml, polymerization time = 72 h, [b]Activity = kg polymer per mol Zr per h, [c]M_w: weight average molecular weight

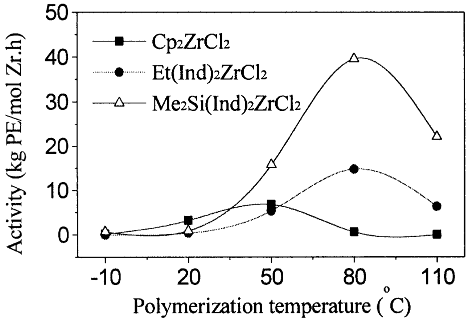


Figure 1. Dependence of the catalytic activity on the polymerization temperature for allylbenzene polymerization

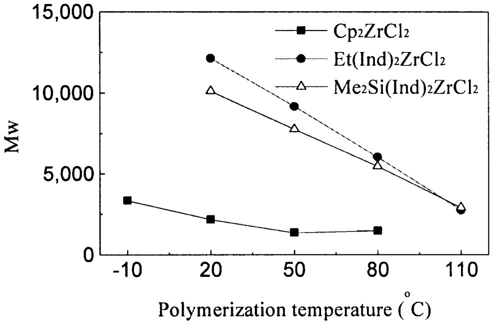


Figure 2. Dependence of the molecular weight on the polymerization temperature for allylbenzene polymerization

The molecular weight of the polymers decreases monotonously with increasing temperature (Figure 2) probably because the activation energy for chain transfer is greater than that for propagation.[9] It is reported that ß-hydride elimination is more frequently occurred with Cp_2ZrCl_2 catalyst than bridged catalysts resulting in lower molecular weight.[10,11] The polymers obtained with Cp_2ZrCl_2 catalyst have MWD less than the most probable value. Narrow molecular weight distribution was also observed in oligomerization of α-olefin, which was explained in terms of a propagation rate dependence of chain length.[12]

Kennedy and Boiteux reported that polymerization of allylbenzene proceeded partly via isomerization of allylbenzene by cationic initiator and Zieglar-Natta catalyst.[3,13,14] Some of allylbenzene partly isomerized to methylstyrene prior to propagation producing the polymers which contain both allylbenzene and rearranged styrene unit.[13,14]

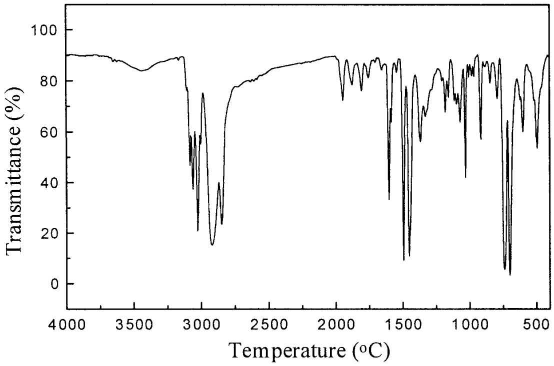


Figure 3. IR spectra of polyallylbenzene prepared by rac-Et(Ind)$_2$ZrCl$_2$/MAO catalyst (run 20)

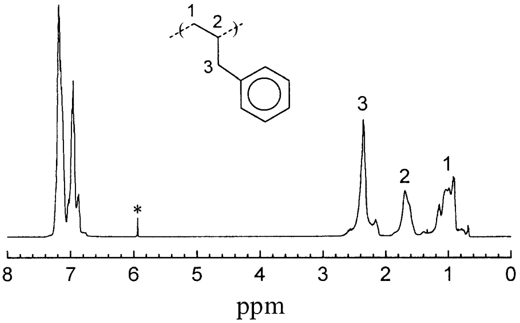


Figure 4. ^{1}H-NMR spectra of polyallylbenzene prepared by rac-Et(Ind)$_2$ZrCl$_2$/MAO catalyst (run 20). The asterisk denotes a solvent peak.

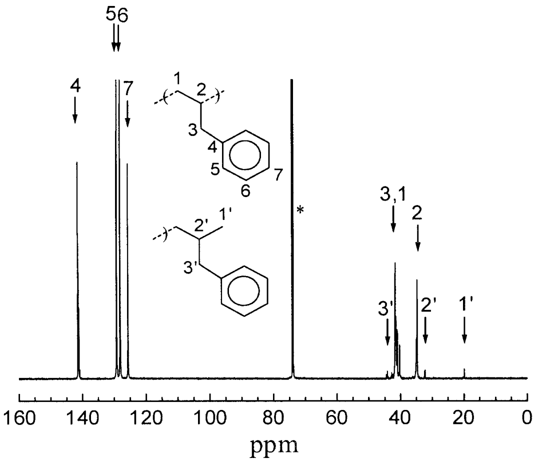
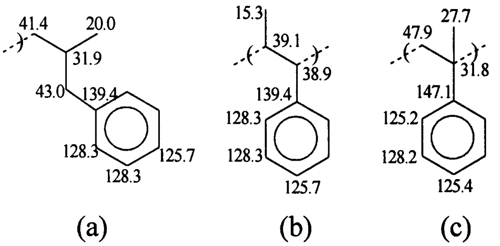


Figure 5. ^{13}C-NMR spectra of polyallylbenzene prepared by rac-Et(Ind)$_2$ZrCl$_2$/MAO catalyst (run 20). The asterisk denotes a solvent peak.



Scheme 1. Calculated chemical shifts of terminal allylbenzene unit (a), β-methylstyrene unit (b), α-methystyrene unit (c)

In order to investigate the structure of the polyallylbenzene produced with a metallocene cataryst, the polymer obtained with Et(Ind)$_2$ZrCl$_2$ catalyst (run 20 in Table 2) was examined with IR and NMR spectroscopy. In the IR spectrum (Figure 3), the characteristic peaks of polyallylbenzene appeared at 3026, 1495, 1452, 739 and 699 cm^{-1}.[3,13] The peaks corresponding to the methyl group of rearranged styrene unit at 2961, 2870 and 1373 cm^{-1} were not observed.[13,14] ^{1}H (Figure 4) and ^{13}C (Figure 5) NMR spectra of polyallylbenzenes prepared by Et(Ind)$_2$ZrCl$_2$/MAO catalyst show the four broad ^{1}H peaks (1.1ppm, methylene; 1.8ppm, methine; 2.5ppm, benzyl; 7.1ppm, phenyl) and the seven major ^{13}C peaks (34.8ppm, methine; 41.0ppm, methylene; 41.7ppm, benzyl; 125.7, 128.1, 129.3, 141.4ppm, phenyl). The ^{13}C NMR spectrum also shows the small additional peaks at 20.0, 32.2, 44,1ppm due to terminal methyl structure, but do not show any characteristic peaks of the rearranged styrene unit at 15.3ppm (ß-methylstyrene unit) and 27.7, 147.1ppm (α-methylstyrene) (cf. Scheme 1). The above IR and NMR analysis data of the polyallylbenzene obtained with the metallocene catalyst indicate that the polymerization of allylbenzene proceeded without isomerization.[3,13,14] The Zieglar-Natta catalyst system[15] might cause the cationic isomerization of allylbenzene during the polymerization due to the heterogeneous character of the catalyst.

Wide angle X-ray diffractometer (WAXD) spectra of the polyallylbenzenes are shown in Figure 6. The WAXD patterns of the polyallylbenzenes show the small crystalline peaks only for the polymers obtained with isospecific catalysts as expected on the basis of stereospecificity of the catalysts.[15,16] Thermal properties of the polyallylbenzenes were measured by differential scanning calorimeter (DSC). The glass-transition temperature (T_g) and the melting points (T_m) are shown in Table 3 and Figure 7.

Table 3. Thermal properties of polyallylbenzenes prepared with various metallocene catalysts

run	catalyst	WAXD	DSC			
			T_g[a]	T_m[b]	ΔH_f[b]	T_c
15	Cp_2ZrCl_2	amorphous	14.4	-	-	-
20	$Et(Ind)_2ZrCl_2$	semi-crystalline	54.0	176.6	8.5	160.3
25	$Me_2Si(Ind)_2ZrCl_2$	semi-crystalline	48.9	174.3	2.9	156.1

[a] Glass-transition temperature recorded at the second heating cycle. [b] Melting temperature and Melting enthalphy recorded at the first heating cycle.

All the polymers obtained are found to have low heat of fusion (ΔH_f) that reflects low crystallinity. The melting temperature and the glass transition temperature of the polyallylbenzenes are in the range of 174 ~ 177°C and 14 ~ 54°C, respectively. The endothermic peaks after T_g of the polymers are due to the quenching effect that was formed during the precipitation of the polymers.

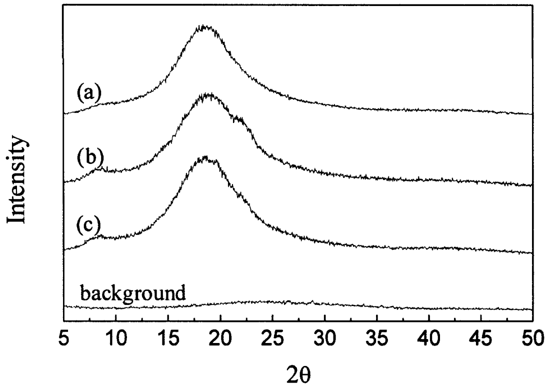


Figure 6. WAXD spectra of polyallylbenzenes obtained with Cp_2ZrCl_2 (a, run 15), rac-$Et(Ind)_2ZrCl_2$ (b, run 20) and rac-$Me_2Si(Ind)_2ZrCl_2$ (c, run 25)

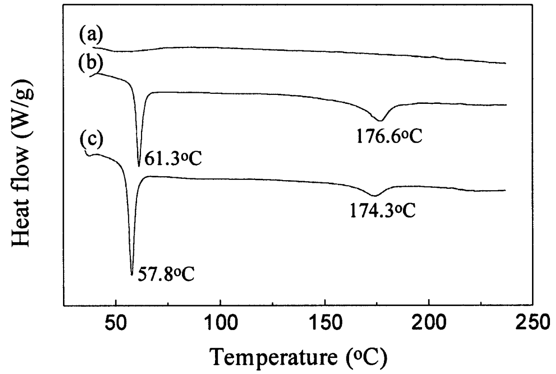


Figure 7. DSC diagrams of polyallylbenzenes obtained with Cp_2ZrCl_2 (a, run 15), rac-$Et(Ind)_2ZrCl_2$ (b, run 20) and rac-$Me_2Si(Ind)_2ZrCl_2$ (c, run 25)

Conclusions

Polymerization of allylbenzene was attempted with various metallocene/MAO catalysts. Among the catalysts investigated, Cp_2ZrCl_2, $Et(Ind)_2ZrCl_2$, $Me_2Si(Ind)_2ZrCl_2$ produced the polyallylbenzene with low molecular weight. The polymerization results was attributed to the accessibility of the bulky monomer to the catalytic site and to the steric interaction between the ligand of the catalyst and the growing polymer chain which affects the chain transfer reactions. But the crystallinity of the polyallylbenzene obtained with the two isospecific catalysts was very low. Spectroscopic analysis of the polymer confirmed that the polymerization with metallocene catalysts proceeded without isomerization.

References

1. Odian G (1991) Principles of polymerization, John Wiley & Sons Press, Singapore: 266
2. D'alelio GF, Finestone AB, Taft L, Miranda TJ (1960) J Polym Sci 14: 83
3. Boiteux G, Seytre G, Berticat P (1979) Makromol Chem 180: 761
4. Tian J, Huang B (1994) Macromol Rapid Commun 15: 923
5. Quijada R, Dupont J, Miranda MSL, Scipion RB, Galland GB (1995) Macromol Chem Phys 196: 3991
6. Reddy SS, Sivaram S (1995) Prog Polym Sci 20: 309
7. Chein JCW, Wang BP (1988) J Polym Sci Polym Chem 26: 3089
8. Mitani M, Oouchi K, Hayagawa M, Yamada T (1996) Macromol Chem Phys 197: 1815
9. D'Agnillo L, Soares JBP, Penlidis A (1998) Macromol Chem Phys 199: 955
10. Hungenberg KD, Kerth J, Langhauser F, Muller HJ, Muller P (1995) Angew Macromol Chem 227: 159
11. Michelotti M, Aotomare A, Ciardelli F, Ferrarini P (1996) Polymer 37: 5011
12. Janiak C, Lange KCH, Marquardt P (1995) Macromol Rapid Commun 16: 643
13. Boiteux G, Pham QT (1984) Macromol Chem 185: 877
14. Kennedy JP (1964) J Polym Sci Polym Chem 2: 5171
15. Subramanian PS, Chou KJ (1995) TRIP 3: 324
16. Kaminsky W (1996) Macromol Chem Phys 197: 3907