9th International Seminar on Polymer Science and Technology
Iran Polymer and Petrochemical Institute, Tehran, Iran
17-21 October 2009

Metallocene catalyst for ethylene, propylene and diene Terpolymerization

S. Ahmadjo[1], H. Arabi[1,*], M. Nekomanesh[1], G.H. Zohuri[2], M.M. Mortazavi[1], A. Farhadi[1]

1. Faculty of Polymerization Engineering, Iran Polymer and Petrochemical Institute, P. O. Box: 14965/115, Tehran, Iran

2. Department of Chemistry, Ferdowsi University of Mashhad, Mashhad, Iran

Abstract

Metallocene catalyst of $(Ind)_2ZrCl_2$/MAO was synthesized and used in ethylene/propylene/diene terpolymerization. The maximum activity for teropolymerization was 1864 kgP/molZr.h in 1 bar of monomer pressure. The terpolymerization activity decreased with increasing P/E feed ratio and diene concentration. Kinetic behaviour of the reaction was a decay type with very short induction period. Ethylene content of the polymer decreased with increasing P/E feed ratio, diene content increased with decreasing ethylene monomer in the P/E feed ratios.

Keywords: Metallocene catalyst, terpolymerization, solution polymerization, EPDM

Introduction

Recently single-site catalysts find more application in industrial polyolefin production. A well-known distinguishing feature of the single-site catalysts is their ability to copolymerize ethylene with α-olefins in a homogeneous fashion[1-2]. These catalysts have ability to effect random distributions of monomers and to provide good control over molecular weight distribution[3-5]. The studies show that metallocene catalyst exhibited higher activities and higher incorporation rates of termonomers in the polymer without any noticeable side reactions[6-7]. In the present work the bis-Ind-$ZrCl_2$ was synthesized and used in the terpolymerization of ethylene, propylene and 5-ethyldiene-2- norbornene monomer .

Experimental

Indene, Zirconium tetrachloride and Methylithium were provided by Merck and used as recievied. All solvents were provided from Luba (India) dried and deoxygenated according to the methods taken from the literature[8]. MAO and 5-ethyldiene-2-norbornene (ENB) purchased from Aldrich. Ethylene and diene contents of the polymer were measured according to ASTM D3900-2002 and ASTM D6047-2002 standards respectively.

Result and Discussion

The bis(indenyl)zirconium dichloride catalyst was synthesized using a modified method of the literature [9]. The obtained solid was washed several times using dry Et_2O to purify as much as possible following to drying. It was characterized by ^{1}HNMR;

6.23 (d, 4H, Cp-H(1,3)); 6.55 (t, 2H, Cp-H(2)); 7.28-7.37 (m, 4H, Ar); 7.60-7.69 (m, 4H, Ar).

Terpolymerization of ethylene, propylene and the diene monomer (ENB), was carried out using the catalyst (Table I). The rate of the reaction based on the monomer consumption in 20/80, 33/67, 50/50, 67/33, P/E feed ratio presented in Figure 1, as can be seen the reaction is a decay type with very short induction period; similar behaviour was reported. The decay behaviour could be due to decrease in the activity of some active center with time[10].

The activity of the catalyst decreased with increasing P/E ratio, this behavior is common in the terpolymerization (Figure 2). Increasing the diene monomer concentration (ENB) decreases the activity of the catalyst (Figure 3). Et content in the polymer decreased with increasing P/E feed ratio, However diene content increased with increasing the P/E feed ratio.

References

1- D. Arrowsmith, W. Kaminsky, A. M. Schauwienold, U. Weingarten, *J. Mol. Catal*. **160**, 97 (2000).

2- N. Friederichs, B. Wang, P. H.M. Budzelaar, B. B. Coussens, *J. Mol. Catal*. A: Chem. **242,** 91 (2005).

* E-mail: H.Arabi, H.Arabi@ippi.ac.ir

3- G. B. Galland, J. H. Z. dos Santos, M. DallAgnol, R. Bisatto, *Macromol. Symp*., **245–246**, 42 (2006).
4- Tritto, L. Boggioni, D. R. Ferro, *Coordination Chemistry Reviews*, **250**, 212 (2006).
5- S. Phoowakeereewiwat, B. Jongsomjit, P. Praserthdam, *J. mater. Process. Tech*. **209**, 520–524 (2009).
6- N. Bavarian, M. C. Baird, J. S. Parent, *Macromol. Chem. Phys*. **202**, 3248 (2001).
19- J. C. W. Chien, Y. Zhengtian, M. Marques, M. D. Rausch, *J. Polym. Sci., Part A*, **33**, 979 (1995).
7- G. H. Zohuri, R. Jamjah, S. Ahmadjo, *Iranian Polym. J*. **14**, 111 (2005).
8- R. Jamjah, G. H. Zohuri, M. Masnadi, S. Ahmadjo, M. Nekoomanesh, *J. Apply. Polym. Sci*. **101**, 2216 (2006).
9- D. Balboni, I. Camurati, A. C. Ingurgio, S. Guidotti, F. Focante, L. Resconi, J. *Organomet. Chem*. **683** 2 (2003).
10- P. J. T. Tait, G. H. Zohuri, A.M. Kells, *Macromol. Symp*. **89**, 125 (1995).

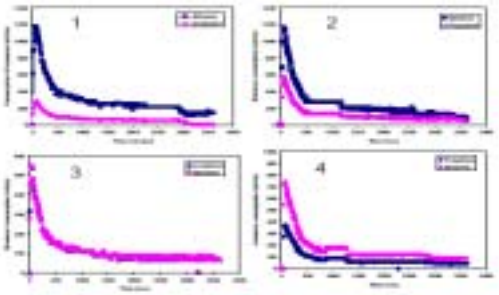

Fig. 1. Effect of reaction time on monomers consumption. Polymerization condition: (1)= P/E= 20/80, (2)= 33/67, (3)= 50/50, (4)=67/33, other condition as in Table I.

Table I. Terpolymerization using $(Ind)_2ZrCl_2$/MAO catalyst

P/E	ENB in reactor (mol/l)	%ENB in polymer (%wt)	Et % in polymer (%wt)	Activity kgP/molZr.h
20:80	0.05	1	83	1864
20:80	0.1	4	85	970
20:80	0.14	5	77	220
20:80	0.19	10	74	320
33:67	0.05	2	72	867
33:67	0.1	6	70	260
50:50	0.05	3	68	230
50:50	0.1	7	66	230
67:33	0.05	4	67	120

Polymerization conditions: Temperature =60 ^{0}C, [Zr],= 10^{-5} mol, MAO,=5 mmol, $P_{internal}$=1 bar, [Al]:[Zr]=500.

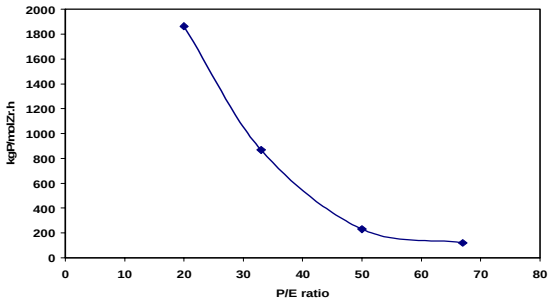

Fig. 2. Effect of P/E ratio on yield of polymerization.

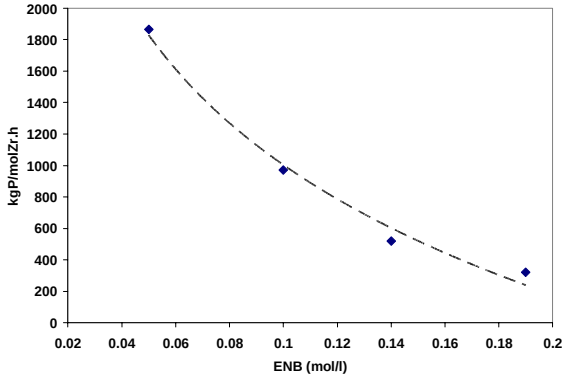

Fig. 3. Effect of diene concentration on yield of polymerization