9th International Seminar on Polymer Science and Technology

Iran Polymer and Petrochemical Institute, Tehran, Iran
17-21 October 2009

Preparation of rubbery (amourphous) polyethylene using late metal catalyst of [(2,6-i-prph)$_2$DABMe$_2$]NiBr$_2$

R. Sandaroos, G. H. Zohuri[*], S. Damavandi
Department of Chemistry, Ferdowsi University of Mashhad, P.O. Box 91775 Mashhad, Iran.

Abstract

Rubber like (amourphous) polyethylene with crystallinity of about 1 to 14% was prepared using a late metal catalyst of bis (2,6-isopropyl phenyl) 1,4-diazobutadine Nickel(II) dibromide [(2,6-i-prph)$_2$ DABMe$_2$]NiBr$_2$. The optimum activity of the catalyst was observed at [Al]:[Ni] = 3333:1 molar ratio and of polymerization temperature of 25°C of polymerization. Higher concentration of MAO than the optimum value not only decreased the activity of the catalyst but also produced polyethylene-wax (PE-Wax). The rate/time profile of the polymerization was a decay type with an acceleration period of about 60 min at polymerization temperature of 25°C. The polyethylene produced at temperature lower than 50°C showed rubberly (amourphous) behavior while the reaction at 65°C produced PE-Wax. Activity of the catalyst was increased with monomer pressure to 5 atmosphere which studied. The viscosity average molecular weight ($\overline{M_V}$) of the polymer obtained was 7.5×10^4 at the monomer pressure of 3 bars and 35°C temperature.

Key words: Rubbery (amourphous) polyethylene, late metal catalyst, Ni-catalyst, ethylene polymerization.

Introduction

Although the industrial process of shell higher olefin process (SHOP) is an example to produce oligomers by using homogeneous chelate of Ni(II) complexes with very high Activity[1,2] but the late metal catalyst systems of Fe, Co, Ni and Pd have developed since the mid - 1990s when Brookhart and his group reported a family of new cationic Pd(II) and Ni(II) α-diimine catalyst for the polymerization of ethylene, α-olefins and even cyclic olefins[1]. Most late metal systems often dimerize or oligomerize olefins, due to competing β-hydride elimination. However, the key to high molecular weight polymer is to use aryl-substituted α-diimine systems incorporation with bulky groups in the ortho position[3]. The bulky groups favors insertion reaction over transfer reaction[4,5].In the present work, as the kind ofproduced polyethylene strongly affected with the structure of α-diimine ligand, two catalysts of [(2,6-i-prph)$_2$DABMe$_2$]NiBr$_2$ and [(2,4,6-trimethyl-ph)$_2$DABMe$_2$]NiBr$_2$ were prepared and used for the polymerization (Fig1). Rubberly (amourphous) polyethylene was prepared with the catalyst contain the bulky group ligand, while, an oligomer was obtained using the other catalyst.

Experimental

Methylaluminoxane (MAO) (10% solution in toluene), triisobutylaluminm (T1BA) (purity 93%), were supplied by Merck Chemical (Darmstadt, Germany). Polymerization grade ethylene (purity 99.9%) was supplied by Iranian Petrochemical Co (Tehran, Iran).

Result and Discussion

Slurry polymerization of ethylene was carried out using the prepared catalyst (cat a) at different conditions in toluene. The polymerization activity increased with addition of MAO to a maximum activity of 5.1×10^3 g PE/(mmol Ni. h) following to a slightly decrease at higher molar ratio than [MAO]:[Ni] = 3333:1. The polyethylene obtained up to [MAO]:[Ni] molar ratio of 3333:1 was rubbery (amourphous) like while the polymer obtained at the ratio of 5000:1 was a waxy polymer. This behaviour could be as result of high chain transfer reactions at the presence of so high amount of MAO that lead to low molecular weight polyethylene.The highest activity of the catalyst was obtained at about 35°C (Fig 2). Higher temperatures provoke easy transfer to catalytic active centers, meanwhile solubility of the monomer gas in the polymerization medium decreased with increasing the temperature[6,7]. The maximum activity of the catalyst was observed after 60, 10 and 5 min of the polymerization for the reaction carried out at 25, 45

---

[*] E-mail: zohuri@um.ac.ir

and 55°C respectively. The waxy polymer obtained at 65°C could be as a result of β-hydride elimination which facilitated by the temperature[7]. In the presence of enough solvent, the activity linearly increased with increasing monomer pressure in the range studied. The polymerization was carried out at [Al]:[Ni] = 1667: 1 and temperature of 25°C. Due to the rubbery (amourphous) nature of the polymer obtained the solvent used was trapped in the polymer and prevent the polymerization to carry out further when 250 ml of toluene was used. The behavior is mainly due to higher concentration of the monomer close to the active centre[6].As the polymerization proceeds, the crystallinity began to decrease. It has been reported that mass transfer limitation could produce amorphous polymer[3] which confirmed by the following results of high crystallinity obtained at higher monomer pressure.

Conclusion

The conclusion obtained from the polymerization of ethylene using the $[(2,6\text{-}i\text{-}prph)_2DABMe_2]NiBr_2$/TIBA/MAO catalyst system are as follows;

The prepared catalyst of $[(2,6\text{-}i\text{-}prph)_2DABMe_2]NiBr_2$ was quite an active catalyst. The catalyst with the bulky substituted ligand groups produces high amourphous rubbery (likepolyethylene, while, the catalyst of $[(2,4,6\text{-}trimethyl\text{-}ph)_2DABMe_2]NiBr_2$ with less bulky substituted ligand produced oligomer of Oily like polyethylene. There is an optimum molar ratio of about [MAO]:[Ni] = 3333:1 obtained the highest yield of the polymer. At high temperature and high concentration of MAO, the cocatalyst, a waxy polyethylene was obtained.The optimum activity of the catalyst was obtained at 35°C. However, a linear increase of the activity was observed with increasing the monomer pressure up to 5 bars which studied. The polymer obtained has low crystallinity of about 1 to 14% depend on polymerization conditions used. A viscosity average molecular weight polymer of 7.5×10^4 was obtained using 35°C temperature and monomer pressure of 3 bar.

References

1. Ittel SD, Johnson LK and Brookhart M, *Chem Rev* **l00**,1169, 2000.
2. Kim IL, Han BH, Ha YS and Ha CS, *Park D W* **281**, 93-95, 2004.
3. *United States Patent 6034259*, 1996.
4. Guan Z and Salo EV, *Organometallics* **22**, 5033 2003.
5. Small BL, Brookhart M and Bennet AMA, *J Am Chem Soc*, ***120***, 4049, 1998.
6. Justino J, RomanoDias A, Ascenso J, Marcues M and Tait PJT, *Polym Int* **44**, 407, 1997.
7. Tsai W, M and Chien JCW, *J Polym Sci* **32**, 179 1194.

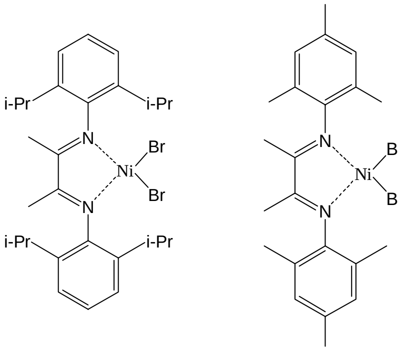

Figure 1. Structure of catalyst a (left) & b (right)

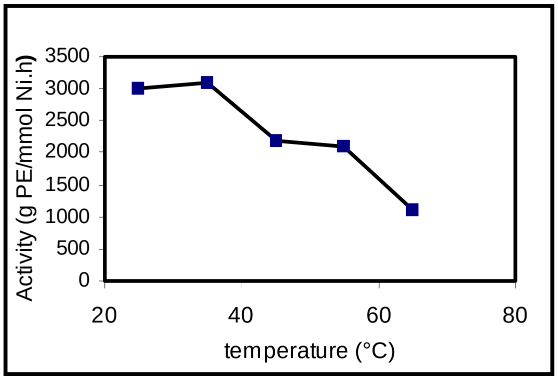

Figure 2. Effect of temperature on Rp