Preparation of rubbery (amorphous) polyethylene using late metal catalyst of \([(2,6-i-prph)_{2}DABMe_{2}]NiBr_{2}\)

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Abstract

Rubber like (amorphous) polyethylene with crystallinity of about 1 to 14% was prepared using a late metal catalyst of bis (2,6-isopropyl phenyl) 1,4-diazobutadiine 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 (amorphous) 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 (\(M_v\)) of the polymer obtained was 7.5 \(\times 10^4\) at the monomer pressure of 3 bars and 35 °C temperature.

Key words: Rubbery (amorphous) 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) \(\alpha\)-diimine catalyst for the polymerization of ethylene, \(\alpha\)-olefins and even cyclic olefins[1]. Most late metal systems often dimerize or oligomerize olefins, due to competing \(\beta\)-hydride elimination. However, the key to high molecular weight polymer is to use aryl-substituted \(\alpha\)-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 of produced polyethylene strongly affected with the structure of \(\alpha\)-diimine ligand, two catalysts of \([(2,6-i-prph)_{2}DABMe_{2}]NiBr_{2}\) and \([(2,4,6-trimethyl-\phi h)_{2}DABMe_{2}]NiBr_{2}\) were prepared and used for the polymerization (Fig1). Rubberly (amorphous) polyethylene was prepared with the catalyst contain the bulky group ligand, while, an oligomer was obtained using the other catalyst.

Experimental

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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 (amorphous) 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-i-prph)2 DABMe2]NiBr2/TIBA/MAO catalyst system are as follows:
The prepared catalyst of [(2,6-i-prph)2 DABMe2]NiBr2 was quite an active catalyst. The catalyst with the bulky substituted ligand groups produces high amorphous rubbery (like polyethylene, while, the catalyst of [(2,4,6-trimethyl-ph)2 DABMe2]NiBr2 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