



Effects of Cocatalyst on Ethylene-1-hexene Copolymerization with MgCl₂-supported Ziegler-Natta Catalyst *

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Introduction

LLDPE has become one of the most widely applied polymeric materials. In industry, LLDPE is mostly made by copolymerizing ethylene and higher α -olefins (1-hexene etc) with Ziegler-Natta catalysts. Since the catalysts have multiple active sites, the copolymer always has a broad chemical composition distribution (CCD) which can cause poor polymer properties. Al-alkyls are well known cocatalysts for Ziegler-Natta olefin polymerization. They affect the activity of the catalyst system and the CCD of the copolymer^[1-3]. An correct understanding of the effects of cocatalyst may be helpful for improving the CCD of LLDPE. For this purpose, the influence of the 1-hexene concentration (C_{Hex}) on ethylene /1-hexene copolymerization with MgCl₂-supported Ti-based Ziegler-Natta catalyst using triethylaluminum (TEA) or triisobutylaluminum (TIBA) as cocatalyst were investigated.

Experimental

Polymerizations were carried out in a 200 mL stainless-steel autoclave equipped with a mechanical propeller stirrer at 60 °C, 0.4 MPa ($[H_2] = 12.5 \text{ mol}\%$). The 1-hexene concentration was varied in the field of 0.3 ~ 2.0 M. About 20 mg catalyst (Ti-content = 5.8 wt %) was used.

All polymers were separated into crystalline and amorphous fractions by Soxhlet extraction with boiling *n*-heptane for 12 h. Compositions of ethylene/1-hexene copolymers and the fractions were measured by IR. Molecular weight and molecular weight distribution were obtained by GPC. The GPC curves were separated into five peaks of corresponding Flory components according to Schulz-Flory distribution.

Results and discussion

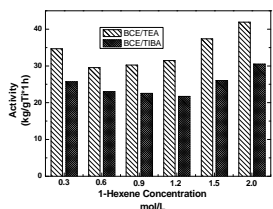


Fig.1 Activity of BCE with TEA or TIBA as cocatalyst

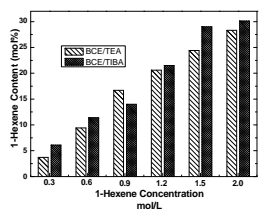


Fig.2 1-Hexene content of ethylene/1-hexene copolymer synthesized with BCE using TEA or TIBA as cocatalyst

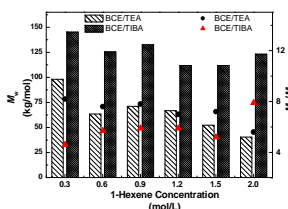


Fig.3 Molecular weight and molecular weight distribution index of ethylene/1-hexene copolymer synthesized with BCE using TEA or TIBA as cocatalyst

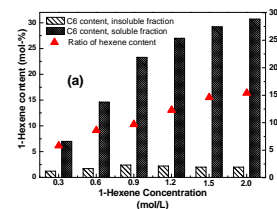


Fig.4 1-Hexene content of two different fractions separated from ethylene/1-hexene copolymer synthesized with BCE using TEA or TIBA as cocatalyst and the ratio of this two fractions (a) Using TEA as cocatalyst; (b) Using TIBA as cocatalyst

It was found TIBA brought about higher 1-hexene incorporation but lower polymerization activity than TEA. As C_{Hex} increased, the polymerization activity increased while the molecular weights of the copolymer were depressed. Beyond that, two additional phenomena were found: (1) using TEA as cocatalyst, the difference in 1-hexene content between the boiling *n*-heptane soluble fraction and the insoluble fraction increased as C_{Hex} increased. While using TIBA as cocatalyst, this difference remained almost unchanged. (2) using TEA as cocatalyst, the DPI of the copolymers were depressed as C_{Hex} increased. While using TIBA as cocatalyst, the situation is just the opposite.

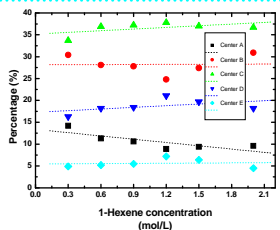


Fig.6 Flory components percentage of ethylene/1-hexene copolymer synthesized with BCE using TEA as cocatalyst

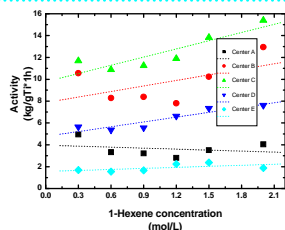


Fig.7 Activity of the corresponding active center to the Flory components of ethylene/1-hexene copolymer synthesized with BCE using TEA as cocatalyst

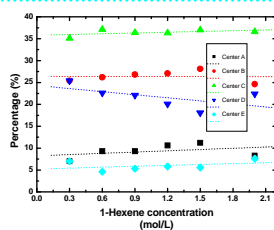


Fig.8 Flory components percentage of ethylene/1-hexene copolymer synthesized with BCE using TIBA as cocatalyst

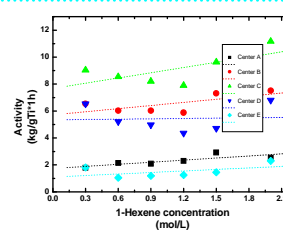


Fig.9 Activity of the corresponding active center to the Flory components of ethylene/1-hexene copolymer synthesized with BCE using TIBA as cocatalyst

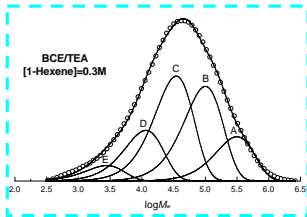


Fig.5 GPC curve and its Flory components separated according to Schulz-Flory distribution

All solid Ti-based Ziegler-Natta catalysts contain several types of active centers, thus all polymers and copolymers produced with such catalysts have broad molecular weight distributions. The GPC curves were separated into peaks of five Flory components. Each Flory component was assumed to be produced by a single type of active center. As previous research, the centers producing polymer molecules of higher molecular weights have lower copolymerization ability. According to our research, using TEA as cocatalyst, increasing comonomer concentration depresses the activity of the centers with poor copolymerize ability (center A). Meanwhile, increasing comonomer concentration also increases the activity of the centers with good copolymerize ability (center D). While using TIBA as cocatalyst, the situation is just the opposite.

Conclusions

TIBA brought about higher 1-hexene incorporation but lower polymerization activity than TEA. Using TEA as cocatalyst, increasing comonomer concentration increases the activity of the centers with good copolymerize ability.

References

- [1] E. Adison, M. Ribeiro, A. DeYeux, M. Fontanille, Polymer 1992, 33, 4337.
- [2] Kolvumaki, J.; Seppala, J. V.; Kuutti, L. Polym Bull 1992, 29, 185.
- [3] Collina, G.; Morini, G.; Ferrara, G. Polym Bull 1995, 35, 115.

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