

Controlling poly(1-hexene) microstructure by polymerization conditions

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Abstract

Effect of polymerization parameters including cocatalyst concentration, polymerization time, temperature and free solvent (bulk) technique on the behavior of a dinuclear α -diimine Ni-based catalyst ((1E,1'E,2E,2'E)-N1,N1'-(2,3,5,6-tetramethyl-1,4-phenylene)bis(N2-(2,6-diisopropylphenyl)acenaphthylene-1,2-diimine) dinickel tetra bromide) was investigated. As there was an optimum [Al]/[Ni] molar ratio, it also observed that higher concentration of diethyl aluminum chloride (DEAC) could decrease the normal insertion through the chain walking. Although, polymerization temperature showed an optimum point (25 °C), monomer conversion increased by time. Branching density (BD) for bulk polymerization was higher indicating normal insertion which led to greater butyl branches on microstructure. Distribution of branches along with BD disclosed that they could reduce the glass transition temperature (T_g) due to increasing chain mobility. Complete chain walking was a reason to reach lower BD, and subsequently, to create methylene sequence and melting area.

Keywords: chain walking, poly(1-hexene), dinuclear catalysts, polymerization condition, microstructure

Introduction

Based on literature, catalyst structure along with the polymerization parameters led to production of amorphous to semi crystalline polymers. In regard to catalyst architecture, multinuclearity as well as the ligand steric and electronic effects are important on the catalyst behaviour [1-4]. Chain walking polymerization of α -olefins is pronounced using different structure of mononuclear Ni and Pd catalysts; however, there is a demand on investigation of the effect of nuclearity on the mechanism of polymerization by the multinuclear catalysts. In addition, the monomer length in regard to the agostic interaction is important as well as the distance between the active centers [5, 6]. Through our recent works which were on polymerization of α -olefins using a series of mono and dinuclear Ni α -diimine based catalysts, the average molecular weight and distribution have been reported [7]. As it has been presented, the Mw and MWD of poly(1-hexene) samples in regard to catalyst structure could be varied. Based on it, the catalysts bearing ortho-substituents only on one side showed a broad to bi-modal distribution, while the catalyst with optimum bulkiness (A) resulted in higher molecular weight and virtually narrow MWD of poly(1-hexene) with the highest activity of catalyst. The supplementary analysis on microstructure and thermal properties of samples at different polymerization condition are discussing as following sections.

Experimental

Ligand and corresponding complex (A) were prepared according to our recent work [6]. The bulk polymerization of 1-Hexene monomer (purified prior to use) was carried out in a round bottom flask. The monomer (10 mL) was injected to the round bottom flask containing 10 mL toluene (solution polymerization) which was conducted under Schleck system. Afterward, the co-catalyst and catalyst were introduced to the flask, respectively. This system was stirred for 24 h. The poly (1-hexene) was precipitated and purified by acidic Methanol (5%).

Table 1. polymerization of 1-hexene at different condition and thermal properties

Entry	[Al]/ [Ni]	Con. (%)	T _g ^a (°C)	T _m ^a (°C)	ΔH^a (J/g)
1	1000	16.6	-56.3	-	-
2	1500	34.8	-56.9	-8.3	13.0
3	2000	32.7	-57.6	-	-
4 ^b	1500	22.8	-55.7	-	-
5 ^c	1500	19.3	-58.1	-17.1	3.3
6 ^d	1500	39.2	-61.8	-	-
7 ^e	1500	32.4	-57.1	-7.8	7.1

Polymerization condition: DEAC as cocatalyst, [catalyst]=3 μ mol, room temperature (25 °C), polymerization time=24 h, 10 cc toluene as solvent, a Determined using DSC, b 10 °C, c 60 °C, d free solvent, e 12h.

Table 2. Microstructure properties of the obtained samples

Entry	BD ^a (/1000 C)	Branch Distribution ^a (%)				
		Methyl	Ethyl	Propyl	Butyl	Long (>C4)
1	109.5	29.3	0	7.3	54.3	9.2
2	96.9	28.1	2.5	7.8	49.0	12.6
3	103.4	39.1	1.3	10.2	44.5	4.9
4	120.4	25.4	0	4.1	60.3	10.2
5	91.7	31.7	4.9	8.1	42.0	13.3
6	123.7	25.9	0	5.0	58.7	10.3
7	101.2	27.6	1.3	9.1	50.1	11.9

^a Obtained by ¹³C NMR instrument

Results and Discussion

Concentration of DEAC in the polymerization media had high impact on the microstructure. Based on this, as the concentration of the DEAC promoted, it induced the Ni center to go through partial chain walking and make the short chain branches, consequently. Higher density and diversity of branching, also, led to higher chain mobility and lower Tg and no significant melting temperature. Higher concentration of monomer through the free solvent technique is one of the substantial polymerization parameter which raised the BD, especially butyl branches. This result can be attributed to the high level of conventional 1,2-insertion [8]. Moreover, the conversion percent increased due to greater accessible monomer at higher concentration of 1-hexene around the active centers. Lower conversion ($\approx 5\%$) and molecular weight of 1-hexene observed when the polymerization quenched after 12 h (entry 16, Table 2). The BD increased, however, distribution not showed significant difference with entry 5. Higher BD according to the SCB curve in Fig. 4 for BC2 which is slightly ascending by increasing the Mw shows that BC2 through less tendency for chain walking favours higher normally insertion. The temperature as it showed the impact on the catalyst isomerization, it dramatically revealed an influence on the poly(1-hexene) microstructure [36, 37]. Based on this, the BD decreased from 120.4 to 91.7/1000 C atom as the temperature increased from 10 °C to 60 °C, while the SCBs increased. It can be concluded that tendency of the catalyst for partial chain walking is a function of temperature and the β -hydride elimination and also reinsertion mechanism increases as the polymerization temperature rises. Furthermore, the Tg and melting area are also consistent on our previous results [8].

Conclusion

Polymerization parameters as a controlling factor on the behavior of catalyst showed a huge impact on poly(1-hexene) microstructure. Chain walking was the reason for production of shorter and longer branches than butyl. Higher

level of the BD and distribution led to greater chain mobility leading to decrease of Tg. Free solvent polymerization due to high concentration of accessible monomer for active center led to higher conversion. Although long chain branches (>C4) percent for the samples were close, but the main difference were on the butyl and shorter branches. As a result, polymerization condition could induce the catalyst A to go through partial chain walking.

References

1. Leone G, Mauri M, Pierro I, Ricci G, Canetti M, Bertini F, *Polymer*, **100**, 37-44, 2016.
2. Wang F, Tanaka R, Li Q, Nakayama Y, Shiono T, *Organometallics*, **36**, 1358-1367, 2018.
3. Khoshsefat M, Zohuri GH, Ramezani N, Ahmadjo S, Haghpanah MJ, *Polym Sci Part A: Polym Chem*, **18**, 3000-3011, 2016.
4. McInnis JP, Delferro M, Marks TJ, *Acc Chem Res*, **47**, 2545-2557, 2014.
5. Han S, Yao E, Qin W, Zhang S, Ma Y, *Macromolecules*, **45**, 4054-4059, 2012.
6. Khoshsefat M, Ahmadjo S, Mortazavi SMM, Zohuri GH, Soares JBP, *New J Chem*, **42**, 8334-8337, 2018.
7. Azoulay JD, Bazan GC, Galland GB, *Macromolecules*, **43**, 2794-2800, 2010.
8. Dechal A, Khoshsefat M, Ahmadjo S, Mortazavi SMM, Zohuri GH, Abedini H, *Appl Organomet Chem*, 2018. DOI: 10.1002/aoc.4355.