

Accepted Article

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To be cited as: *ChemCatChem* 10.1002/cctc.202001281

Link to VoR: <https://doi.org/10.1002/cctc.202001281>

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Zn-assisted cooperative effect for copolymers made by heterodinuclear Fe-Ni catalyst

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Abstract: Mononuclear Fe and Ni based catalysts (M_1 and M_2) in the form of single and dual catalytic systems were employed in the presence and absence of diethyl zinc (DEZ) for polymerization of ethylene. Besides, corresponding homo- (M_3 and M_4) and heterodinuclear catalysts (M_7) along with the mononuclear analogues (M_5 and M_6) were used to explore the effect of adjacency of second metal center on the chain transfer efficiency. Totally, DEZ had stronger influence on the behavior of mono- and dinuclear Fe-based structures and corresponding thermal and microstructural properties of the PE samples than Ni complexes. In addition, a mechanism was proposed for M_5 as the vinyl-terminated polymer chains augmented in the presence of DEZ. More interestingly, M_7 not only showed a cooperative effect for production of a random copolymer containing short and long chain branches but also at low and high concentration of DEZ, a blocky copolymer was obtained through CCTP and CSP. All these were consistent on ^{13}C NMR, DMTA, SSA and CEF results.

Introduction

One of the fascinating area in the polymerization of olefins is synthesis of olefin block copolymers (OBCs) through chain shuttling and coordinative chain transfer polymerizations (CSP and CCTP). This approach, i.e. CSP or CCTP, leads to fine-tuning polyolefin and polydiene microstructures enabling better control on the polymer properties.^[1] It is a result of regulating the backbones and well-defined branches onto it.

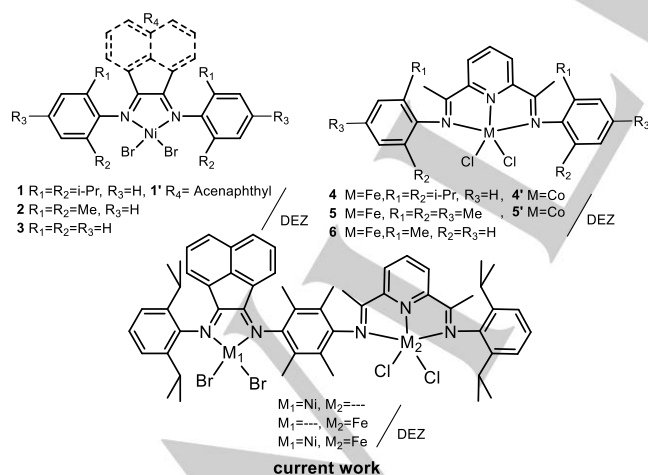
In these systems, different kinds of catalysts based on rare-earth and transition metals have been used where a single or a mixture of two catalysts are employed in the presence of chain transfer agents (CTAs) in the form of main group metal alkyls.^[2-23] Although the catalysts based on rare-earth metals have shown good results in these kinds of polymerizations but transition metals especially the late ones are much more interesting and

attractive. This interest is due to their outstanding behaviour in polymerization of olefins for production of linear to hyperbranched and low to high molecular weight (M_w) polyolefins, introduction of polar and even bio-sourced comonomers into the backbone of polyolefins.^[24-32] Based on this, there are many papers on the study of these catalysts behaviour. Moreover, they kept their position in the mentioned systems for production of olefinic copolymers. For instance, Wang et al. reported a linear-hyperbranched polyethylene (PE) produced using α -diimine nickel catalyst **1** (scheme 1) and an ethylene-bridged indenyl zirconium catalysts in the presence of DEZ as chain shuttling agent (CSA).^[7] Mortazavi and co-workers reported a linear-branched PE block copolymer made by **1'** and the same zirconium catalyst. Similar catalytic systems based on an α -diimine Ni structure and a zirconocene catalyst in the presence of DEZ also have been reported, however, they were much more suitable for a control production of bimodal PE.^[21,23] With respect to bimodality, bimodal PE represents an important class of polyolefin material with many unique properties and wide applications such as bimodal film resins, pipes and large part blow-molding articles.^[33] The molecular weight distribution (MWD) as well as the branching type, density and distribution significantly affect the polymer properties (thermal, rheology, mechanical and etc.).^[33-36] In another report, Ahmadi et al. prepared a branch-on-branch PE microstructure via a new dual catalytic system including catalyst **1'** and a Fe-based vinyl-producer complex in a CCTP.^[37] The structural properties of catalysts can control the rate and efficiency of chain transfer as there is a competition among the chain transfer, propagation and chain termination. According to this, Tonks and co-workers disclosed that changing of *iso*-propyl groups on side aryl rings of α -diimine Ni catalyst (**1**) into methyl substituents (**2**) could increase the chain transfer to propagation rate.^[17] While, in the case of hydrogen substituents (**3**), chain termination through the β -H elimination was dominant. The effect of substituents also could be observed in the work of Xiao and co-

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workers where using **1** and **2** afforded branched-hyperbranched PE block copolymers in the presence of DEZ.^[19] There are some other reports on using other late transition metals such as Co and Fe (**4-6**, **4'** and **5'**) which only Fe catalysts successfully acted toward CSAs.^[2,4,5] Even in the case of Fe catalysts, *iso*-propyl substituents on side aryl rings (**4**) demonstrated good response in this manner, while the efficiency decreased for methyl groups (**5** and **6**).⁵ In addition to catalyst structure, polymerization parameters such as CSA type and concentration, ratio of the catalysts, polymerization time, temperature and monomer pressure have striking effects on the chain transfer efficiency (CTE), length of the olefinic blocks and polymer properties.^[2,15,17,21,37-40]

On the other side, multinuclear catalysts have shown remarkable behaviour such as cooperative effects.^[41,42] This metal...metal interactions may change the polymerization mechanism and cause an increasing of catalytic features and polymer properties such as catalyst activity, selectivity of chain branching, Mw, tacticity and so on.^[43-45] Regarding the multinuclear catalysts architectures, there are homo- and heteromultinuclear structures which completely could affect the cooperation between the centers. Through an ideal style of cooperative effect, the product of first center can be consumed by the second center.^[46,47] The efficiency of cooperative effect depends on some factors including the tendency of each center for cooperation, distance between the centers, the nature of centers and the products of each active site and etc.^[41,42] All these could be summarized in electronic and steric effects. Presence of CSA in the polymerization media and its interaction via CSP or CCTP along with the possibility of cooperative effects in multinuclear catalysts are very controversial. Although both scenarios have a similar concept, fundamentally, the synergistic or frustrating impacts could be considered. To interpret the effects, in addition to well-known catalyst behaviour, the experiments must be carried out under suitable and determined conditions as the catalyst behaviour and the aforementioned effects are very dependent on polymerization parameters.



Scheme 1. Fe/DEZ and Ni/DEZ catalyst systems vs. the current work.

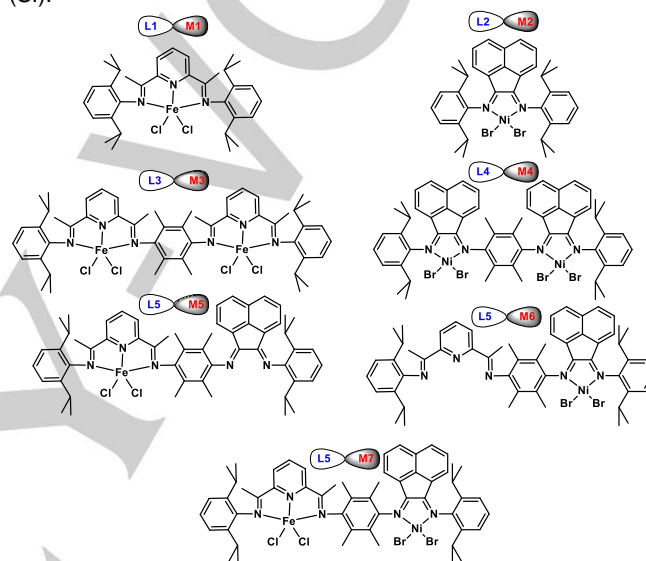
Herein, we designed a series of heterodinuclear and mononuclear catalyst structures (scheme 1; current work) based on our previous reports and literatures. These complexes are bearing methyl and *iso*-propyl on the side aryl rings showing optimum bulkiness (in respect of activity and CTE) which used in the presence and absence of DEZ for polymerization of

ethylene.^[5,17,28,29,42] These catalysts were compared with further mono- and homodinuclear structures (scheme 2). The effect of CSA on the behaviour of each catalyst and molecular, thermal and mechanical properties of the polymer obtained were studied, comprehensively.

Results and Discussion

Preparation of ligands and complexes

All the ligands (L_1 - L_4) and complexes (M_1 - M_4) were prepared according to our previous papers (scheme 2) except those new structures (L_5 and M_5 - M_7) which the details on syntheses and characterizations are provided in the supporting information (SI).^[28,29]



Scheme 2. Mono- and dinuclear catalysts used in the polymerization of ethylene.

Effect of DEZ on the catalyst behaviour and polymer properties

Catalyst activity and ethylene flow profile

First of all, it should be noted that all the $[Al]/[M]$ molar ratios were chosen based on the highest catalyst activity observed in our previous reports.^[29,42] The effect of DEZ on the catalyst activity, as it mentioned previously, is completely different regarding the nature of active center and concentration of DEZ.^[5,15] In some cases, addition of DEZ has caused an increasing in productivity of the catalysts, while in the other cases, activities have dropped. Herein, we also dealt with different affinities, as for M_1 , activity decreased and for M_2 productivity improved (table 1).

It previously has been reported that at lower DEZ concentration (100 equiv.), activity of M_1 increases and it also shows lower productivity at higher equivalent of DEZ (i.e. 500 equiv.).^[4] In our case, as we used 200 equiv. of DEZ, activity for M_1 decreased. It also has been reported for M_1 that there are two different active sites: the more active (and unstable) centers operated at the early stages of polymerization, gradually transforming into the less active sites; the former sites afford the low- M_w PE fraction, while the latter sites are responsible for the high- M_w PE fraction.^[48] In order to interpret the results for activity, it can be suggested that the presence of DEZ may cease transformation of first active centers into second ones. Therefore, there are only first active centers affording low- M_w PE. This also can be seen in the profile of ethylene flow in the presence and absence of DEZ (figure 1-a).

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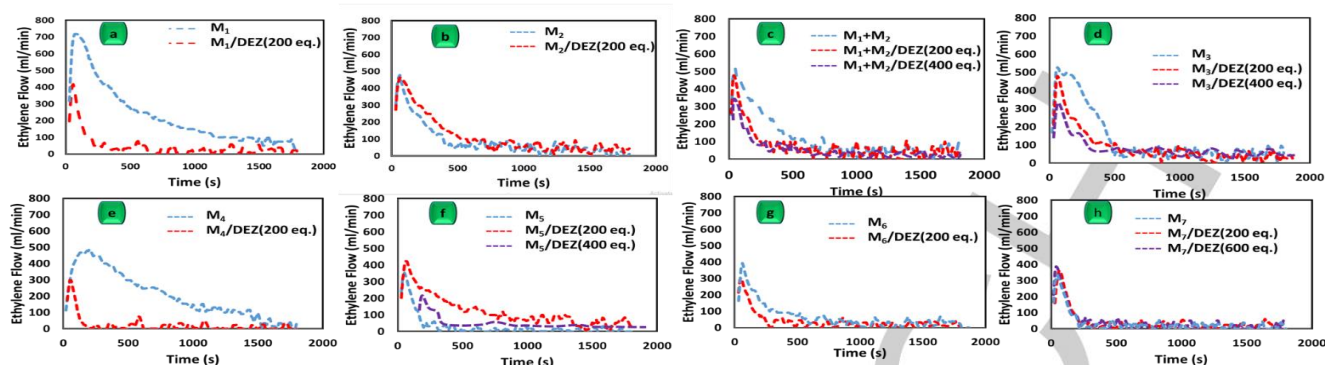


Figure 1. Ethylene flow profile for mono- and dinuclear catalysts (M_n , $n=1-7$).

Table 1. Results of ethylene polymerization using mono- and dinuclear catalysts (M_n , $n=1-7$)^[a]

Entry	Cat.	[Zn]/[M]	[Al]/[M]	Yield (g)	Activity (g P mmol ⁻¹ M h ⁻¹)	M_w ^[b]	MWD ^[b]	CH ₃ ^[b] (/1000C)	T_m ^[c] (°C)	X_c ^[c] (%)
1	M ₁	0	1000	5.5	2619.0	143000	21.7	5.5	137.0	67.8
2	M ₁	200	1000	1.9	904.7	2300	1.5	39.1	87.5	65.6
3	M ₂	0	1500	4.7	2220	112000	2.2	66.3	45.0	<0.1
4	M ₂	200	1500	5.5	2600	117000	2.5	72.3	-	-
5	M ₁ +M ₂	0	1500	5.2	2472	190000	60.5	31.6	131.5	26.3
6	M ₁ +M ₂	200	1500	5.0	2377	153000	41.7	23.2	92.1, 124.2	15.2
7	M ₁ +M ₂	400	1500	3.7	1759	76000	34.0	30.5	80.7, 127.0	37.5
8	M ₃	0	1000	10.3	4904.8	104000	12.0	4.6	138.0	79.8
9	M ₃	200	1000	4.6	2214.3	94000	21.0	11.2	93.8, 132.1	86.3
10	M ₃	400	1000	3.1	1476.2	4900	1.9	19.3	91.5	75.2
11	M ₄	0	1500	6.9	3280	501000	2.4	32.5	121.0	24.7
12	M ₄	200	1500	4.2	1996.5	82000	6.5	21.9	124.2	5.1
13	M ₅	0	1000	1.9	922.2	551000	48.3	21.3	136.0	40.0
14	M ₅	200	1000	3.9	1853.9	73000	19	23.4	128.3	25.8
15	M ₅	400	1000	1.6	760.6	1200	1.2	44.2	81.7	18.3
16	M ₆	0	1500	2.0	950.8	293000	2.4	26.0	119.0	18.2
17	M ₆	200	1500	1.1	522.9	227000	4.3	40.2	125.1	5.5
18	M ₇	0	1500	1.4	674.7	268000	4.1	29.5	124.1	4.8
19	M ₇	200	1500	1.7	810.6	238000	3.7	20.1	120.2	8.2
20	M ₇	600	1500	1.7	834.9	150000	2.5	12.1	119.1	13.3

^[a] Polymerization condition: [Al]/[M]=1500 (MMAO), ethylene pressure 1.5 bar, 30 min, toluene 80 ml, 30 °C, [M]= 4.2 μmol. ^[b] Determined by GPC-IR. ^[c] Determined by DSC.

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According to it, ethylene is consumed by the active centers at the early stages of polymerization, however, for M_1 /DEZ system, ethylene consumption decreased strongly, afterward. It also has been claimed that there is a possible complexation of active center and DEZ leading to an inactive site.^[5,18,21] For M_2 , catalyst activity increased in the presence of DEZ. It has been reported that CSA cannot act as an activator or a cocatalyst, individually, so it may imply that DEZ acts as CTA and polymerization can last for longer time (figure 1-b).^[5,18] For dual catalytic system (M_1+M_2), overall activities (table 1; entries 6 and 7) decreased (figure 1-c) as DEZ augmented in the polymerization media (200 and 400 equiv.s of DEZ). It is clear that the observations for the dual catalytic system are due to strong reduction of activity for M_1 against moderate enhancing of productivity for M_2 . Although for dinuclear catalyst M_3 (figure 1-d), activity decreased similarly to its mononuclear counterpart (i.e. M_1), for M_5 , surprisingly, activity increased two-fold in the presence of DEZ (table 1; entry 14 and figure 1-f). An opposite behaviour was observed for M_4 and M_6 in comparison to M_2 where the productivities decreased significantly. Decreasing of activity for dinuclear catalysts M_3 and M_4 in the presence of DEZ may be attributed to an interruption of dinuclearity and synergistic effects of the second metal center, and agostic interaction. All these also could be observed in the ethylene profiles depicted in figure 1 (e and g). For heterodinuclear catalyst M_7 , productivity increased smoothly as DEZ introduced into the reactor at 200 and 600 equiv.s of DEZ (table 1; 19-20 and figure 1-h). Moreover, not only activity of M_7 was lower than its mononuclear analogues (M_5 and M_6) but also lower than homodinuclear catalysts (M_3 and M_4), dual and single catalytic systems (M_1 and M_2). Totally, it could be concluded that in addition to nature of metal center, *ortho*-substituents and dinuclearity effects are the further controlling factors on the behavior of catalysts against DEZ.

Molecular weight (M_w) and molecular weight distribution (MWD)

To investigate the effect of DEZ on M_w and MWD, all the samples were analysed by gel permeation chromatography- infra red (GPC-IR) machine. As DEZ acts as CTA, through transferring of polymer chain to Zn, it can cause a decreasing of M_w by suppressing of propagation. In other side, this reduction in terms of intensity, strongly, relies on the catalyst affinity and reversibility of chain transfer reactions (CTRs) which control the interaction of catalyst...CTA (CSA) and may allow the transferred chains to grow on the metal centers. In addition to M_w , MWD is one of challengeable factors that not only depends on the catalyst affinity but also concentration of CSA that affects the features of polymer, crucially. These facts can be seen in figure 2 and table 1. To clarify, for M_1 , as DEZ introduced, M_w dropped drastically from 1.4×10^5 g mol⁻¹ to 2.4×10^3 g mol⁻¹. MWD of the PE made by M_1 /DEZ also was narrow (1.5) and unimodal while in the absence of DEZ, MWD was very broad and about 22 (see figure 2-A). Aforementioned reasons for the activity of M_1 may also implied here as it seems that there is only one active center producing low M_w fraction in the presence of DEZ. For M_2 , decreasing of M_w also observed, however, it was not like M_1 as MWD of the given sample was slightly broader in the presence of DEZ (from 2.2 to 2.5). It may be attributed to the lower affinity of M_2 for CTR that few numbers of active centers effectively reacted with DEZ. These results completely showed the difference of DEZ action against different catalysts. As each catalyst acted individually in the dual catalytic system (M_1+M_2), a very broad MWD (bimodal) was

observed. At 200 and 400 equiv.s of DEZ, MWD decreased significantly that can be seen in the GPC curves (figure 2-A). Reduction of M_w and MWD was a sign of chain transfer to Zn (CTZ) in the system. The scenarios for M_5 /DEZ and M_6 /DEZ were the same as described for M_1 /DEZ and M_2 /DEZ except the intensity of the interactions was stronger and M_w and MWD changed dramatically. Although, M_5 needed more amount of DEZ to act as a single site catalyst affording a narrow MWD, M_w of the neat PE made by M_5 was higher than M_1 . All these may be attributed to the optimum bulkiness provided by *iso*-propyl and methyl groups on *ortho*-positions along with the electronic effects of bulky ligand.^[5,17]

Homodinuclear catalyst M_3 showed a similar behaviour to M_1 , though at higher concentration of DEZ (figure 2-B). Reduction of M_w and MWD were not as strong as M_1 and M_5 . This could be attributed to the interference of DEZ action with dinuclearity effect. As it could be observed in figure 2-B, the GPC curves have shifted toward lower M_w as DEZ augmented in the system. GPC-IR curves also showed the same trends for M_3 similar to M_1 and M_5 . Although, DEZ caused to reduction of M_w for the PE made by M_4 , MWD of the sample broadened even with more intensity than M_2 . The observed differences between the mononuclear (M_1 and M_2) and dinuclear (M_3 and M_4) catalysts regarding the intensity of interaction with DEZ could be attributed to the combination of steric (optimum bulkiness) and electronic effects (second metal center).

Regarding the nature of active centers, totally, Fe-based catalysts (i.e. M_1 , M_3 and M_5) exhibited more intense reduction of M_w along with narrowing of MWD. It revealed that at a desired concentration of DEZ, there is only one active center. An explanation for the results can be expressed as bond dissociation energy of Fe-C and Zn-C are much closer than Ni-C and Zn-C which facilitates CTR and suppresses propagation (effective CTZ).^[2,49]

Heterodinuclear Fe-Ni catalyst (M_7) produced PE with an almost higher M_w and extremely narrower MWD in comparison to the mixture of mononuclear Fe and Ni catalysts (M_1+M_2). It also can be observed that M_w of the sample (entry 18) is between the M_w 's obtained for mononuclear analogues (M_5 and M_6) and much closer to M_6 (figure 2-C). However, there is a different behavior from M_5 and M_6 as DEZ introduced into the reactor. This observation is about the disappearance of low M_w -fraction along with narrowing of MWD where at higher DEZ concentration, it showed a unimodal MWD. This may be attributed to the incorporation of the hard or soft segments into the final microstructure of copolymer through CSP or CCTP that leads to formation of random or block copolymer. This is called "Zn-assisted cooperative effect" which needed more evidences as is described in the following.

Melting point (T_m) and crystallinity (X_c)

Thermal properties such as T_m and X_c could be good clues for the changes in microstructure of the obtained samples. Decreasing of T_m and X_c can be attributed to the decreasing of methylene sequences and as a result of branched microstructure or lowering of M_w . T_m of HDPE obtained by Fe-based catalysts (i.e. M_1 , M_3 and M_5) decreased as DEZ was added into the polymerization systems. However, X_c not showed a significant change. Shortening of polymer chains due to lowering of M_w by CTZ, along with a slight increasing of branching density (BD) were the reasons for the observations. On the other side, Ni-based catalysts showed a different behavior in this manner. Where these α -diimine Ni structures are candidates for production of branched

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PE, interference of DEZ performance with chain walking mechanism led to sporadic thermal properties. To clarify, M_2 produced an amorphous PE with higher BD in the presence of DEZ, higher T_m 's with lower X_c were seen for M_4 /DEZ and M_6 /DEZ systems. As broad to bimodal MWDs were observed for the dual catalytic systems (i.e. entries 5, 6 and 7), different endotherm peaks were observed in the thermograms. Heterodinuclear catalyst M_7 made PE with low X_c (4.8%) and high T_m (124.1 °C). Although, X_c increased as DEZ introduced into the reactor, T_m

decreased from 124.1 to 119.1 °C. Regarding the X_c values for M_7 and M_7 /DEZ, there are two possibilities; first, incorporation of linear microstructure into the polymer chain (backbone or long chain branch (LCB)) dedicated by Fe center through cooperative effect and second, no chain walking or complete chain walking (chain straightening) leading to linearity of polymer chains. These two scenarios are the plausible mechanisms for formation of random or block copolymers.

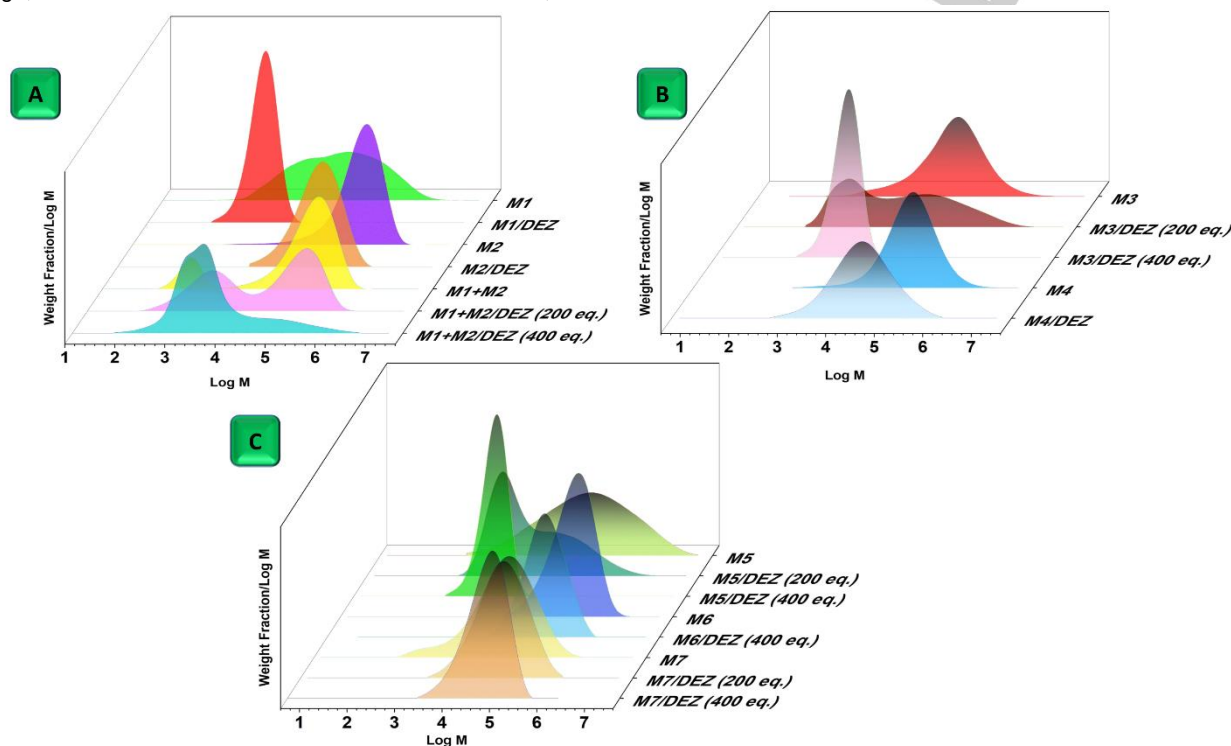


Figure 2. GPC results of PE made by mono- and dinuclear catalysts (M_n , $n=1-7$)

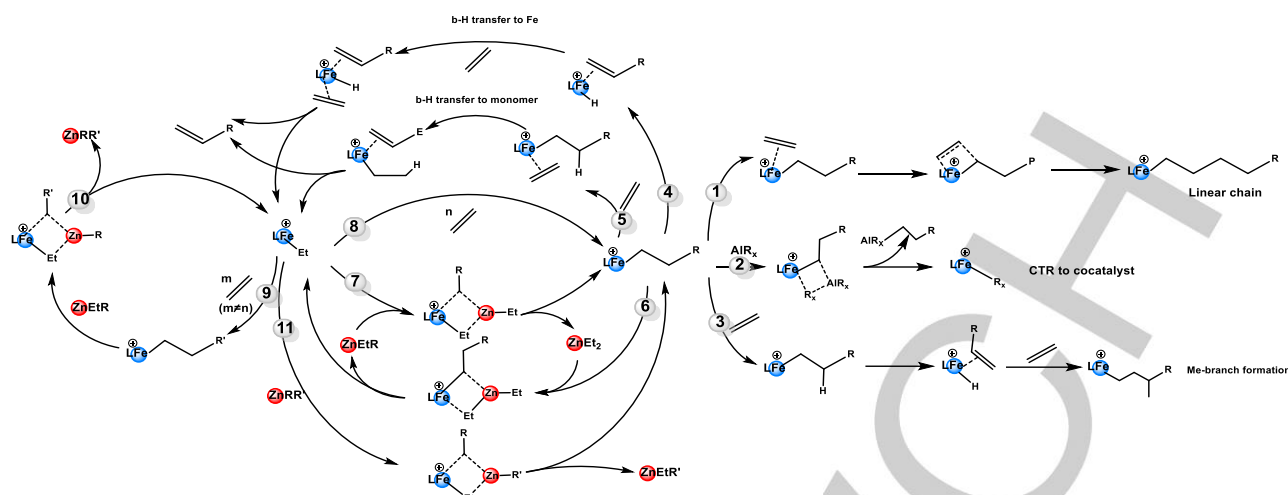
Branching density (BD) and distribution

According to GPC-IR, two different catalyst structures with different behaviours in respect of microstructural properties of PE can be seen where each catalyst (i.e. Ni and Fe) produces its own polymer in the presence of DEZ (table 1 and figure S2). Although, high methyl-end ($CH_3/1000C$) at high concentration of DEZ was due to great share of low M_w in the samples made by Fe-based catalysts, for Ni comparators, greater values of methyl-end and $CH_3/1000C$ curves were related to high BD.

In order to take a deeper look at microstructure of the polymers, ^{13}C NMR analysis was used for some samples including entries 1-4, 13, 15-17, 18 and 20 (figure S2). All the peaks were assigned to the corresponding microstructure and the results were tabulated in table S1. Low BD affording linear microstructures (few methyl (Me) branches) obtained for entries 1 and 2 which are the most probable type of branches forming by the iron catalysts (table 2). Plausible mechanism for the iron catalysts is given in scheme 3. Paths 1, 2 and 3 are showing propagation (linear microstructure) and CTR to Aluminum (Al) and Me branch formation routes, respectively. For catalyst M_2 (i.e. entries 3 and 4), the BD increased in the presence of DEZ. Moreover, branching distribution demonstrated that M_2 dominantly tends to produce Me branches as its Me branch percent enhanced from 50.8 to 83.9%. It may be interpreted from this point of view that CTZ could

increase the polymer chains initiated per nickel catalysts.¹⁷ This may cause an interruption to chain walking mechanism and conducting first chain walking on the new polymer chain, possibly. Based on this, nickel active centers not have enough time to walk on the polymer chains and DEZ tunes the Me branch formation. In a similar manner to M_1 , M_5 also reacted strongly with DEZ, however, the BD was higher. Besides, branching distribution was similar as high level of Me branches obtained. More interestingly, in the presence of DEZ, the production of vinyl-terminated polymer chains improved. This behavior for Fe-based catalysts has been observed for a few structures while for the most cases, saturated polymer chains have been obtained.^[50] It can be speculated that Zn has assisted M_5 to produce higher unsaturated polymer chains. In scheme 3, all the possible routes for CTRs are presented. As it can be observed, CTRs could occur within 4, 5, 6 and 10. Within a normal route, a vinyl-end polymer chain obtains through β -H transfers to Fe or to monomer (4 and 5). In the presence of DEZ, although, unsaturated polymer chains could not be obtained, it augmented Fe-Et cationic specie in the system through CTZ. This specie then could undergo a series of reactions including 7, 8, 9 and 11 to reproduce the Fe-polymeryl species (i.e. Fe-R or Fe-R'). Based on this, these new Fe-polymeryl chains may go through the β -H transfer reactions affording vinyl-terminated polymer chains.

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Scheme 3. Proposed mechanism of polymerization routes for Fe catalysts in the presence of DEZ.

In spite of M_2 , M_6 produced PE with lower BD and higher selectivity for Me branches. It also can be observed in table 2 that the BD decreased for M_6 /DEZ and affinity for Me branches shifted to other types of branches such as ethyl and butyl. This may be attributed to the lower steric and higher electronic effects provided by *ortho*-substituents and bulky backbone in M_6 . On the other side, no vinyl-end polymer chains observed for Ni catalysts in the presence or absence of DEZ. A similar mechanism as described in scheme 3 could be considered. However, there are some differences between these nickel and iron complexes including different affinity for macromer incorporation, chain walking and efficiency of CTZ. For M_7 , microstructure of the polymer was containing high level of Me branches and low level of LCBs affording an almost average BD. Moreover, unsaturated chains not observed for M_7 and M_7 /DEZ systems. In the presence of DEZ, not only Me branches were still the dominant SCBs but also LCBs slightly increased in the microstructure of the sample (table 2; entries 19 and 20). This may imply that as Fe centers could produce higher vinyl-end polymer chains in the presence of DEZ similar to M_5 which could incorporate in the polymer backbone as LCBs.

Table 2. Branching density and distribution of selected samples.

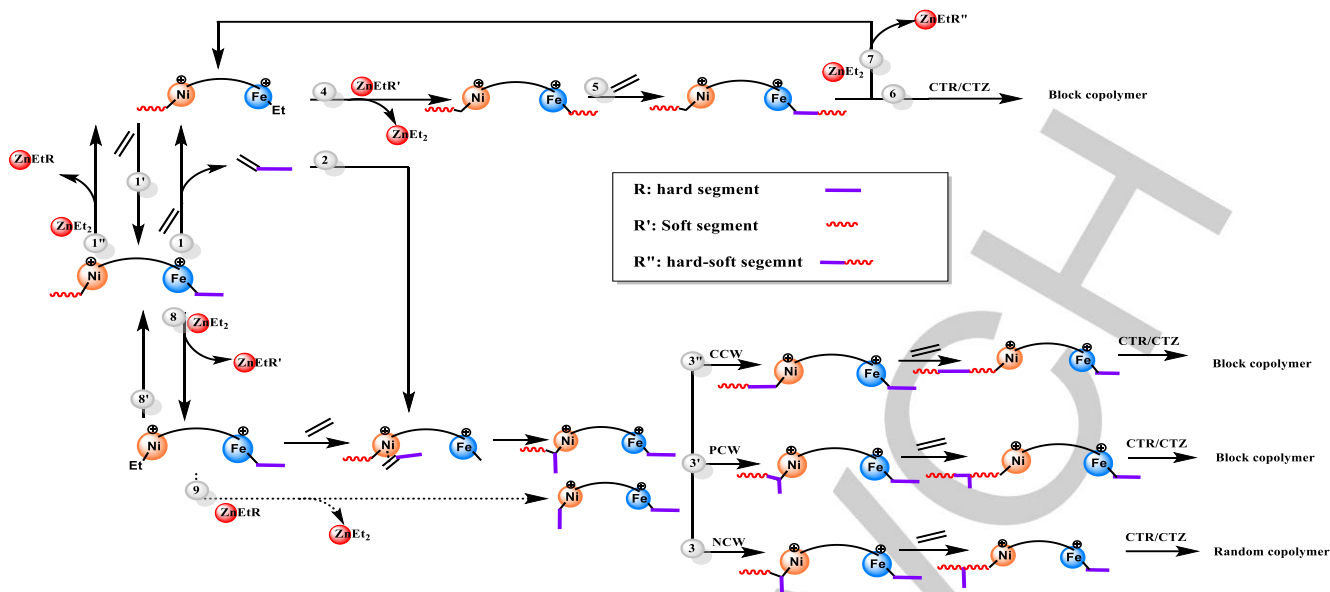
Entry	Branching Density (/1000C)	Branching distribution (%)					
		Me (i-Me)	Et	Pr	Bu	Am	L
1	4.3	100 (100)	0	0	0	0	0
2	5.2	98.8 (100)	1.2	0	0	0	0
3	75.2	50.8 (85.1)	11.6	12.7	13.0	2.4	9.5
4	84.6	83.9 (91.5)	9.2	0	6.3	0	0.6
13	9.3	98.2 (100)	1.8	0	0	0	0
15	12.4	99.7 (100)	0.3	0	0	0	0
16	56.0	74.5 (82.1)	14.7	0	4.3	6.2	0.3
17	59.2	68.4 (90.0)	18.2	1.2	10.0	1.1	1.1
18	39.5	88.2 (84.2)	2.4	0	1.5	3.2	4.7
20	25.7	87.3 (92.5)	1.4	0	2.9	0	8.4

On the other side, regarding the Me branches in the microstructure of samples, isolated Me (i-Me) branches increased

for entry 20 (92.5%) rather than 18 (84.2%). i-Me branches for M_5 was the only type of Me branches (100%). In contrast to M_5 , Me branches for M_6 were various from i-Me (81.2%) to paired 1,4-Me (11.6%), 1,5-Me (4.1%) and 1,6-Me (3.1%). Generally, Ni catalysts are capable for production of highly branched PE (soft segment) and are good incorporators while, Fe catalysts are poor incorporator and are able to produce linear microstructure (hard segment). Besides, iron catalysts better act against CTZ reactions. Based on the thermal and microstructural properties of the sample made by M_7 , incorporation of macromers made by Fe center into the backbone of main branched polymer chain could be considered. According to schemes 3 and 4, a vinyl-end polymer chain could supply by the Fe center through β -H transfer reactions (scheme 4; 1). After this transfer, Fe center could again undergo propagation to produce another hard segment (1'). The hard macromer (linear) may enchain into the Ni-linked branched polymer chain (soft segment) (2). In case of no chain walking (NCW), the final microstructure could contain macromers as LCBs (3) and produce random copolymer. Similarly, for partial chain walking (PCW), LCB could be formed with lower length (3') while, complete chain walking (CCW) leads to chain straightening and formation of linear microstructure and block copolymer structure (3''). Besides, block copolymer could be obtained by soft segment (produced by Ni and transferred to Zn) transferring to Fe (4 and 5).

In the presented Fe-Ni structure, totally, two different scenarios could be considered for M_7 /DEZ. First, Fe center like its mononuclear (M_5) could act as a linear macromer producer (hard segment) and Ni center was able to incorporate the macromeres with or without CW. Second, due to reversibility and high CTE of Fe, the soft segment (made by Ni) could be transferred to Fe center and through the propagation reactions, a hard block could be obtained after the soft segment. The probable reverse route for transferring of hard segment to Ni could be considered (9) but it is rare as the interaction of Ni and Zn is not as strong as Fe and Zn, and chain transfer for Ni center is almost irreversible. It could be concluded that the copolymer is a result of cooperative effect in the absence of DEZ, and in the presence of DEZ, Zn-assisted cooperative effect, CSP and CCTP are responsible for the production of copolymers.

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Scheme 4. Proposed mechanism for production of random and block copolymer made by M_7 and M_7/DEZ .

Crystal fractionation

For better understanding of microstructural properties, successive self-nucleation and annealing (SSA) technique was used as fractionation of different lamellae can give good details on various methylene sequences. Interestingly, for entry 2 where the DEZ reacted with M_1 , no fractionation observed and there was only a shift for T_m (figure 3-A). Therefore, the high crystalline HDPE changed to high crystalline low M_w PE wax. However, for M_2 , the scenario was different as addition of DEZ led to higher level of BD, and no melting point and fraction were observed. In the other word, some few weak fractionated lamellae observed in the absence of DEZ disappeared in SSA thermogram. According to DSC results for M_1+M_2 and M_1+M_2/DEZ showing bimodal to broad endotherm peaks, the same trends with some fractionations were observed in SSA thermograms. However, fractionations were based on the share of each catalyst in the final polymer blends and linear to branched microstructure of PEs. The SSA thermograms for M_3/DEZ and M_5/DEZ were similar to M_1 except for M_5 , X_c decreased at higher concentration of DEZ (figures 3-B and 3-C). Besides, at low concentration of DEZ, some fractions obtained in the range of 70-130 °C where the share of fraction with $T_m=127.1$ °C was the greatest. A slight increasing of BD (Me branches) and decreasing of M_w (chains with shorter length) could be the reasons for decreasing of X_c . For M_4 and M_6 , a same trend to M_2 observed in respect of intense decreasing of fractions (figures 3-B and 3-C). Low intensity for fraction melted at 127 °C (entry 18) enhanced by DEZ (figure 3-C) and gave various fractions melted at different temperatures. Besides, some fractions melting at lower temperature appeared for entry 20. These observations are consistent on the aforementioned mechanisms and reasons as linear macromers and hard segments introduced into the microstructure of polymer which formed block copolymer.

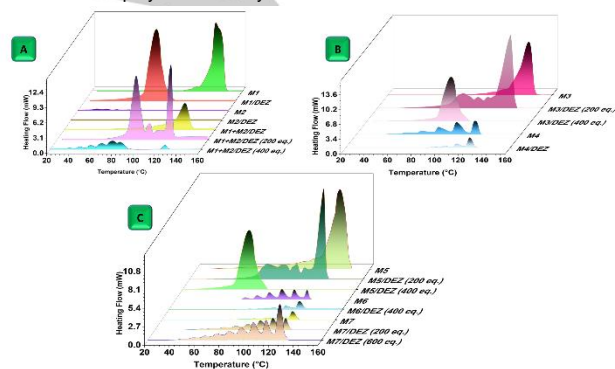


Figure 3. SSA thermograms of PEs made by mono- and dinuclear catalysts (M_n , $n=1-7$).

In order to supplement the results and explanations, crystallization elution fractionation (CEF) analysis was employed. The elugrams are presented in figures 5 and S3-8. This method is known for chemical composition distribution (CCD) determination that relies on the distribution of crystallizability of polymer chains in a dilute solution.^[51] Based on this, soluble fraction eliminates as it does not incorporate in crystalline fractions. The soluble fraction could be due to high level of comonomer or branches in the microstructure or very low M_w fraction (under 6000 g mol⁻¹) as they are soluble in the solvent. For instance, entry 2 showed more than 85% soluble fraction without any peaks in the elugram while it owned high X_c (65.6%, figure S3). On the other side, as the BD were high in the presence or absence of DEZ (entries 3 and 4), increasing of soluble fraction and disappearance of crystalline share was a clue showing that there is a soluble highly branched polymer (figure S4). Low concentration of DEZ led to formation of different sites in M_3 and M_5 . Therefore, different composition of polymer chains led to different peaks in the elugrams (figures S5 and S7). At higher concentration of DEZ, all the sites transformed to a unique active center and it was expected to observe a unimodal peak in CEF elugram, however, due to low M_w fraction obtained at high concentration of DEZ, no peaks were observed.

As it could be expected that lowering of X_c and promoting of BD for entries 12 and 17 (i.e. M_4/DEZ and M_6/DEZ) lead to increasing of soluble fraction like M_2 to more than 90% where no crystal fractionation occurred by CEF (figures S6 and S8). However, for

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neat M_4 and M_6 catalysts, broad chemical composition distributions were observed. For M_7 , although, a broad CEF profile was observed in the absence of DEZ (figure 4), as DEZ introduced into the catalyst system, narrowing of CCD was obvious. Therefore, CCD and branching distribution were regulated by DEZ as the hard segment incorporated into the microstructure of PE.

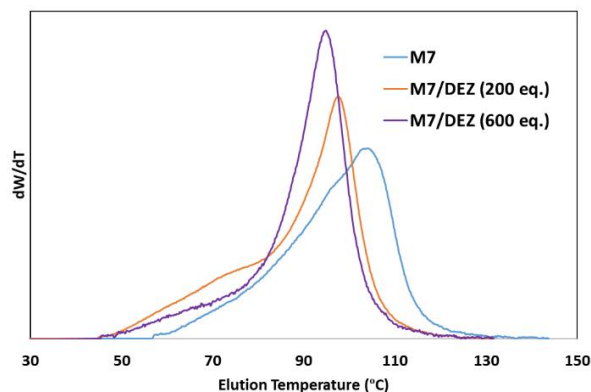


Figure 4. Effect of DEZ on CEF profile of PE samples made by M_7 .

Dynamic mechanical thermal properties (DMTA)

According to DMTA, it can give good details on microstructure of chains based on stress-relaxation mechanisms. α , β and γ transitions are related to the mobility of chains in crystalline phase, mobility of chain ends in crystalline phase and mobility of chains in amorphous phase, respectively.^[52] As M_7 displayed much more interesting results regarding the microstructure of polymer obtained, two DMTA were carried out on the entries 18 and 20. According to figure 5-A, there is a weak β -transition peak in $\tan \delta$ curve for M_7 (-41.5°C) that weakened and almost disappeared for M_7/DEZ . This could be attributed to the incorporation of hard segments into the microstructure of polymer. It previously has been reported that by increasing the hard segments, intensity of β -transition decreases and shifts to higher temperature.^[53] A broadened γ transition peak (-120 to -110°C), also may be due to presence of random and block copolymers having high mobility in the amorphous phase.^[54] Storage and loss modulus (E' and E'') curves (figures 5-B and 5-C) of the sample made by M_7/DEZ owing more X_c (hard segment) showed a gentle downward slope, while for neat M_7 (entry 18), steep slope obtained. The results are consistent on the previous observations about the hard and soft segments in the microstructure of PE.^[55,56] Totally, there is no doubt that the polymer made by M_7/DEZ system (entry 20) contains higher share of hard segments than M_7 (entry 18). Besides, it is confirmable that there is blocky microstructure for entry 20 according to the results including narrow MWD (table 1 and figure 2), uniform $\text{CH}_3/1000\text{C}$ in GPC-IR curve (figure S1-C), low BD (containing LCB and isolated Me branches) along with disappearance of vinyl-end polymer chains (table 2 and figure S2), increasing of X_c in the form of different lamellae thickness in SSA thermogram (table 1 and figure 3), narrowing of CEF profile (figure 4) and weakening of β -transition and amplification of crystalline phase or hard segments (figure 5).

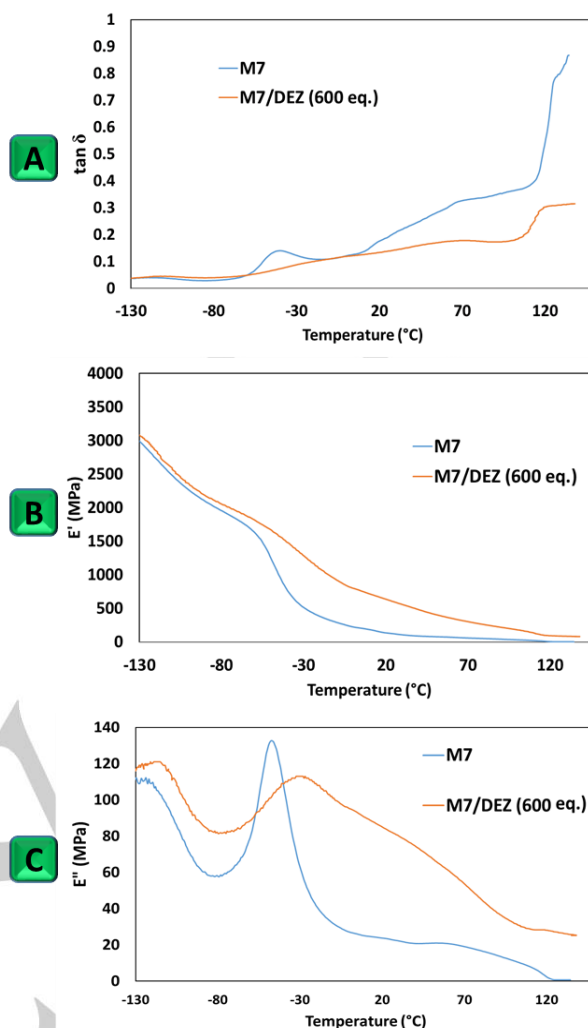


Figure 5. Dynamic mechanical thermal behaviour of the copolymers made by M_7 in the presence and absence of DEZ (entries 18 and 20) (A) $\tan \delta$, (B) storage modulus (E') and (C) loss modulus (E'').

Conclusion

In conclusion, it can be said that not only optimum bulkiness around the active centers (*iso*-propyl and methyl groups on *ortho*-position) along with dinuclearity can improve the catalyst activity but also have synergistic impact on the cooperative effect and CTE. Besides, CTE and reversibility strongly depend on the metal center affinity which for all mono- and dinuclear Fe-based catalysts, higher CTE was observed in comparison with Ni complexes. Accordingly, DEZ could show various impacts on activity and behavior of the catalysts. As CTZ could increase the number of polymer chains initiated per metal center, for Fe-based catalysts (M_1 , M_3 and M_5), CTZ led to shortening of PE chain length and dropping of M_w , MWD and T_m of the samples. Besides, vinyl-end polymer chains could augment by DEZ (M_5). In contrast, the impact of DEZ on M_w and MWD of the samples made by Ni-based catalysts were weaker. However, DEZ exhibited a strong influence on the branching density and distribution in related to the chain waling mechanism. Increasing of branching density (Me-branches) in the microstructure of these samples was a clue to the competition of chain walking and CTZ leading to first chain walking on the macromers. Dinuclearity effect of different active centers with various affinities led to formation of a random copolymer containing LCBs through cooperative effect. Besides,

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DEZ could assist the active centers via different ways for production of random and block copolymers. To sum up, using a heterodinuclear catalyst is a promising approach for the production of olefinic random and block copolymers.

Acknowledgements

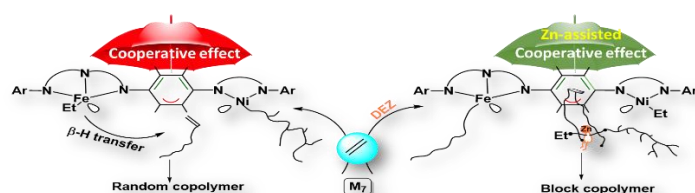
The authors are thankful of Dr. Saeid Mehdiabadi, Dr. Vahid Vajihinejad and University of Alberta for all their cooperation.

Keywords: cooperative effect • heterodinuclear catalyst • block copolymer • diethyl zinc • polyethylene

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Table of Contents



Adjacency of two active centers owing different catalytic performance in polymerization of ethylene leads to new polyolefin material via cooperative effect. Herein, a random copolymer containing LCB was obtained using heterodinuclear catalyst M_7 . Additionally, DEZ showed a strong interplay for production of blocky copolymers.