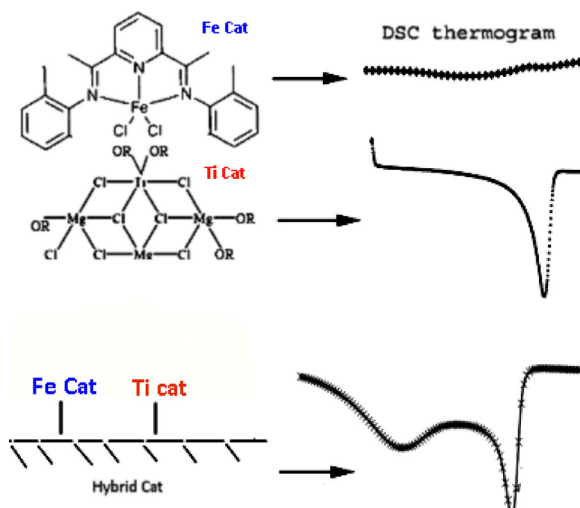


# Thermal Behavior of Polyethylene Reactor Alloys Polymerized by Ziegler–Natta/Late Transition Metal Hybrid Catalyst

Saeid Ahmadjo, Samaneh Dehghani, Gholam Hossein Zohuri, Gholam Reza Nejabat, Hamed Jafarian, Mostafa Ahmadi, Seyed Mohammad Mahdi Mortazavi\*

Polyethylene reactor alloys are synthesized through heterogeneous ethylene polymerization with a new type of Ziegler–Natta (ZN)/late transition metal (LTM) hybrid catalyst. The effect of various parameters including catalyst composition (LTM/ZN = 0.01, 0.02, 0.04), polymerization temperature (TP = 30, 30–60, 60 °C) and loading temperature (TL = 30, 60 °C) on catalyst activity, chain's vinyl content, viscosity average molecular weight ( $M_v$ ) and thermal properties are investigated. Two distinct melting peaks were observed in the ranges of 110–140 °C and 60–90 °C, indicating presence of two different lamellar structures. LTM/ZN ratio shifted melting peaks toward lower values. Rheological properties confirmed homogeneity of polymer blend's microstructure as they follow time temperature superposition.



## 1. Introduction

Six decades after invention of Ziegler–Natta (ZN) catalyst, polyolefins have the largest share in polymer production in

the world and is expected to reach to the fabulous value around 160 Mt/year in 2018.<sup>[1]</sup> Well-defined molecular structure and predetermined properties that can be achieved by tailoring catalyst structure and controlling polymerization conditions are the main reasons for this accomplishment. In other words, it can be said that the scientific and technological developments are based on an understanding first of the catalyst and then of the process, the products, and the product applications. Developments have been and are carefully planned by proper understanding and management of the catalyst, which brings the best process creation and product generation, the real keys to all the consequent market success.<sup>[2]</sup>

One of the main strategies used for the development of polyolefin catalyst, which is still being studied in the lab scale is the use of combination of different types of catalysts

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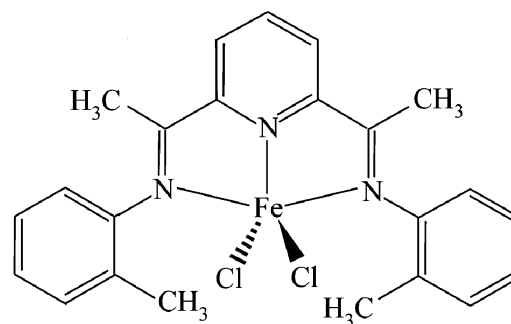
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during polymerization. Catalyst alloys, hybrid catalysts, and multi-catalyst systems are the common expressions used in this respect.<sup>[3–7]</sup> In these systems, each of the catalysts produces polymers with different properties and therefore the final polymer is a blend of two or more kinds of polymers.

En route making new types of polyolefins different strategies have been used for making polymeric reactor alloys. We may categorize the strategies as operational strategies and catalytical strategies. In the operational strategies, the reactors and reaction conditions play the main roles while in the catalytical strategies the catalyst and its structure plays the main role. Employing a series of reactors (tandem or cascade reactor systems) is one of the operational routes in which each reactor runs under different polymerization reaction conditions, generating the desired bimodal polymers with different MWs and microstructures.<sup>[8–10]</sup> However, using this method at the pilot plant level has been revealed as expensive, cumbersome, and time-consuming.<sup>[11]</sup> Another operational route utilizes the variation of operation conditions, such as temperature, comonomer concentration, and hydrogen pressure, in a single reactor during polymerization. However, it is difficult for this method to obtain ideal polymers because this method faces difficulties in controlling the MW and branch degree of the polymers, owing to the value of MW, which usually decreases with the increase of the branched degree.<sup>[11]</sup> The catalytical routes have more variety due to multiple combinations that can be made in the making or selection of the catalysts. For example, using multi-catalyst or hybrid systems are of this routes in which when polymerization conditions are met, each of the various catalytic sites are responsible for producing polymers with different microstructure,<sup>[12–16]</sup> e.g., polymers with different molecular weight distributions, which can result in bimodal polymers.<sup>[12,15]</sup> An alternative strategy is loading the other catalyst on polymer particles,<sup>[17–19]</sup> in this case the primitive polymer particles act as a reaction bed for the loaded catalyst. A final route is through changing the feed of the reactor that is used in conventional reactor granule technology (RGT) in which one type of catalyst is responsible for producing different types of polymers usually polypropylene and ethylene-propylene rubber.<sup>[20,21]</sup>

Up to now various types of hybrid catalysts including Ziegler–Natta/metallocene,<sup>[3–8,22–26]</sup> metallocene/metallocene,<sup>[27–37]</sup> metallocene/LTM,<sup>[38–44]</sup> and finally LTM/LTM<sup>[11]</sup> have been studied in polymerizing different types of monomers and comonomers for producing polymeric reactor alloys; however to the best of our knowledge, no report could be found on the application of any kind of Ziegler–Natta/LTM hybrid catalyst in polymerization of alpha-olefins. In the present article, a Ziegler–Natta/LTM hybrid catalyst of the type fourth generation ZN catalyst



■ Scheme 1. Structure of late transition metal catalyst.

pretreated with triethylaluminum (TEA) before combining with the late transition metal (LTM) catalyst (I) (Scheme 1). Ethylene polymerization was investigated using the synthesized hybrid catalysts and the obtained polymers are thoroughly investigated by DSC.

## 2. Experimental Section

### 2.1. Materials

Methylaluminoxane (MAO; 10 wt% solution in toluene) and TEA were purchased from Aldrich Chemical Company. Toluene was provided by Bandar Imam Petrochemical Company (BIPC, Iran) and was refluxed and distilled over sodium before use and kept over 4A/13X activated molecular sieves. The fourth generation ZN catalyst and ethylene were obtained from Jam Petrochemical Company (Iran). Aniline derivatives were supplied by Merck Chemicals and vacuum-distilled before use. 2,6-Diacetylpyridine (purity >99%) was prepared from Acros (Somerville, NJ). LTM catalyst prepared according previous report (Scheme 1).<sup>[45]</sup> The gases were purified as explained elsewhere.<sup>[46]</sup>

### 2.2. Hybrid Catalyst

The hybrid catalysts were prepared as follows: TEA (5 mmol) was added drop wise to 1 g ZN catalyst (dispersed in 10 ml toluene) at room temperature along with gentle mechanical stirring. The mixture was warmed up and after 1 h was washed five times each time with 20 ml toluene and finally the solid powder was dried. Then specified amounts of pretreated ZN catalyst (e.g., 0.25 g) were dispersed in toluene and specified amount of the LTM catalyst (e.g., 0.005 g in dichloromethane) was added to it (weight ratios of the catalysts are shown in Table 1). The reaction mixture was allowed to stir for 6 h. After 6 h, the reaction mixture was fully filtered, washed with toluene, and dried.

### 2.3. Polymerization

Catalyst component handling and polymerization procedures were carried out as previously described.<sup>[47]</sup> Polymerization reactions were performed in a 150 ml steel reactor equipped with controlling

**Table 1.** The mixing weight ratios and amount of the different elements weight ratio in the final hybrid catalysts using ICP.

Entry	LTM/ZN [wt%] (mixing ratio)	TL [°C]	Ti [wt%]	Fe [wt%]	Al [wt%]
1	0.01	30	2.19	0.06	3.38
2	0.02	30	2.10	0.15	3.40
3	0.04	30	2.05	0.34	3.42
4	0.01	60	2.14	0.12	3.97

TL, loading temperature.

systems for temperature, stirring speed, and reaction pressure. One hundred twenty milliliters of dried toluene were charged into the reactor. The desired amount of co-catalyst was introduced. A measured amount of catalyst was injected and then the polymerization reaction was conducted at 3 bar of ethylene, for 30 min. The obtained polymers were poured into acidified methanol, collected by filtration, dried, and weighed.

## 2.4. Characterization

The weight percents of Ti, Fe, and Al elements in each hybrid catalyst were determined through inductively coupled plasma ICP-OES using an ICAP 6000 instrument. Thermal properties of the polyethylene samples were determined by differential scanning calorimetry (DSC) (Universal V4IDTA). The samples were heated from room temperature to 160 °C by the rate of 10 °C min<sup>-1</sup> and remained for 10 min at the temperature; followed by cooling to 25 °C with a cooling rate of 10 °C min<sup>-1</sup>. Finally, the polymer was reheated to 160 °C using the same heating rate. The melting point was determined according to the results obtained in the last heating cycle. FTIR analyses of the samples were recorded using a FTIR Bruker 55 instrument (model EQUINOX) to determine the vinyl content of polyethylene samples.<sup>[48]</sup> The intrinsic viscosities were determined in decahydronaphthalene at 135 ± 0.1 °C using an Ubbelohde viscometer. Mark-Houwink-Sakurada equation was used for calculation of viscosity average molecular weight,  $M_v$ . The requisite constants  $\alpha$  and  $K$  for polyethylene were adopted from elsewhere ( $\alpha = 0.7$  and  $K = 0.062 \text{ ml g}^{-1}$ ).<sup>[49]</sup>

Linear viscoelastic properties were measured by small amplitude oscillatory shear (SAOS) experiment using Anton Paar's MCR 301 rheometer at strain control configuration by 25 mm parallel plate tools and 1 mm gap. All samples were stabilized with necessary amount of traditional polyolefin antioxidants and all measurements were performed under purge of nitrogen. Disk samples of about 1.1 mm thickness were prepared by compression molding at 190 °C. Amplitude sweep measurements were performed at frequency of 1 rad s<sup>-1</sup> in advance to determine the linear response region, and all measurements were done in this region. SAOS measurements were performed at four temperatures of 130, 160, 190, and 220 °C from 0.1 to 100 rad s<sup>-1</sup>. The corresponding mastercurves calculated based on time-temperature superposition rule (TTS) using Arrhenius equation.

## 3. Results and Discussions

### 3.1. Effect of LTM/ZN Mixing Ratio on Composition and Performance of the Hybrid Catalysts in Ethylene Polymerization

Results obtained from ICP analysis of the synthesized hybrid catalysts (Table 1) show that as the LTM/ZN mixing ratio increased from 0.01 to 0.04 the amount of loaded Fe on the MgCl<sub>2</sub> support (within ZN catalyst) increased from 0.06 to 0.34 and a proportional decrease was detected for Ti from 2.19 to 2.05, respectively. Similar behaviors can be found elsewhere.<sup>[50,51]</sup>

Table 2 displays the results of ethylene polymerization using three different hybrid catalysts at different polymerization temperatures (TP). Catalytic activity increased with increase in the proportion of LTM in the hybrid catalyst, except at the TP = 60 °C due to decrease of LTM catalyst activity at high polymerization temperature. Unsaturated chain ends, caused by  $\beta$ -hydrogen elimination transfer reactions to the metal center or to the monomer, which produces one unsaturated end per polymer chain (vinyl end groups), is more pronounced in polymers produced by LTM catalysts.<sup>[48,52]</sup> It is apparent from Table 2 that as the fraction of LTM catalyst increased in the hybrid catalyst the vinyl content of the produced polyethylenes increased considerably. For example, by decreasing the LTM/ZN weight ratio from 0.04 to 0.01 the vinyl content of polyethylenes, synthesized at 30–60 and 30 °C, decreased from 40 to 15 and from 61.40 to 20%, respectively. Vinyl content of polyethylenes synthesized by pure ZN catalyst at 30–60 and 30 °C were very low (1.1–1.3) and almost constant. While for the case of LTM catalyst the vinyl content was considerably high (60–87%) and variable. Vinyl content of the samples produced by the LTM catalyst at 60 °C was rather low and equal to 28%.

It is evident from Table 2 that  $M_v$  of PEs increases as the LTM fraction in the hybrid catalyst decreases. For example at TP = 30–60 °C, the pure LTM catalyst (ZN fraction = 0) produced PE with  $M_v = 6\,000$ ; as the ZN fraction increased,

Table 2. Results of ethylene polymerization with hybrid catalysts (catalyst loading temperature (TL) = 30 °C).

Entry	LTM/ZN [wt%]	TP [°C]	Activity <sup>a)</sup>	$M_v$ [kg mol <sup>-1</sup> ]	$T_m$ [°C]	Vinyl content
1	0.04	30	295	46	83, 109, 112	61.4
2	0.04	30–60 <sup>b)</sup>	440	19	85, 110, 112, 115	40.1
3	0.04	60	133.1	13	88, 98, 111, 115	18.8
4	0.02	30	266.7	161	78, 120	44.0
5	0.02	30–60	366.7	63	72, 120	37.3
6	0.02	60	126.2	52	91, 121	11.6
7	0.01	30	181.7	437	60, 118	20.0
8	0.01	30–60	285.2	355	75, 122	15.0
9	0.01	60	250	335	120	1.8
10	ZN (pure)	30	46.7	3 589	130	1.3
11	ZN (pure)	30–60	121.7	1 564	136	1.1
12	ZN (pure)	60	183.4	1 104	136	1.1
13	LTM (pure)	30	5555.6	–	20, 55 (wide) 85	87.0
14	LTM (pure)	30–60	4888.8	6	75, 105, 117	63.0
15	LTM (pure)	60	–	–	10, 50 (wide) 80	28.0

Polymerization condition: hybrid catalyst: 0.04 g, cocatalyst: 4.5 mmol (MAO), solvent: 120 ml toluene, time of polymerization: 30 min, pressure: 3 bar, TL = 30 °C, TP, polymerization temperature. <sup>a)</sup>Activity: (g PE/g cat bar h); <sup>b)</sup>TP (30–60): (15 min at 30 °C and 15 min at 60 °C).

i.e., LTM/ZN = 0.04, 0.02, and 0.01,  $M_v$  increased and became 19 000, 63 000, and 355 000, respectively. When ZN catalyst was used alone, the produced PE samples showed a considerably high  $M_v$  (about 1 564 000). A same trend was seen by Cho<sup>[53]</sup> for ZN/metallocene hybrid catalyst in ethylene polymerization.

Figure 1–3 depict thermal behaviors of synthesized polyethylenes as measured by DSC. The related melting points are listed in Table 2. It is clear that by increasing LTM fraction in hybrid catalyst the unimodal melting point appeared at high temperatures, i.e., 120–136 °C, turns into a multimodal peak, which appears at lower temperature

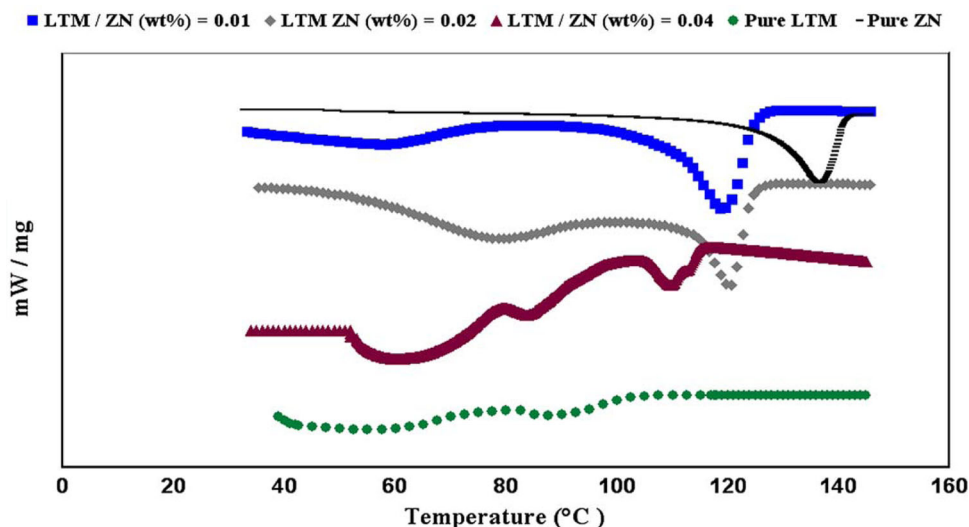


Figure 1. Thermal behavior of PE samples produced by LTM/ZN hybrid catalysts (loading temperature (TL): 30 °C). Polymerization conditions: TP = 30 °C, P = 3 bar, polymerization period = 30 min, co-catalyst: MAO.

- Pure ZN ▲ LTM / ZN (wt%) = 0.04 ◆ LTM / ZN (wt%) = 0.01 ● LTM / ZN (wt%) = 0.02 ■ Pure LTM

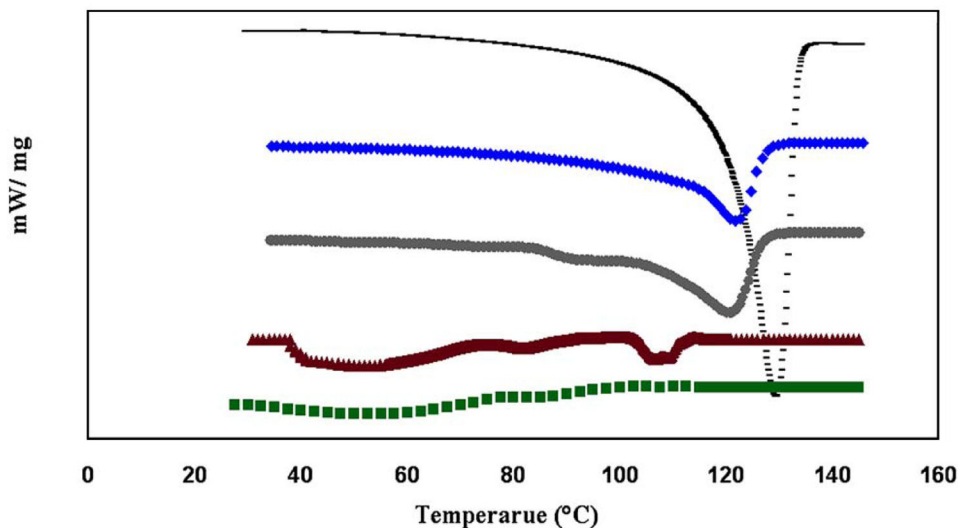


Figure 2. Thermal behavior of PE samples produced by LTM/ZN hybrid catalysts (loading temperature (TL): 30 °C). Polymerization conditions: TP = 60 °C, P = 3 bar, polymerization period = 30 min, co-catalyst: MAO.

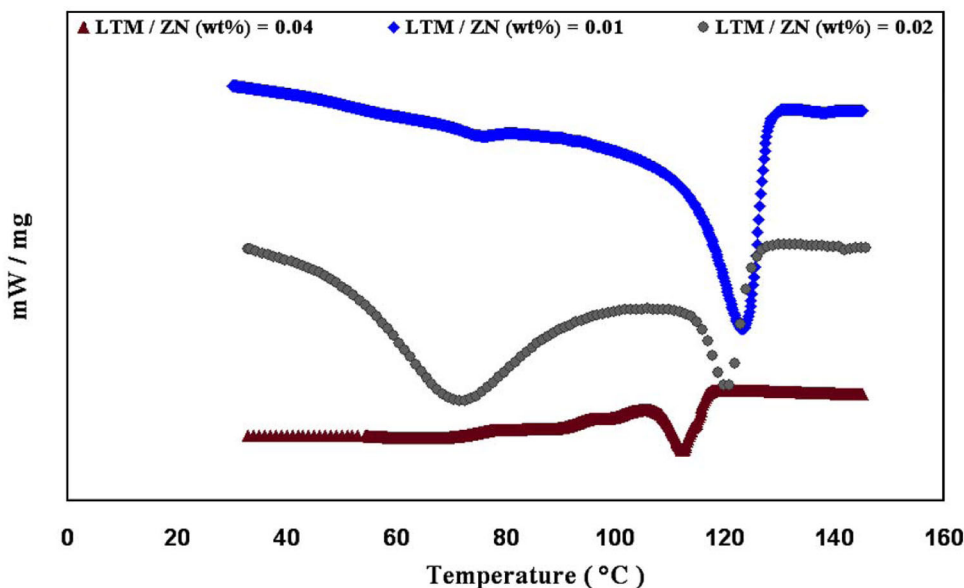


Figure 3. Thermal behavior of PE samples produced by LTM/ZN hybrid catalysts (loading temperature (TL): 30 °C). Polymerization conditions: TP = 30–60 °C, P = 3 bar, polymerization period = 30 min, co-catalyst: MAO.

regions. Of course this behavior is more pronounced for the samples prepared at TP = 30 °C and TP = 30–60 °C at which the LTM component is more active. The observed multimodal melting points can be related to the presence of branched or lower molecular weight polymer chains produced by LTM catalyst<sup>[13]</sup> or in other words due to the different microstructures obtained from various LTM and ZN active sites supported on the hybrid catalyst.

Usually hybridizing catalysts causes each component to show unusual polymerizing behaviors due to the presence of different chemical moiety around each of the active centers. At low LTM fractions, i.e., 0.01 and 0.02, the multimodal melting peak is less pronounced but in all the samples the depression of the maximum melting point is common. It can be said that the hybrid catalyst produces polymers with melting points between the

Table 3. Ethylene polymerization results using hybrid catalysts at different TL and TP.

Entry	TL [°C]	TP [°C]	Activity <sup>a)</sup>	Vinyl content	$M_v$ [kg mol <sup>-1</sup> ]	$T_m$ [°C]	$\Delta H_m$ [J g <sup>-1</sup> ]
1	30	30	182.2	20.0	437	60, 118	-51.98
2	30	30–60 <sup>b)</sup>	285.0	15.0	355	75, 122	-29.03
3	30	60	126.7	1.8	335	120 (wide)	-87.58
4	60	30	83.4	27.0	152	80, 120	-150.0
5	60	30–60	161.7	25.0	135	75, 115	-122.4
6	60	60	56.7	2.4	185	93, 120	-87.65

LTM/ZN weight ratio = 0.01. Polymerization conditions: hybrid catalyst 0.04 g, activator: 4.5 mmol, solvent: 120 ml toluene, polymerization period: 30 min, TL, loading temperature; TP, polymerization temperature. <sup>a)</sup>Activity: g PE/g cat bar h; <sup>b)</sup>15 min at 30 °C and 15 min at 60 °C, P: 3 bar.

polymers produced with each of the individual catalysts separately.<sup>[8,12,15]</sup>

### 3.2. Effect of Catalyst Loading Temperature on the Composition and Performance of Hybrid Catalysts in Ethylene Polymerization

Table 1 also shows the amount of Fe loaded on ZN catalyst at different mixing ratios and loading temperatures. It is clear that by increasing the loading temperature (TL), the amount of loaded Fe increases as well. For example, a twofold increase is observed when TL is increased from 30 to 60 °C in the mixing ratio of LTM/ZN = 0.01.

Investigating the effect of TL on the overall activities of hybrid catalysts (as depicted in Table 3) showed that by

decrease of TL from 60 to 30 °C for samples with the mixing ratio of LTM/ZN = 0.01 and TP = 30, 30–60, 60 °C, twofold increase in catalyst activities were observed.

It is evident from Table 1 that as TL increases from 30 to 60 °C, the amount of loaded LTM on ZN catalyst increases. On the other hand, Table 3 shows that the vinyl content of polymers produced by the hybrid catalysts loaded at 60 °C is higher. Therefore, FTIR and ICP results approve each other. Accordingly, the  $M_v$  of PE produced with catalysts loaded at higher TL was lower. This can be attributed to the higher amount of LTM catalyst loaded on ZN catalyst.

As is clear from Table 3 and Figure 4 by increasing TL from 30 to 60 °C, the higher melting point of PEs does not change but the lower one increases considerably, furthermore the overall heat of melt ( $\Delta H_m$ ) increases considerably.

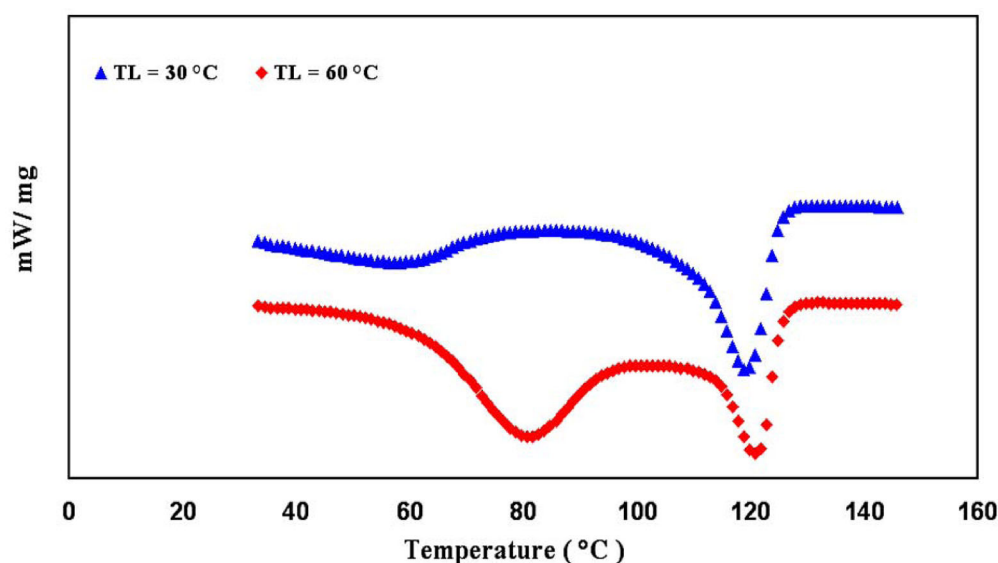


Figure 4. Thermal behaviors of polyethylene samples synthesized by hybrid catalysts (LTM/ZN wt% = 0.01) with different loading temperatures (TL = 30 °C, 60 °C). Polymerization conditions: TP = 30 °C, P = 3 bar, polymerization period: 30 min.

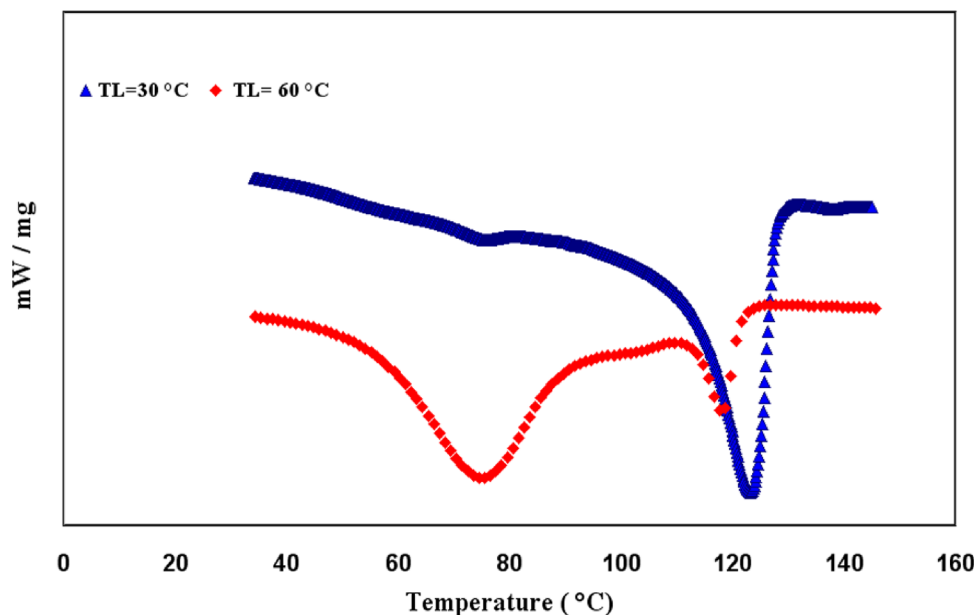


Figure 5. Thermal behaviors of polyethylene samples synthesized by hybrid catalysts (LTM/ZN wt% = 0.01) with different loading temperatures (TL = 30 °C, 60 °C). Polymerization conditions: TP = 30–60 °C, P = 3 bar, polymerization period: 30 min.

This implies that as TL increases, the synthesized hybrid catalyst produces more crystalline PEs and as is clear from Figure 4, the LTM part seems to be responsible for the most of the increase. The same trend can be seen for the samples prepared at TP = 30–60 °C. Of course as is shown in Figure 5 and Table 3  $T_m$  has not changed significantly, which can be attributed to its lower  $M_v$ . For the samples prepared at TP = 60 °C (Table 3 and Figure 6) as TL increases neither  $T_m$

nor  $\Delta H_m$ . It can be concluded that at higher TP, the crystallinity and melting behavior of the samples is governed only by the ZN part and is rarely affected by LTM component. Also as is clear from Table 3, by increasing TL from 30 to 60 °C, the vinyl content increased. This can be a proof for higher contents of LTM in the hybrid catalysts produced at higher TL, which is in agreement with ICP results (Table 1).

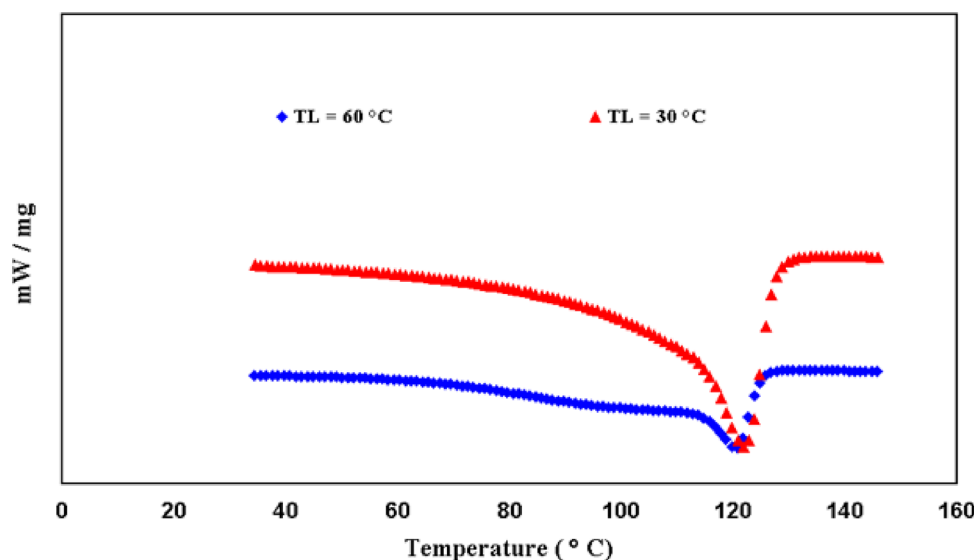


Figure 6. Thermal behaviors of polyethylene samples synthesized by hybrid catalysts (LTM/ZN wt% = 0.01) with different loading temperatures (TL = 30, 60 °C). Polymerization conditions: TP = 60 °C, P = 3 bar, polymerization period: 30 min.

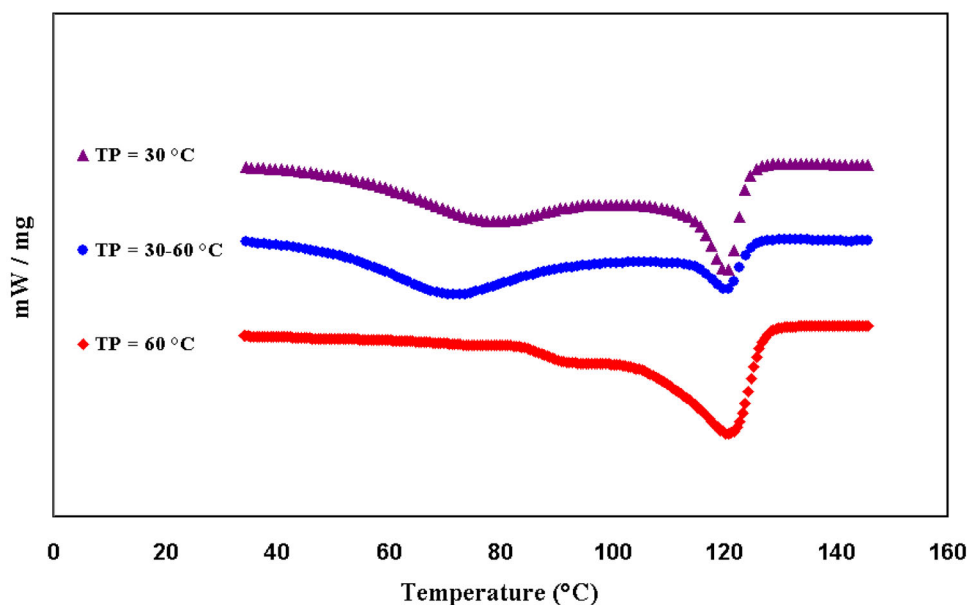


Figure 7. Thermal behaviors of polyethylene samples synthesized by hybrid catalysts (LTM/ZN wt% = 0.02) with same loading temperatures (TL = 30 °C) and different polymerization temperatures (TP), i.e., 30, 30–60, and 60 °C,  $P = 3$  bar, polymerization period: 30 min.

### 3.3. Effect of Polymerization Temperature on the Performance of Hybrid Catalysts in Ethylene Polymerization

Generally as TP increases the activity of LTM catalyst decreases,<sup>[45,48]</sup> and a reverse trend is observed for the ZN component. According to Table 3, maximum activities were obtained when TP = 30–60 °C and other TPs (i.e., 30 and 60 °C) resulted in lower activities. As is clear from the Table 2 for LTM/ZN = 0.04 and TP = 30–60 °C, the activity is 440 g PE/g cat bar h, when TP is changed to 30 and 60 °C activity drops considerably and reaches 295 and 133 g PE/g cat bar h, respectively. At 60 °C, deactivation of LTM catalyst is very probable while 30 °C is not an optimum TP for ZN component. When TP = 30–60 °C used both of the catalyst have the chance to play a role in polymerization of ethylene.

Table 2 also depicts the effect of TP on vinyl content of PEs. As can be seen when TP increases the vinyl content of PEs decreases. The highest content was observed for polymers obtained at TP = 30 °C at which the LTM component is more active. For example, when LTM/ZN = 0.01 and TP = 30 °C, the obtained vinyl content was 20 while the content was 15 and 1.75 for TP = 30–60 and 60 °C, respectively. It can be said that due to more  $\beta$ -transfer reactions of LTM part, more vinyl content is obtained when this part has more chance to be active.

Also as TP increased, catalyst activity and viscosity average molecular weight ( $M_v$ ) decreased. It can be said that at higher TPs, rates of propagation and chain transfer

increase, but higher activation energy of transfer reaction leads to more progress of transfer rate constant, which results in decrease of molecular weight.<sup>[54]</sup> However, there can be other factors that may counterbalance the mentioned reasoning. First, at higher TPs ethylene solubility decreases, which can lead to lower activities and second, higher TPs can result in higher rates of catalyst deactivation.<sup>[48]</sup>

As is clear from Figure 2, polymerization using LTM at 60 °C produces polymers with the widest melting point. It can be said that polymerization using LTM at high temperatures causes the catalyst to have lower control on the polymer microstructure. Figure 7 shows the effect of TP on thermal behaviors of obtained polyethylenes at the LTM/ZN = 0.02. It is clear that by changing the TP = 30 to 30–60 °C the melting temperatures do not change but as TP changes to 60 °C, the thermal behavior of the sample changes considerably and the two distinct peaks observed for the other TPs merge and a wide peak is obtained (the lower peak merges with the higher peak). It can be said that when TP is 30 or 30–60 °C, the LTM part can play a completely distinct role but at 60 °C, it is not the case.

### 3.4. Effect of LTM/ZN Mixing Ratio and Polymerization Conditions on Rheological Properties

Rheological properties are known to be severely dependent on small changes in microstructural properties like MWD and extent of branching. Therefore, we evaluated the



rheological properties of some selected samples to investigate the effects of catalyst properties and polymerization conditions on the microstructure of the synthesized samples. Selected samples include entries 4 and 5 from Table 2, which have LTM/ZN ratio of 0.02 and differ in TP, being 30 and 30–60 °C, and entries 7 and 8, which have LTM/ZN ratio of 0.01 and differ similarly in TP. In this way, we can study the effect of catalyst mixing ratio and also polymerization temperature protocol on rheological properties.

Figure 8 shows the van Gurp–Palmen plot of phase angle versus absolute amount of complex shear modulus for all samples measured at four temperatures of 130, 160, 190, and 220 °C. As the corresponding curves of all temperatures superimpose nicely for each sample, it can be concluded that our samples are thermo-rheologically simple. In other words, the temperature dependence of relaxation mechanisms of all components present in the mixture are the same, which infer that there is no substantial difference in the microstructure of chains produced with LTM and ZN components of the hybrid catalysts. As the melting points of chains associated with LTM component are significantly lower than the corresponding value for ZN component of hybrid catalyst, they should have explicitly lower molecular weights without any degree of branching. Fe-based LTM catalysts (with the ligand used here) are prone to produce oligomeric  $\alpha$ -olefins with length distribution according to Flory's equation.

Figure 9 shows the mastercurves of dynamic shear moduli, obtained by TTS rule, calculated using Arrhenius equation, for each sample. Measurements at each temperature superimpose nicely to give a uniform mastercurve for both storage and loss moduli. First of all, the vertical

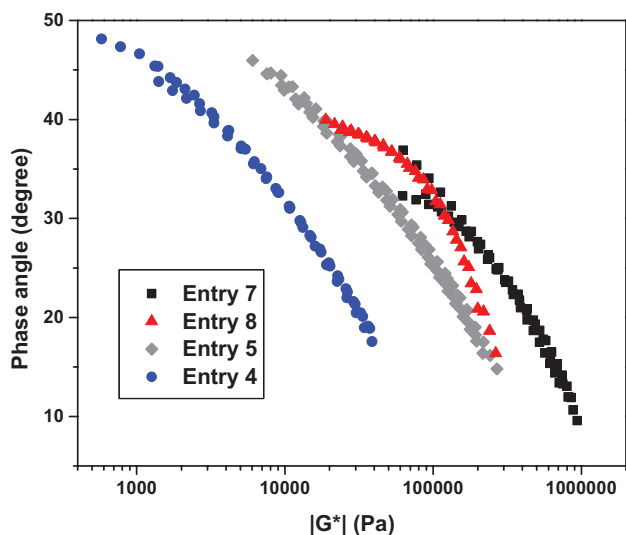


Figure 8. van Gurp–Palmen plot of phase angle versus complex modulus for four temperature measurements of all samples.

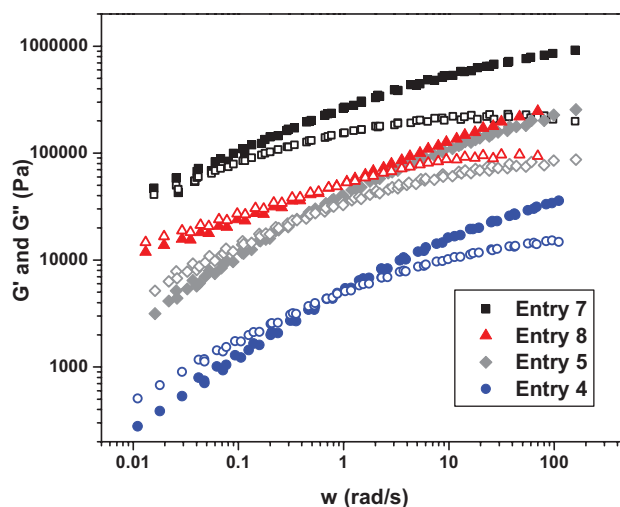


Figure 9. Mastercurves of storage (closed symbols) and loss (open symbols) moduli calculated for all samples at reference temperature of 190 °C.

positioning of each curve is a quantitative reflect of fraction of chains with low molecular weight (LMW). Plateau modulus scales with the fraction of long chains with the exponent of  $(1 + \alpha)$ , where  $\alpha$  is the dilution exponent with a value between 1 and 4/3.<sup>[55,56]</sup> Consequently, entry 4 with highest LTM fraction, utilized for polymerization at 30 °C, has the highest LMW fraction, and accordingly, entry 7, with lower LTM fraction has the lowest LMW portion. As a rough guess (for comparison purpose) entry 7 should have about 20% of LMW component as the plateau modulus for well-entangled PE is about 0.2 MPa. Compared to entry 7, using the scaling relationship, the corresponding LMW fraction for entries 4, 5, and 8 would be roughly 0.80, 0.56, and 0.52, respectively.

The crossover frequency and terminal relaxation time in single component polymer melt is a measure of molecular weight, however for the case of binary blends, like our cases, the interpretation is quite complicated as they depend on the LMW fraction, as well. Terminal relaxation time for entangled linear chains scales with molecular weight with the exponent of 3.4 and also scales with the fraction of high molecular weight (HMW) component with the exponent of  $\alpha$ .<sup>[55,56]</sup> Figure 10 shows the calculated complex viscosities, which provide a better view of terminal relaxation. As zero-shear rate viscosity is equal to product of reptation time and plateau modulus, it scales with the fraction of HMW component with the exponent of  $1 + 2\alpha$ . If we normalize the viscosity data with weight fraction of HMW chains with the exponent of  $1 + 2\alpha$ , we can remove the effect of LMW fraction on terminal relaxation and have a better estimate from the molecular weight of long chains, if all LMW chains are short enough to be considered all relaxed in the final relaxation of HMW chains. The corresponding normalized

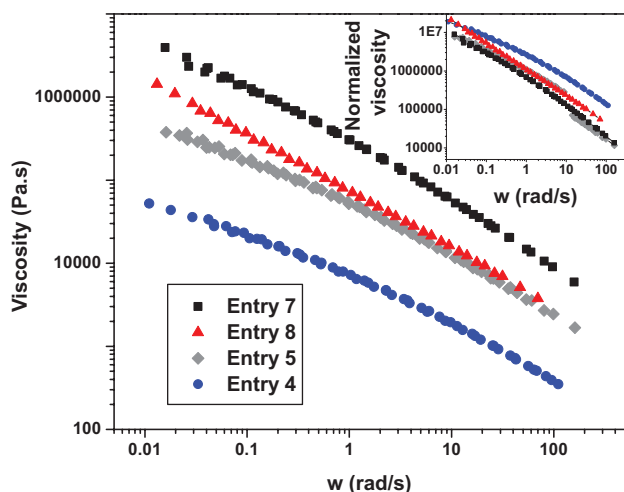


Figure 10. Complex viscosity (main plot) and viscosity normalized by weight fraction of HMW chains with exponent of  $(1 + 2\alpha)$  (inset plot) versus frequency.

viscosities are plotted in the inset. Unlike the viscosity curves in the main plot, all curves converge in the low frequency region of normalized viscosity. Despite the fact that we are still far from the plateau in low frequency region of viscosity curves (which scales with molecular weight), we can expect the lower frequency viscosity values stem from HMW chains produced by ZN fraction of hybrid catalyst, and the convergence could be attributed to the aforementioned reason. However, the fact that, the ratios of the lowest frequency normalized viscosities do not follow the  $M_v$  trend provided in Table 2, clarifies that LTM derived chains have significant contribution to the average  $M_v$ s.

#### 4. Conclusion

A new combination of Ziegler–Natta/LTM (ZN/LTM) hybrid catalyst was used in ethylene polymerization. The ethylene polymerization behavior of the catalysts and thermal properties of produced polyethylenes were investigated. Increasing LTM share in hybrid catalyst led to increase in activity and vinyl content at all TPs. Maximum activity of hybrid catalyst was observed at TP = 30–60 °C for all loading temperatures (TL). Investigating viscosity average molecular weights ( $M_v$ ) of PEs showed a sharp decrease in  $M_v$ s upon increasing LTM share in the hybrid catalyst. Increasing TL caused a decrease in  $M_v$ s but the vinyl content increased. Therefore, it can be concluded that TP and TL can play decisive roles in composition engineering of PEs using ZN/LTM hybrid catalysts. Assessment of rheological properties revealed that samples are thermo-rheologically simple and there should be no substantial microstructure difference between polymers produced by two components

of the hybrid catalyst. The obtained mastercurves of dynamic moduli showed vertical shifts toward lower values due to presence of chains with low molecular weight fraction.

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