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Performance of Post Phthalate Ziegler Natta Catalysts with Activity Limiting Agents for Propylene Gas Phase Polymerization

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Abstract

The performance of isopropyl myristate, methyl trimethylacetate, and dibutyl sebacate (IPM, MTMA, and DBS respectively) as activity limiting agents (ALA) were evaluated using a post phthalate Ziegler Natta catalyst system for the gas phase polymerization of propylene at different ALA ratios to titanium (ALA/Ti), and different temperatures. ALAs are used to limit catalyst activity and prevent formation of agglomerates in the reactor in cases of thermal runaways. All the ALAs were effective at retarding the catalyst activity at temperatures higher than 90 °C when used with n-propyltrimethoxysilane (N-donor) as an external donor, even at the lowest ALA/Ti. The lowest drop in catalyst activity at the lowest reaction temperature was observed with IPM, while the highest drop was observed with MTMA. Moreover, when used without an external donor the ALAs show a retarding effect of the catalyst at higher temperatures but to a lesser extent as when the external donor is used. Furthermore, none of the ALAs had a significant impact on the molecular weight averages or distributions, the bulk density nor the fines content. On the other hand, the isotacticity, evaluated in terms of the isotactic pentads and the average meso sequence length (MSL), was found to increase slightly with MTMA and DBS. Finally, it was observed that the reaction between the co-catalyst and the ALA is very crucial in determining the retarding effects of the ALA.

Keywords: Ziegler-Natta catalysts, gas phase polymerization, activity limiting agent, polypropylene, post phthalate Catalysts.

1. Introduction

The combination of the highly exothermic nature of Ziegler Natta (ZN) catalyzed polymerizations and the need to operate at high polymerization rates make the possibility of thermal runaway a real risk, particularly in gas phase reactors. Thermal runaway in fluidized bed reactors while the catalyst is still highly active lead to many problems ranging from increased fouling to complete loss of fluidization due to the formation of agglomerates. For propylene polymerization, the use of activity limiting agents (ALA), also called thermal runaway reducing agents (TRRA) have proven to be quite effective in deactivating the catalyst at elevated reaction temperatures: higher than 80 °C which provides an effective solution to the mentioned problems. This effect is generally referred to as the self-extinguishing property of a catalyst system [1]. Such modifiers are electron donating compounds similar to the external electron donors that are used in propylene polymerization to control stereoregularity but have not been proven to be effective tacticity control agents on their own [2], hence, mostly they are injected in addition to the classical tacticity control agents such as alkoxysilanes.

In an overview of the recent advances in fluidized bed polymerization technology, Cai et al. [3] presented the advantage of using DOW's (the technology now is owned by W.R. Grace) proprietary Advance Donor Technology (ADT) with Ziegler Natta catalysts for propylene polymerization where the catalyst deactivates, or, as the authors coined it, it self-extinguishes as the temperature increases. They stated that such optimization of catalyst kinetics reduces particle agglomeration by killing the active sites before the particle temperature can reach the softening point. Another advantage they have also mentioned is the increased flexibility in the reactor operating envelope, such as increasing

the production rate without decreasing the polymer bed inventory or working at higher fluidized bed densities while maintaining a high production rate.

Chen and Campbell [4] in their patent (US 7,491,670 B2, entitled "A self limiting catalyst composition and propylene polymerization process) disclosed a catalyst composition that includes an Activity Limiting Agent (ALA) to control polymerization in addition the normal modifiers used for propylene polymerization (i.e., co-catalyst, and selectivity control agents). This ALA renders the catalyst almost inactive at elevated temperatures. They discussed that the use of para ethoxy ethyl benzoate (PEEB) as an external donor with third generation ZN catalysts that provides the desired self-extinguishing property with respect to reaction temperature, but that is ineffective for tacticity control with the later generations of ZN catalysts. They presented many examples for combinations of different selectivity control agents, including silanes, and ALAs such as dibutylsebacate (DBS), and methytrimethylacetate (MTMA) that seem to lead to a significant (self-extinguishing) decrease in catalyst activity at high reaction temperatures. Looking at their data, one can see when the selectivity control agents are solely used, the catalyst still retains enough activity at temperatures close to the softening temperature of polypropylene which may lead to agglomeration and fouling, but this was not the case when ALAs were used.

Cai et al. [5] disclosed a gas phase polymerization process where the fluidized bed density is higher than 128 kg/m³. Operating at high bed density for a fluidized bed reactor means lower superficial gas velocity which in turn means less heat is removed from the bed. On the other hand, as long as one maintains stable reactor operation, a high bed density means high space time yields that are economically desirable. However, as in the mentioned patent, the inventors employ a mixed external donor system where one of these donors is an ALA which allows for operating the reaction beds at higher bed densities without encountering continuity issues. The use of the ALA provides the needed protection from temperature excursions as the catalyst is deactivated at elevated temperatures before reaching the softening point of the polymer. They presented two examples of using DBS with homo-polymerization and random copolymerization of propylene in vertically and horizontally stirred reactors, and compared these to two similar examples without the ALA.

They showed that after a problem occurring to the agitator, the kill gas is immediately introduced and an attempt to start agitation is done after fixing the problem. Agitation could have not been started when no ALA is used due to the blocking of the reactor with agglomerates and chunks, which was not the case when the ALA was used and agitation in this case was re-started without issues.

In a patent by Basell, Morini et al. [2] highlighted two negative aspects of using ALAs to control the reaction at elevated temperatures: the drop in base catalyst activity at normal operating temperatures, and the drop in stereoregularity when attempting to lower the mixed donor ratio to the catalyst. In their patent, they disclosed a catalyst composition for polymerization of propylene containing a diether internal donor that exhibits the desired self-extinguishing property without the addition of specific donors like in the case of using ALAs. They presented several examples whereby showing the residual activity of their catalyst system drops to as low as 43% at 90 °C.

Several other patents disclose novel mixtures of external donors and processes where an ALA is used, including in the production of impact propylene copolymers [6], in the production of high melt flow propylene polymers [7], in the production of ethylene based polymers [8], the discontinuous addition of thermal runaway control agents in commercial production of polypropylene [9], the use of monoether compounds as ALAs [10], utilizing fluorinated fatty acids as ALAs [11], and an improved multi-zone olefins polymerization process operating in deep condensed modes employing several thermal runaway control agents [12].

Although there is a significant surge in patent applications disclosing processes and compounds where the desired self-extinguishing property can be achieved in olefin polymerization reactors since 2005 (c.f. **Figure 1**), there are no clear hypotheses of their mechanism of action. Vipin Raj et al. [13] conducted DFT studies on two novel ALAs and concluded that interactions between the ALA and dimeric TEA leads to a decomposition reaction with the help of another TEA molecule, producing either a ketone or an aldehyde. Similarly, the interaction of the ALA with Ti on the 110 surfaces of MgCl₂ produces more favorably a ketone. The decomposition reactions products lead to the poisoning of active

sites as both ketones and aldehydes are known to be able to poison Ziegler Natta active sites. They also explained the efficacy of one ALA over the other in their study by thermodynamic binding preferences supported by the computational study. Such decomposition reactions have been experimentally observed as a result of the reaction between the alkyl aluminum and esters by Chien et al. [14] where they also suggested the pathways by which such reactions occur and the role of temperature in the decomposition rates.

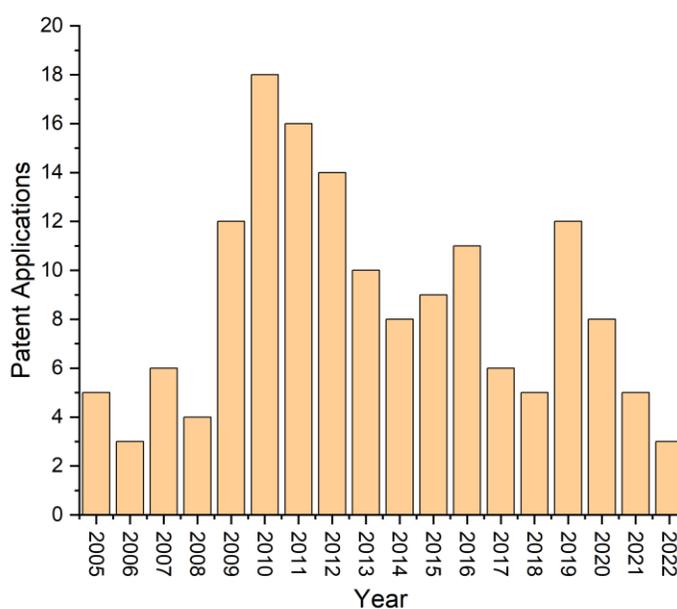


Figure 1. Patent applications for ALA and self-extinguishing catalyst formulations.

In this work, we are evaluating the performance of a 6th generation Ziegler Natta catalyst for propylene polymerization in gas phase developed by SABIC with three activity limiting agents. The ALAs were chosen from the cited patents and have been proven to work effectively with the corresponding catalyst systems used in the aforementioned patents. The main property we will look at is the so-called self-extinguishing property of the catalyst system. This will be conducted by varying the amounts of ALAs and combinations with the selectivity control agent at different reaction temperatures. We will

also take a closer look at the polymer microstructure and powder morphology (mainly the bulk density and fines content) to identify any eventual effects of ALA, if any.

2. Experimental

2.1. Materials

The catalyst used in this study is a sixth generation (phthalate free) Ziegler Natta catalyst developed by SABIC. The titanium content of this catalyst is around 3 wt% and it is formulated with two different internal electron donors. Triethylaluminum purchased from Witco was diluted to around 1 M in n-heptane which is purified using Mbraun solvent purification unit. The external electron donor (ED): n-propyltrimethoxysilane (N-Donor) was purchased from ABCR and stored over molecular sieves after bubbling for a couple of hours using Argon to get rid of free oxygen. The ALAs: isopropyl myristate (IPM), methyl trimethylacetate (MTMA), and dibutyl sebacate (DBS) were purchased from ABCR and were treated similarly to the electron donor. Both the ED and ALA compounds were diluted in purified heptane before introduction to the polymerization experiments.

2.2. Polymerization Setup and Procedure

The polymerization setup and procedures of preparation, conducting the experiments, and post treatment of the polymers are the same as described in a previous publication [15].

2.3. Polymer Characterization

The polymers in this study were characterized for molecular weight using GPC, stereoregularity using ^{13}C NMR, bulk density using a standard volume recipient, and particle size distribution using a Malvern Mastersizer 3000 particle analyzer. All the characterization methods have been described in a previous publication [15].

2.4. Diffuse Reflectance Infrared Transmittance (DRIFT)

DRIFT analyses were performed using a Nicolet 6700 FTIR where data are collected using OMNIC software. The treated samples were placed in the airtight DRIFT cells with a

CaF₂ window inside the glove box. For each spectra, 64 scans were collected with a resolution of 4 cm⁻¹. All the treatments of the catalyst for DRIFT analysis were performed at room temperature.

2.5. Experiments

The three main variables in this study are reaction temperature, use of electron donor (an alkoxy silane), and the ALA/Ti ratio. All the core experiments of this work were conducted with 20 g of NaCl as a seedbed under a propylene pressure of 8.0 barg, and 2.0 mol% of hydrogen. The molar ratios for the co-catalyst and the ED to Ti were 51, and 3, respectively. As shown in **Table 1**, experiments 1 to 3 are the reference experiments where N-Donor is used and the reaction temperature is varied at three levels: 58, 78, and 94 °C. Experiments 4 to 6 are similar to the reference experiment except no ED was added. In this experimental program, three ALAs were used: IPM, MTMA, and DBS, their chemical structures are shown in **Figure 2**. The rest of the experiments from number 7 to 18 are repeated for each ALA, the numbering of these experiments for later sections of this work will be consisting of two digits, the first one refers to the numbers shown in Table 1, and the second digit will refer to the ALA; 1 for IPM, 2 for MTMA, and 3 for DBS. For example, experiment number 7.3 refers to the conditions of experiment 7 with DBS as an ALA. The ALA/Ti molar ratio was varied for these experiments at three different levels: 0.3, 3.0, and 9.0 for the different reaction temperatures. For each ALA, a set of three experiments where no ED was used were also conducted. All the experiments are conducted for 60 minutes.

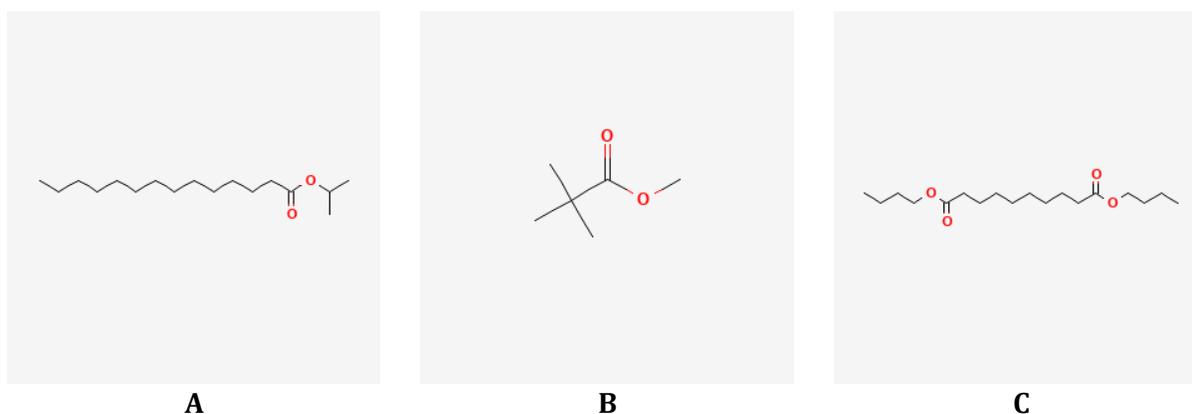


Figure 2. Chemical structures for the ALAs used in this study: A. Isopropylmyristate (IPM), B. methyltrimethylacetate (MTMA), and C. dibutylsebacate (DBS).

Table 1. Experiments on the effects of different ALAs in gas phase propylene polymerization.

SN	ED/Ti	ALA/Ti	T (°C)
1	3.0	0	58
2	3.0	0	78
3	3.0	0	94
4	0	0	58
5	0	0	78
6	0	0	94
7	3.0	0.3	58
8	3.0	0.3	78
9	3.0	0.3	94
10	3.0	3.0	58
11	3.0	3.0	78
12	3.0	3.0	94
13	3.0	9.0	58
14	3.0	9.0	78
15	3.0	9.0	94
16	0	3.0	58
17	0	3.0	78
18	0	3.0	94

A second set of experiments was carried out, as shown in **Table 2**, with the objective of discriminating the possible reactions of ALA during the gas phase polymerization of propylene. This set of experiments was conducted using the same catalyst with 6 barg of propylene, 20 g of NaCl as seedbed, where no hydrogen nor a selectivity control agent (alkoxysilane; namely N-Donor) have been introduced in an attempt to minimize the variables. All the experiments were conducted with one ALA, dibutylsebacate (DBS) and triethylaluminum (TEA) as the co-catalyst. The four main variables considered here are the Al/Ti ratio, ALA/Ti ratio, reaction temperature, and method of addition for the co-catalyst and the ALA. The methods of addition of modifiers will be described below:

1. **Method A:** the catalyst is pre-contacted with the ALA and then vacuum dried, the catalyst then is introduced to the reactor one hour after the pre-contacting step, and the co-catalyst is injected before the start of polymerization.

2. **Method B:** the catalyst is pre-activated with the co-catalyst which is then vacuum dried before introduction to the reactor with a time of contacting around 10 minutes, then the reaction is started without an ALA until around minute 30 where it is introduced.
3. **Method C:** similar to method B (catalyst pre-activated with Al/Ti of 2) except that the ALA added during the reaction is mixed with the co-catalyst to make up the total Al/Ti of 50 and injected at around minute 15 of the reaction.
4. **Method D:** similar to method B except that the ALA addition is done at around minute 15 of the reaction followed by a TEA injection around minute 25.

Table 2. Experiments with DBS with different methods of additions for Al and ALA.

SN	Al/Ti	ALA/Ti	T (°C)	Al and ALA Addition Method
19	50	9	36	Method A
20	50	9	96	Method A
21	2	9	36	Method B
22	2	9	96	Method B
23	2 and 48	9	36	Method C
24	2 and 48	9	96	Method C
25	2 and 48	9	36	Method D
26	2 and 48	9	96	Method D

3. Results and Discussions

3.1. Reaction Rates

3.1.1. Temperature Effect with and without N-Donor (ED)

The reaction rate profile for this catalyst exhibit two types of behavior when N-donor is used as shown in **Figure 3-A**, at the low temperature (i.e. 56 °C), it shows the typical high initial activity followed by decay, whereas at the higher reaction temperatures, 78 and 94 °C, there are two regions; a very short mild decay followed by a build up kinetic profile. The appearance of a second peak in the reaction rate has been reported by some researchers for ethylene and ethylene-propylene polymerizations where mainly two explanations have been put forth: the changes in Ti oxidation state and the role of hydrogen in re-oxidation of Ti ^[16], and perhaps the existence of two different types of active

sites ^[17]. This behavior could be of a chemical origin where reactivation of some catalytic sites takes place later on during polymerization resulting in an increased rate of activation over deactivation. The external donor role in this behavior is important which could be participating in the activation of such sites as such behavior is not observed when no external donor is used as shown in Figure 3-B. The reaction rates are higher in the absence of the electron donor by a maximum increase of around 30% at the lowest reaction temperature which is due to the deactivating ability of the N-donor which has 3 alkoxy groups, two of which can participate in the deactivation of catalytic sites ^[18]. However, at the highest temperature, the reaction rate without an external donor is significantly decreased. This might be due to self poisoning of the catalyst with one of the internal donors or its decomposition products.

Figure 3-C shows the catalyst productivity as a function of temperature for the two sets of experiments: with and without an external donor, the activity in both cases follow a decreasing trend but the decrease in the presence of the ED at 94 °C compared to 58 °C is around 26% whereas it is around 89% in the absence of the ED. This behavior could mean the catalyst itself exhibit a self-extinguishing property in the absence of external donors. This catalyst has two types of internal donors, one that is not affected by the co-catalyst, and the other one which can be removed by the co-catalyst, we believe it is possible for this second donor to poison the active sites at the higher temperature because of the possible higher rate of removal of this second internal donor at elevated temperatures by the co-catalyst.

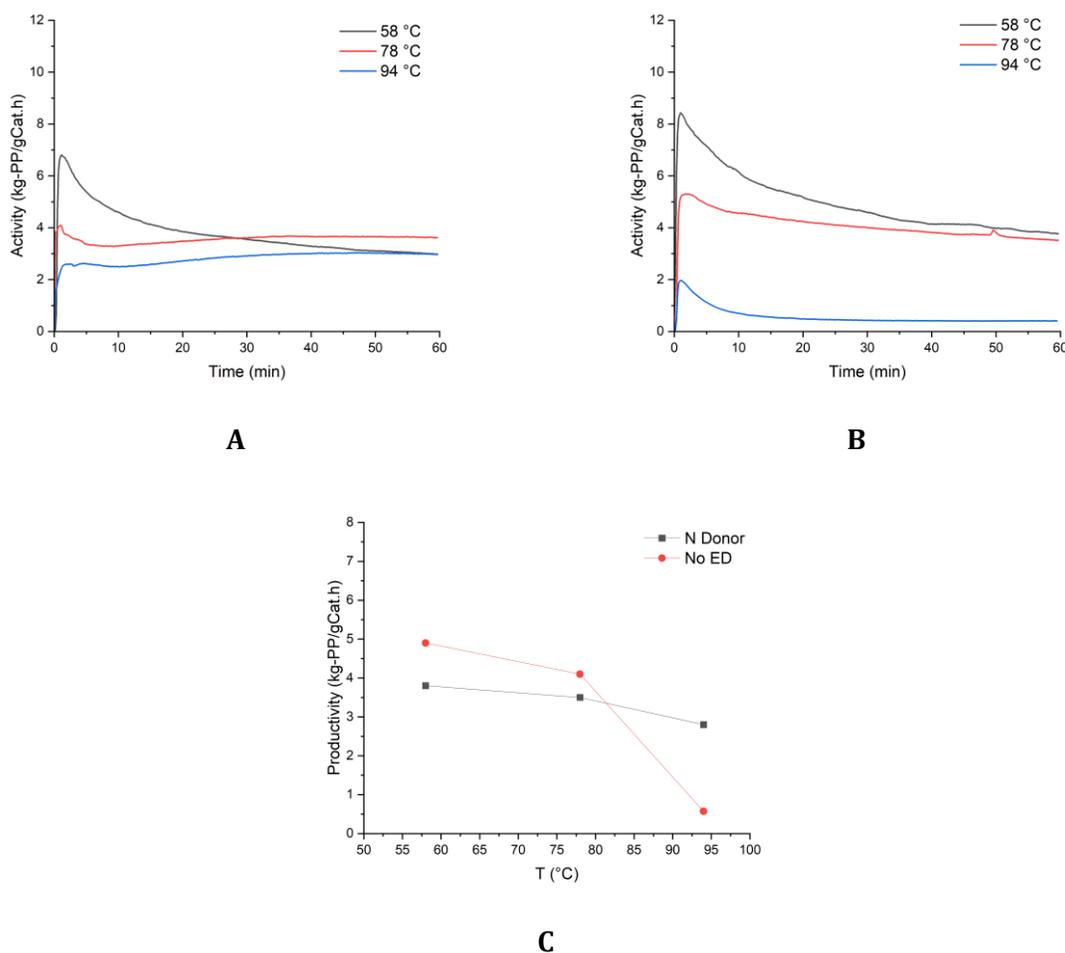


Figure 3. Experimental reaction rates for: **A.** the reference experiments with N-Donor and no ALA, **B.** No N-Donor nor ALA, and **C.** the catalyst productivities for these experiments plotted against reaction temperature.

3.1.2. Temperature Effect with IPM

The effect of different IPM molar ratios to Ti at different temperatures is shown in **Figure 4-A, B, C, and D.** At the lowest IPM molar ratio, the reaction rate at the lowest temperature does not change but as the temperature increases, the activity decreases reaching a significant drop of 67% at the highest reaction temperature as shown in **Table 3.** Moreover, all the kinetic curves are showing a decay type with two distinct regions: a quick decay until around 10 minutes followed by a very stable region with the rate of decay slowing down as the reaction temperature is increased. Increasing the molar ratio of IPM to

1.0 results in a very mild decrease in activity while the reaction rates are practically the same as shown in Figure 4-B. Similarly, the highest ALA/Ti molar ratio we have used in this study of 9 shows similar trends for the lower temperatures while the significant impact of ALA on the reaction rate is observed at the highest reaction temperature, 94 °C, as shown in Figure 4-C.

Using IPM in absence of N-donor leads to around 20% increase in the catalyst productivity as shown in Figure 4-E, while the reaction rate curves at 58, and 78 °C show similar behavior to the rest of experiments where we have used N-donor. However, at the highest temperature, we see the appearance of a second activation evident by the slightly increasing reaction rate after the first 5 minutes of reaction.

One of the parameters we are using in this study to measure the extent of catalyst self-extinguishing property in the percentage of activity decrease at 94 °C in relation to the standard experiment at the same temperature. As we can see in Table 3 for IPM, even at the lowest ratio of ALA/Ti, a 67% drop in activity takes place compared to the standard system (STD) while the activity at the lowest temperature is not affected. Further increasing the amount of IPM increases the activity drop to 74, and 93 %, however, at the highest ratio of IPM where the best self-extinguishing performance is seen, it comes at the expense of activity at the lower temperature (i.e., normal operating temperatures) with a drop of around 19% compared to the standard experiments. Finally, using IPM without an external donor does not seem to be very effective in controlling the activity at higher temperatures with the activity dropping around 40% while activity at the lowest temperature increased by 23%. The increase in activity at the lower temperatures is due to the lower total ED+ALA molar ratio to Ti which lowers the poisoning effect of those external bases leading to an increase in activity. However, the inefficient behavior of the ALA when no external donor is used is due to two factors: the increase of TEA concentration reacting with IPM which will be discussed later, and the lower ratio of ALA to Ti.

Table 3. Percentage of changes in catalyst productivity with IPM as an ALA.

Experiments Set	Productivity Drop at 94 °C (%)	Productivity Change at 58 °C (%)
ALA/Ti = 0.3 + N-Donor	67	+2.00
ALA/Ti = 3.0 + N-Donor	74	-14.0
ALA/Ti = 9.0 + N-Donor	93	-19.0
ALA/Ti = 3.0	40	+23.0

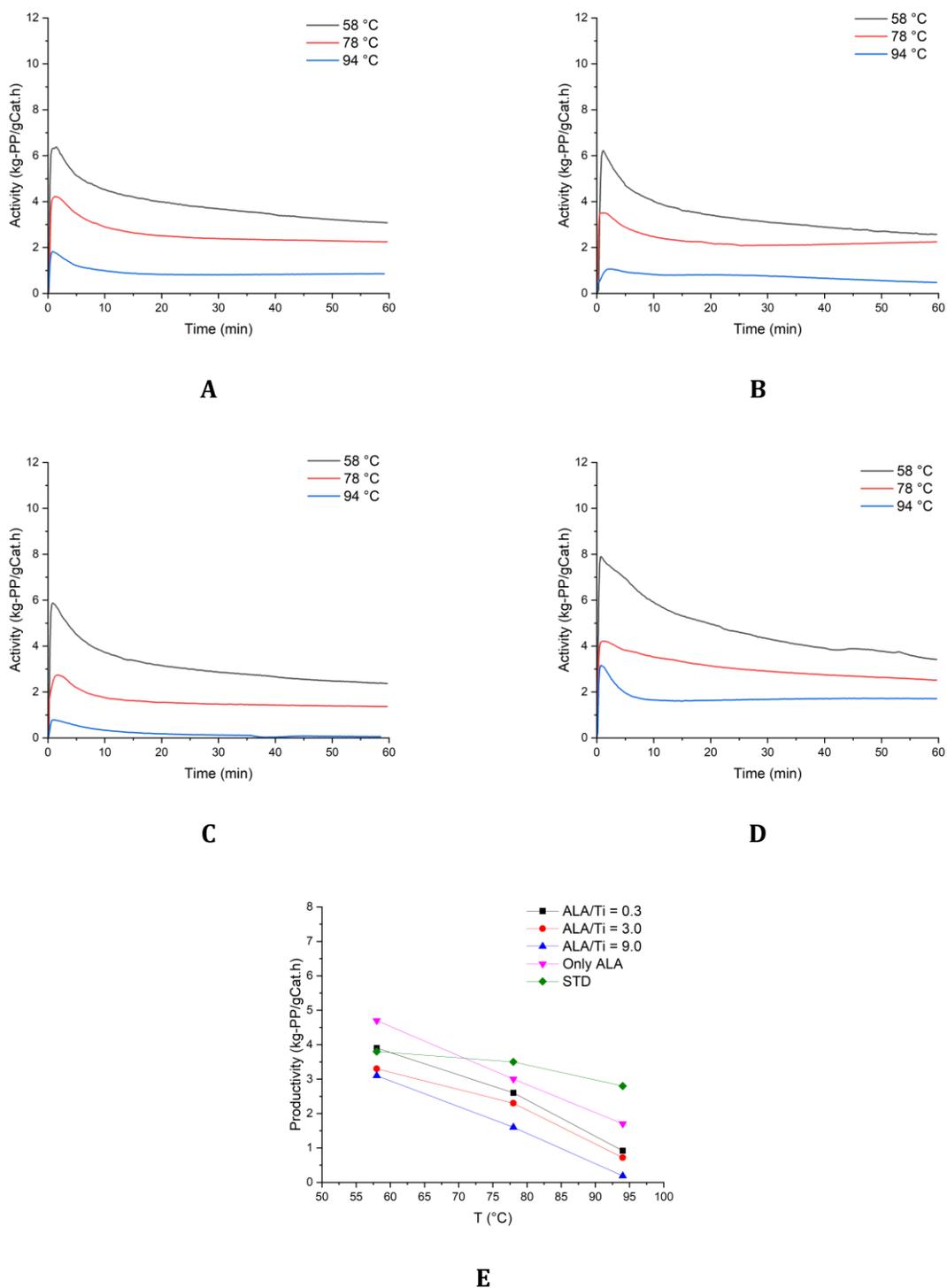


Figure 4. Experimental reaction rates for: **A**. ALA/Ti=0.3 with N-donor, **B**. ALA/Ti=3.0 with N-donor, **C**. ALA/Ti=9.0 with N-donor, **D**. ALA/Ti=3.0 without N-donor, and **E**. the catalyst productivities for these experiments plotted against reaction temperature.

3.1.3. Temperature Effect with MTMA

MTMA is a monoester similar to IPM but is a smaller molecule in comparison and has been reported to show a self-extinguishing property with ZN catalyst systems [4]. Similar to IPM, the kinetic behavior of the catalyst with MTMA at the lowest temperature as seen in **Figure 5** exhibits the classical rate decay over time, however, at the higher temperatures, 78 and 94 °C for ALA/Ti of 0.3 and 3.0, we start to see the two peaks reaction rate where a second reactivation peak appears followed by very minimal decay as shown in Figure 5-A, and B. This behavior does not seem to be present in absence of the external donor with MTMA, as shown in Figure 5-C.

The efficacy of MTMA in inducing self-extinguishing of the catalyst can be observed in Figure 5-E and **Table 4** where a significant drop of activity can be seen, even at the lowest ALA/Ti. However, the highest activity drop is observed at the highest ALA/Ti with about 96% loss of activity compared to the standard catalyst experiment at the same temperature (i.e., experiment number 3). Though the behavior of retarding activity at higher temperatures seems to be similar to IPM, the negative influence on the activity at the lowest temperature is quite significant where 50% of the activity is lost as shown in Table 4 compared to the standard system with an increase of 30% compared to the loss with IPM at the highest ALA/Ti. We believe this effect is dependant on two main factors: the reactivity of MTMA with TEA, and the higher diffusivity of the MTMA. We will discuss in a later section of this work the possible mechanisms of actions for ALA which will shed some light on some of the differences in their self-extinguishing behavior. Moreover, MTMA seems to be quite effective when used in absence of the external donor contrary to IPM where we see 80% drop in activity at 94 °C while the negative effect on activity at 58 °C is only a 14% decrease.

Table 4. Percentage of changes in catalyst productivity with MTMA as an ALA.

Experiments Set	Productivity Drop at 94 °C (%)	Productivity Change at 58 °C (%)
ALA/Ti = 0.3 + N-Donor	50	+18.0
ALA/Ti = 3.0 + N-Donor	60	-20.0
ALA/Ti = 9.0 + N-Donor	96	-50.0
ALA/Ti = 3.0	80	-14.0

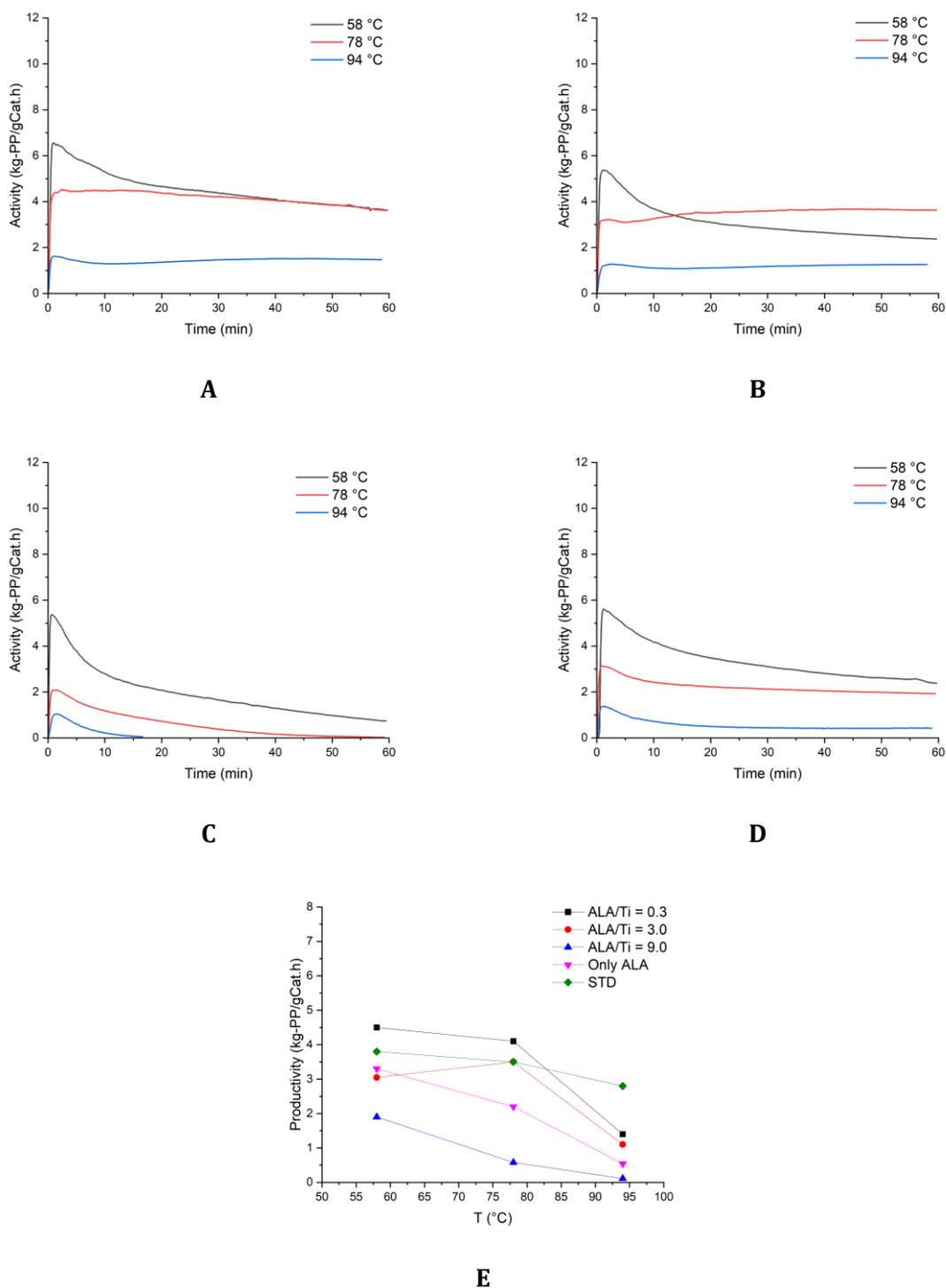


Figure 5. Experimental reaction rates for: **A.** ALA/Ti=0.1 with N-donor, **B.** ALA/Ti=1.0 with N-donor, **C.** ALA/Ti=3.0 with N-donor, **D.** ALA/Ti=3.0 without N-donor, and **E.** the catalyst productivities for these experiments plotted against reaction temperature.

3.1.4. Temperature Effect with DBS

The reaction rates for the experiments where DBS is used are shown in **Figure 6-A,B,C, and D**. Similar to the reference experiments, we can see a reactivation period for the lower ALA/Ti ratios that disappears when ALA/Ti is increased to 9. DBS shows a similar behavior in terms of inducing the self-extinguishing property as IPM with one exception, the drop in activity at 58 °C is more than that of IPM as shown in **Table 5**. It is possible that having two functional groups leads to more catalyst deactivation at the lower temperatures especially if the TEA only binds to one of them leaving the other free to adsorb on the active site. Another interesting difference is the significant increase in activity when DBS is used alone, one of the reasons could be the stronger ability of DBS to control isotacticity compared to the other ALAs while having a lower chance of deactivating the catalyst as compared to the ED which has three alkoxy groups which means higher chance of deactivating the catalyst [18].

Table 5. Percentage of changes in catalyst productivity with DBS as an ALA.

Experiments Set	Productivity Drop at 94 °C (%)	Productivity Change at 58 °C (%)
ALA/Ti = 0.3 + N-Donor	17	-21.0
ALA/Ti = 3.0 + N-Donor	69	-14.0
ALA/Ti = 9.0 + N-Donor	97	-40.0
ALA/Ti = 3.0	50	+98.0

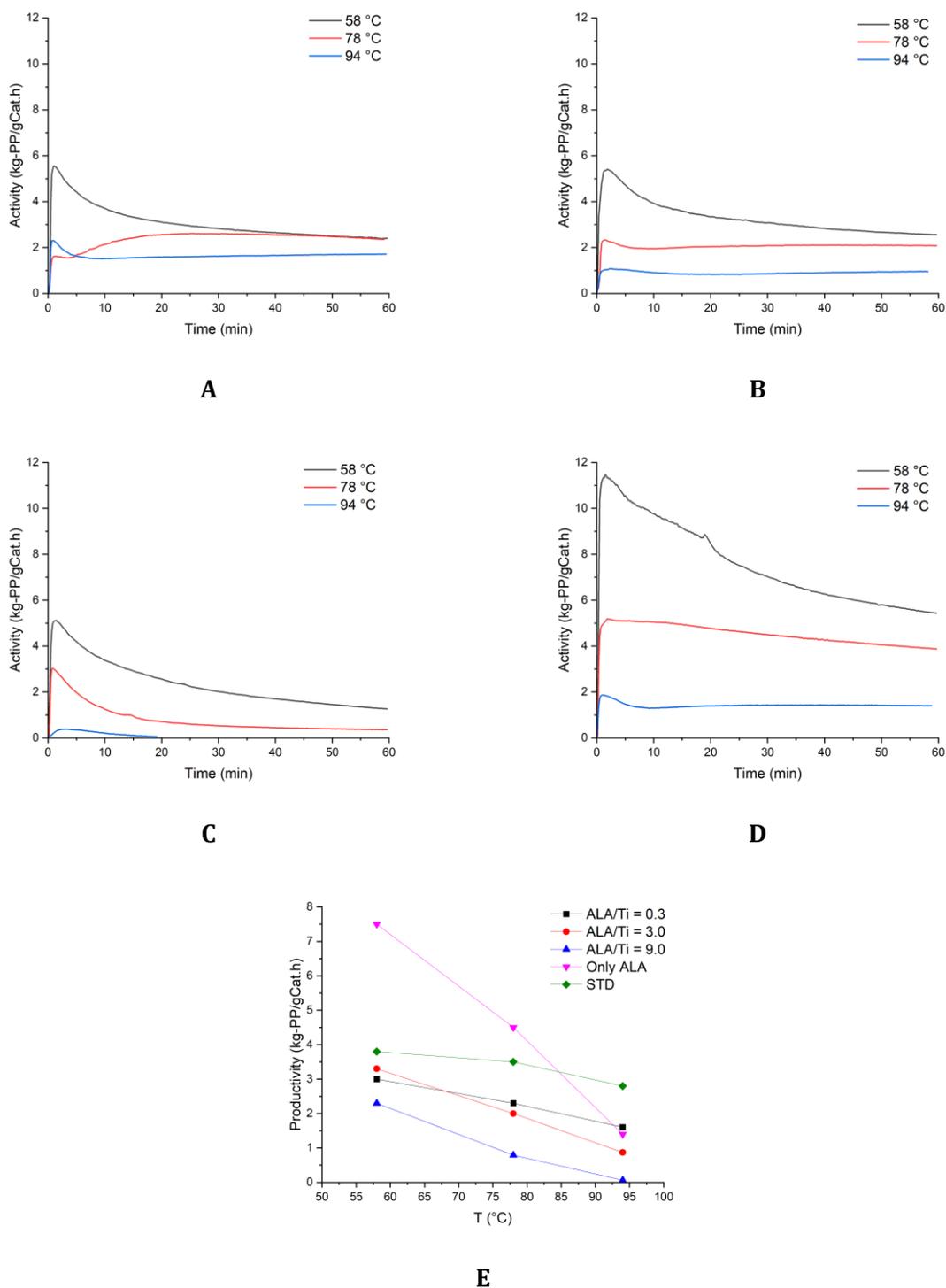


Figure 6. Experimental reaction rates for: **A.** ALA/Ti=0.3 with N-donor, **B.** ALA/Ti=3.0 with N-donor, **C.** ALA/Ti=9.0 with N-donor, **D.** ALA/Ti=3.0 without N-donor, and **E.** the catalyst productivities for these experiments plotted against reaction temperature.

3.2. Polymer Microstructure and Morphology

The microstructure (molecular weight and tacticity) and morphology (bulk density and fines content) analyses were performed on the most meaningful subsets of experiments, which are listed below:

- The reference experiments: 1 to 3.
- The reference experiments without an external donor: 4 to 6.
- ALAs experiments with the highest ALA/Ti, which is 9.
- ALAs experiments in absence of the external donor.

3.2.1. Molecular Weight

Molecular weight results are shown in **Table 6** where the number average molecular weight (M_n), weight average molecular weight (M_w), and molecular weight distribution (MWD) are reported for the analyzed experimental subsets. As we can see in the table, both M_n and M_w decrease for all experiments as the reaction temperature increases. There are mainly two factors that underlie such a trend: the transfer reactions, and the concentrations of active sites with different tacticities. The increase in reaction temperature leads to an increase in the transfer reactions especially with the co-catalyst [19]. Additionally, the drop in isotactic sites concentration, demonstrated by the isotactic pentads results which will be discussed next, that are known to produce higher molecular weight leads to the observed drop in M_w . We can also observe this in the molecular weight results of the experiments where no external donor was used where we see on average a 25% decrease in M_w compared to the reference experiments (i.e., experiments 1 to 3).

The MWD results are comparable for all experiments where we do not see any major effect of ALAs or temperature except for MTMA when used with the external donor where a slight broadening is observed due to the atypical response in effect of temperature on M_n and M_w . Additionally, when DBS is used in absence of external donor, the MWD shows mild narrowing at the reaction temperature of 78 °C. It is possible that ALAs participate in transfer reactions which could explain some of the subtle differences observed.

Table 6. Molecular weight characteristics.

SN	ED	ALA	ALA/Ti	M _n (kDa)	M _w (kDa)	MWD
1	N	None	0	40	217	5.4
2	N	None	0	33	166	5.0
3	N	None	0	24	124	5.3
4	None	None	0	32	163	5.1
5	None	None	0	27	138	5.2
6	None	None	0	13	83	6.2
13.1	N	IPM	9.0	31	213	6.9
14.1	N	IPM	9.0	29	190	6.5
15.1	N	IPM	9.0	26	130	5.0
16.1	None	IPM	3.0	35	191	5.5
17.1	None	IPM	3.0	29	152	5.2
18.1	None	IPM	3.0	20	115	5.7
13.2	N	MTMA	9.0	39	301	7.7
14.2	N	MTMA	9.0	22	164	7.6
15.2	N	MTMA	9.0	22	113	5.2
16.2	None	MTMA	3.0	30	187	6.3
17.2	None	MTMA	3.0	28	147	5.2
18.2	None	MTMA	3.0	15	103	6.9
13.3	N	DBS	9.0	43	233	5.3
14.3	N	DBS	9.0	39	212	5.4
15.3	N	DBS	9.0	26	151	5.8
16.3	None	DBS	3.0	34	177	5.3
17.3	None	DBS	3.0	34	142	4.2
18.3	None	DBS	3.0	21	104	4.9

3.2.2. Stereoregularity

One of the important properties of polypropylene is the stereoregularity of the polymer, which is measured using various characterization techniques, most notably for quick indication of tacticity, Xylene Soluble (XS) are usually performed in industrial plants. However, for more detailed and accurate quantification of the stereo-errors in the polymer, ¹³C NMR is used which we have utilized in this study. The assignment of the pentads was performed as described elsewhere [20]. In addition to the isotactic pentads, mmmm, we are reporting the Meso Sequence Length (MSL). MSL indicates the length of isotactic portions of the polymer chain which correlates to the isotactic pentads but is affected significantly with stereo-errors, and is calculated using the equation that follows [21-23].

$$MSL = \frac{mmmm + \frac{3}{2}mrrr + 2rmmr + \frac{1}{2}rmrm + \frac{1}{2}rmrr}{\frac{1}{2}rmrm + \frac{1}{2}rmrr + rmmr + \frac{1}{2}mmmr}$$

Table 7. isotactic pentads and MSL results.

SN	ED	ALA	ALA/Ti	mmmm	MSL
1	N	None	0	93	85
2	N	None	0	92	72
3	N	None	0	91	65
4	None	None	0	92	70
5	None	None	0	91	63
6	None	None	0	89	47
13.1	N	IPM	9.0	94	99
14.1	N	IPM	9.0	94	101
15.1	N	IPM	9.0	93	88
16.1	None	IPM	3.0	92	73
17.1	None	IPM	3.0	92	70
18.1	None	IPM	3.0	90	52
13.2	N	MTMA	9.0	95	138
14.2	N	MTMA	9.0	94	119
15.2	N	MTMA	9.0	94	115
16.2	None	MTMA	3.0	92	69
17.2	None	MTMA	3.0	91	61
18.2	None	MTMA	3.0	90	52
13.3	N	DBS	9.0	95	145
14.3	N	DBS	9.0	94	110
15.3	N	DBS	9.0	93	84
16.3	None	DBS	3.0	93	67
17.3	None	DBS	3.0	92	65
18.3	None	DBS	3.0	92	60

The catalyst used in this study has two internal donors to control the isotacticity of the polymer, one of them is hardly affected by the TEA whereas the other one can be extracted by TEA, and because of this we can see that the mmmm pentads fluctuate within a narrow range as shown in **Table 7**. For all the experiments, the temperature seems to negatively affect the isotactic pentads, which is most likely due to the extraction of one of the internal donors by the co-catalyst, TEA. It is also possible that as temperature increases, TEA decomposition reactions are more favored ^[24], which lowers the efficiency of the

external donor in isotacticity control, as the complex between TEA and the external donor is thought to play an important role in regulating isotacticity [25].

The standard catalytic system with N-donor as an external donor gives a maximum mmmm content of 93%, which drops to 91% at the highest polymerization temperature as shown in Table 7. However, in absence of the external donor, the isotactic pentads did not drop significantly which as we mentioned earlier is due to the inability of TEA to extract one of the internal donors, thus, retaining a high isotacticity. A major difference when the external donor is not used is the drop in the MSL which indicates the presence of higher stereo-errors in the absence of the external donor; this correlation is shown in **Figure 7** for all the experiments where the MSL correlates very well to the mr diads which represent the stereo-irregular diads. The addition of the ALAs with the external donor increased the isotactic pentads marginally but the significant increase can be observed in the MSL which is indicative of the ability of the ALAs, when added with an external donor, to control the polymer stereoregularity. On the other hand, using the ALAs without an external donor leads to a similar content of isotactic pentads as in the experiments without an external donor. This shows that the ability of ALAs to regulate tacticity is nonexistent in absence of an external donor. Nevertheless, the highest isotacticity in terms of mmmm pentads and MSL is observed when MTMA and DBS are used with the external donor.

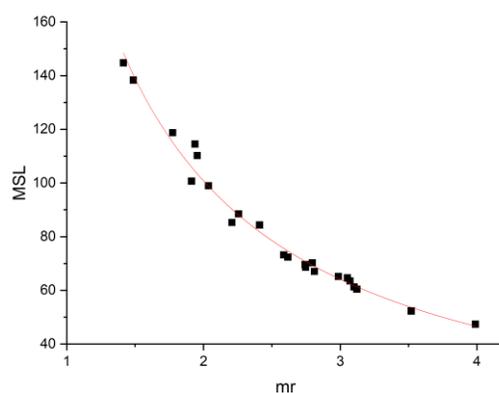


Figure 7. MSL plotted as a function of mr diads (i.e., stereo-irregular diads).

3.2.3. Resin Morphology

The powder morphology is quite important for gas phase processes and can be evaluated using several characterization techniques, some of the most commonly used in industrial plants are powder settled bulk density and fines content (less than 45 μm particles for this scale and conditions). It is always desired to maximize the bulk density and minimize the content of fines in gas phase fluidized bed reactors. As we can see in **Figure 8-A**, the bulk density follows a similar decreasing trend with reaction temperature for all the experiments. The decrease in bulk density as the reaction temperature increases is perhaps related to changes in the fragmentation of the growing catalyst particles, which is clearly affected by the initial reaction rate as shown in **Figure 9-A**, and B. The polymer produced using this catalyst system shows a high bulk density overall, however, due to the mechanically stable structure of the catalyst support, higher initial reaction rates result in a more uniform fragmentation, whereas lower initial reaction rate probably leads to a non-uniform process of fragmentation which is reflected on the lower bulk densities. For example, when DBS is used without an external donor where the highest initial activities are observed at 58 and 78 $^{\circ}\text{C}$, we can see a clear significant improvement in bulk density compared the standard experiments where the external donor is used.

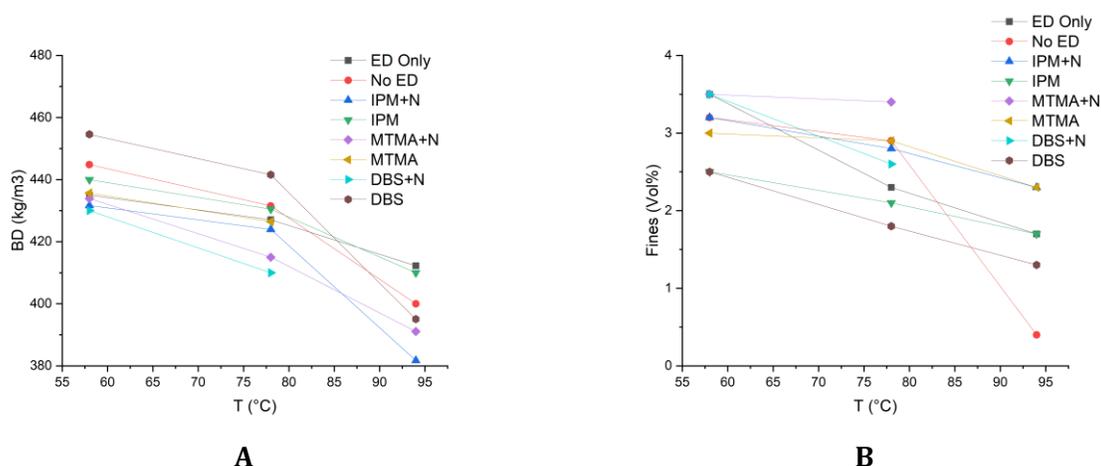


Figure 8. A. Bulk density, and B. fines content, as a function of temperature for the combinations of ALAs and ED.

Fines content, as shown in Figure 8-B, follows a similar decreasing trend with reaction temperature as the bulk density. There are no major differences between all the

experiments as the fines content is fluctuating within 2 vol% for most experiments. Overall, we can see that ALAs have no positive nor negative influence on the bulk density of the powder or the fines content. The bulk density is showing a strong trend with the initial reaction activity regardless of the ALA or ED use, as we can see in Figure 9-A, and B, where the lower reaction temperatures give better bulk density due to the higher initial reaction rate.

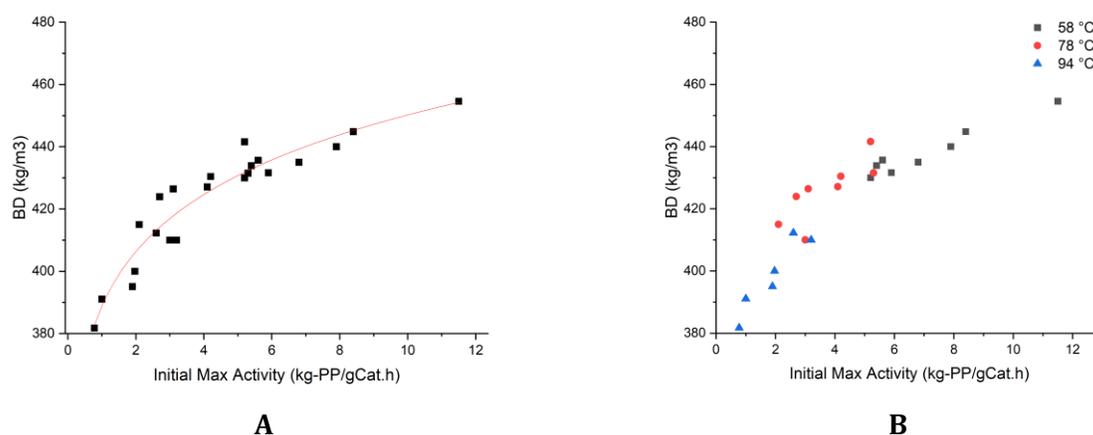


Figure 9. A. Bulk density as a function of initial maximum activity, and B. with temperature, for the analyzed experiments of ALAs and ED combinations.

3.3. Possible Mechanisms of ALAs

To investigate the possible mechanisms of ALA with the catalyst we have used, we have performed a series of experiments that we have described in the experimental section, experiments 19 to 26. Additionally, the catalyst was analyzed using DRIFT without any treatment (R530 curve in **Figure 10**), and with DBS treatment (DBS curve in Figure 10). The treatment with DBS was done in a glove box at room temperature where a ratio of DBS/Ti of 9 was used, after the DBS is contacted with the catalyst under mixing, the catalyst is dried and sampled for the DRIFT analysis. The DRIFT spectra as shown in Figure 10 has the following distinct peaks that are identified based on the functional groups of the internal donors and the DBS:

1. Peaks 1024 and 1060 belong to the first internal donor used in this catalyst.
2. Peak 1611 belongs to the second internal donor.

3. The peak appearing after DBS treatment, 1690, belongs to DBS.
4. Peaks between 3400 and 3600 belong to traces of OH on the catalyst surface [26].

The addition of DBS does not influence the internal donors used in this catalyst; however, DBS seems to bind to the catalyst surface. Since no Ti vacancies are available in a non activated catalyst as is the case here, the DBS is most likely bound to the Mg. As we will see from the experiments next, the DBS binding to the Mg does not seem to influence the self-extinguishing property of the catalyst.

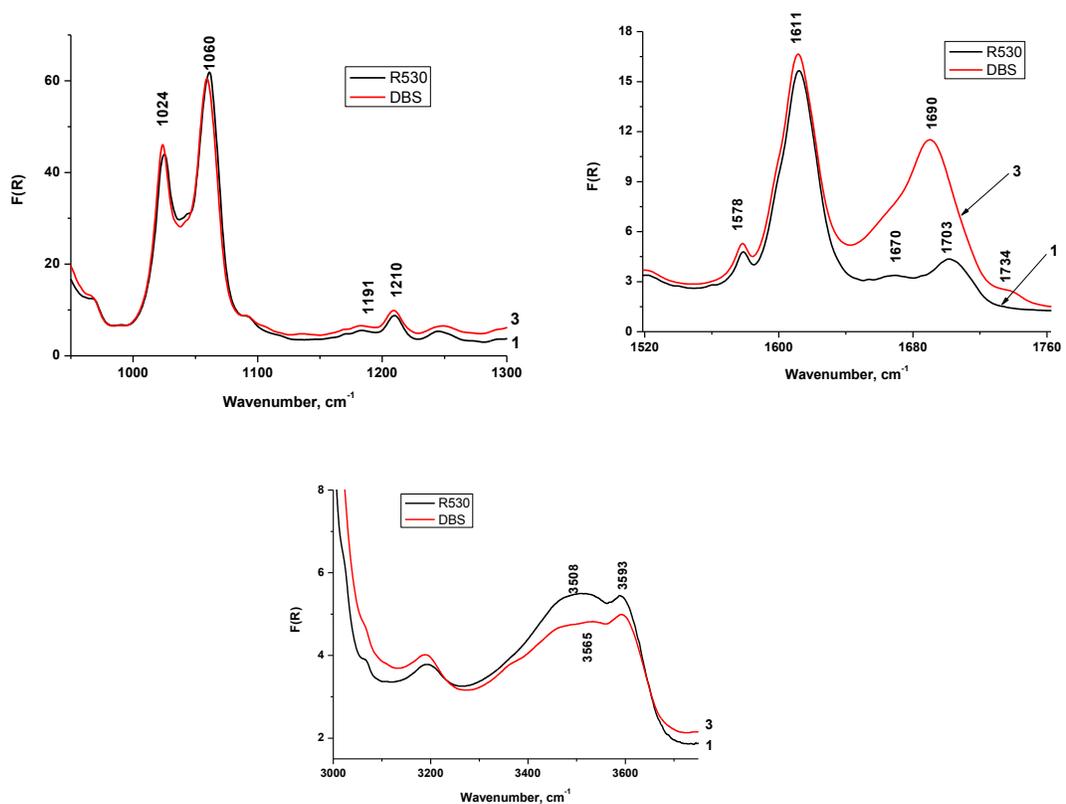


Figure 10. DRIFT spectra of the catalyst with and without DBS treatment.

In **Figure 11-A**, we can see the two experiments performed at low and high temperatures where the catalyst was treated with DBS in the glove box and dried before use in polymerization. Since we have used the highest DBS/Ti molar ratio of 9 and in

reference to the earlier experiments described in the prior sections, at the highest temperature with DBS, we would expect a complete extinction of the polymerization before 60 minutes which is not the case. This indicates that treating the catalyst with DBS does not affect the self-extinguishing property of the catalyst significantly. This is most likely the case as the DBS is bound to Mg where the effect is limited to stereoregular control. In the second set of experiments shown in the same figure, B, addition of the DBS during the polymerization where no TEA is present as the catalyst is preactivated and dried in the glove box before injection shows that the DBS is able to retard the polymerization independent of the polymerization temperature. This means that the DBS is able to adsorb on the active site directly and suppress activity completely. To further distinguish which reaction is more critical with the DBS, some TEA was mixed with the DBS before injection during the reaction as seen in graph C, where at the lower temperature, the reaction proceeds as if there was no DBS added, however, at the higher temperature, we get the same effect as in graph B where the reaction rate goes to zero after the addition of the DBS mixed with TEA. Though we have no direct evidence, these experiments strongly suggest that the most critical reaction happens between the DBS and TEA, where either this reaction is not favored at elevated temperatures which allows the free DBS molecule to adsorb on the active site and suppress the activity, or the decomposition reaction that occurs between the TEA and the DBS is causing the observed deactivation, however, the decomposition reaction doesn't explain the catalyst deactivation by DBS at the lowest reaction temperature where the catalyst is pre-activated with TEA and dried unless the decomposition can occur at the active sites without the aid of the co-catalyst at low temperatures.

Finally, to understand how reversible this retarding reaction by DBS is, we have performed the last set of experiments shown in graph D, where DBS is added in the middle of the reaction which leads to complete suppression of the reaction at both operating temperatures, followed by two injections of TEA at a molar ratio of 48 to Ti. We can see in the case of the lower temperature, TEA seems to reactivate the catalyst slowly but steadily, even in the case of the higher temperature, we can see some reactivation, but it is extremely low. Though we cannot rule out the decomposition of DBS into some poisonous

compounds when reacting on the active species, however, it is difficult to imagine such a decomposition reaction is fast acting especially at the lower reaction temperature of around 36 °C. Instead, it is more likely that the DBS is adsorbing directly on the active species in absence of TEA and rendering it inactive.

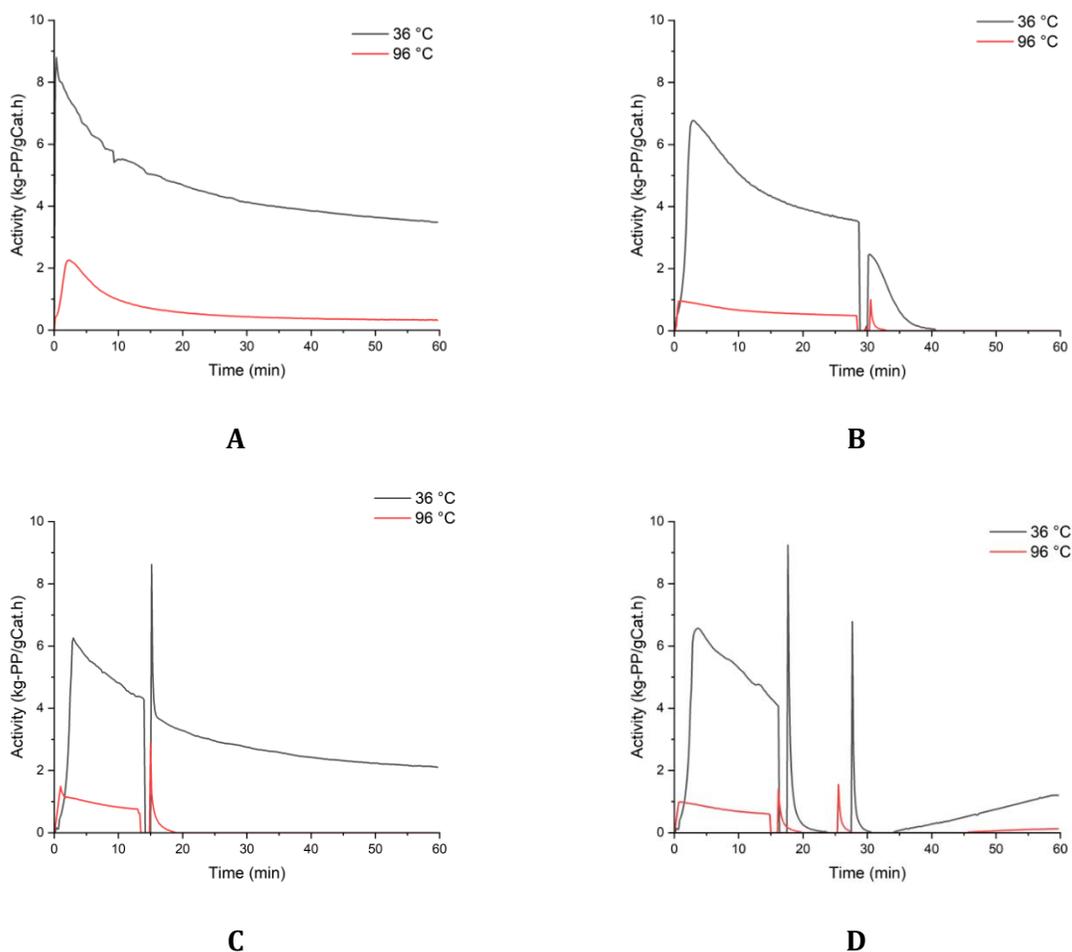
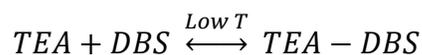


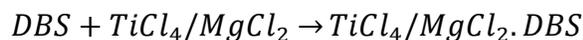
Figure 11. DBS experiments with different methodologies; A. experiments number 19 and 20, B. experiments number 21 and 22, C. experiments number 23 and 24, and D. experiments number 25 and 26.

Based on the experiments performed in this study and in addition to the decomposition reactions that are favored at higher temperatures, we believe the following reactions might take place as well when an ALA is introduced to the reaction environment:

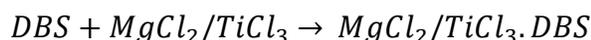
- A reversible ALA-TEA complex formation that is favored at low temperatures.



- Reacting with the Mg in an analogous way to the alkoxy silanes which are used as external donors; this reaction could be the reason ALAs exhibit mild stereoregular control.



- Adsorption on the alkylated active Ti species which leads to the complete suppression of the reaction at higher temperatures.



In addition to the expected reactions that take place with the ALAs, the diffusion of these molecules could play an important role as most of them are quite large molecules as we have seen a difference in the behavior of the smaller molecule we have used in this study, MTMA, compared to the aliphatic mono and diesters, IPM and DBS. Additionally, the number of functional groups could play a significant role in the reactions taken place, for example, we know from studies conducted on alkoxy silanes (i.e. external donors) that an increased number of functional groups leads to increased and unselective deactivation of active species [18].

4. Conclusions

The performance of three activity limiting agents (ALA) with a sixth generation Ziegler Natta catalyst system was evaluated during the gas phase polymerization of propylene. The retarding effect of ALAs on the catalyst at elevated temperatures in order to prevent reactor instabilities in the case of thermal runaways were also studied. Additionally, we have investigated the effects of ALAs on the polymer microstructure, and the morphology of the powder reactor product. Finally, we have looked at the possible pathways by which the retarding effect of the ALA is taking place.

The activity of this catalyst system when used with an external donor decreases mildly as the reaction temperature increases from 58 to 94 °C, however, when we introduce the ALAs even at the lowest ALA/Ti of 0.3 along with the external donor, we observe a decrease in the catalyst productivity of 67, 50, and 17 % in comparison to the standard system productivity at the same temperature for IPM, MTMA, and DBS, respectively. Further increasing ALA/Ti intensifies this retarding effect of activity at the highest reaction temperature, for instance at an ALA/Ti of 9.0, the drop in productivity at the highest temperature in comparison to the standard system is 93, 96, and 96 % for IMP, MTMA, and DBS, respectively. This significant drop in catalyst activity at the high reaction temperature is desirable in order to prevent the softening of the polymer which subsequently leads to the formation of agglomerates. However, this effect comes at the expense of a drop in catalyst productivity at the normal operating temperature of 58 °C; 19, 50, and 40 % for IPM, MTMA, and DBS. An optimum balance between the retardation effect of catalyst activity at higher temperatures and the least negative effect at the normal operating temperatures is achieved at an ALA/Ti of around 3.0. We have only tested three levels of ALA/Ti in a very wide range, the balance of activity at normal operating temperatures and the desired retardation effect can be adjusted for the operation of an industrial plant in favor of retardation when the process is facing some instabilities, and towards the least negative impact on activity at normal temperatures when the process is operating smoothly. Furthermore, the retarding effect is still observed when we use the ALA without an external donor at an ALA/Ti ratio of 3.0, we do see the desirable retarding effect of activity but to a lesser extent than when the external donor is used except for MTMA; the achieved drop in productivity is 40, 80, 50 % for IPM, MTMA, and DBS, respectively. Nonetheless, when the ALAs are used without the external donor, the activity at 58 °C increases by 23, and 98 % for IPM, and DBS, respectively, and drop by 14 % for MTMA.

The use of ALAs with this catalyst system does not lead to any significant effects on the bulk density of the powder, and the fines content. Similarly, no significant effects were observed on the molecular weight averages and distributions. However, when the ALA are used with the external donor, we observe a mild increase in the isotacticity which is

reflected in the isotactic pentads and more so in the MSL. The increase in isotacticity is more pronounced with MTMA, and DBS, than with IPM. Moreover, the use of ALAs without an external donor does not lead to any significant reduction in the isotacticity of polypropylene. Finally, it seems that besides the suspected decomposition reactions' products that could poison the active sites at higher temperatures, the ALA itself is capable of reversibly deactivating the active site, this reaction is seemingly prevented when the ALA complexes with the co-catalyst which is probably more favored at lower temperatures.

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