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Condensed Mode Cooling for Ethylene Polymerization: Part VI. Impact of Induced Condensing Agents on Comonomer Incorporation and Polymer Properties

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Abstract: Gas phase copolymerizations of ethylene and an α -olefin comonomer were performed using a commercial Ziegler-Natta catalyst in the presence of different Induced Condensing Agents (ICA). The impact of these factors the yield and final polyethylene properties such as the melt flow index, crystallinity, and incorporation of comonomer was studied. It has been shown that the increase in the rate of polymerization is even more pronounced the presence of ICA. It also appears that adding ICA to the copolymerizations changes the comonomer incorporation with respect to similar copolymerizations performed without ICA due to competing cosolubility effects.

Keywords: induced condensing agents (ICA); linear low density polyethylene; condensed cooling; gas phase polymerization; comonomer incorporation

1 Introduction

Linear low-density polyethylene (LLDPE) is copolymer of ethylene and an α -olefin comonomer, that typically has a density on the order of 0.91-0.94 g/cm³. The final properties of the polymer can be fine-tuned by adjusting the amount of comonomer added to the final product; increased comonomer content leads to the formation of short chain branches, a decreased density and higher degrees of amorphous material. It is clearly of great importance to be able to accurately predict and control the levels of comonomer incorporation from a commercial standpoint, and as such to plainly identify the different process-related parameters that can have an impact on this aspect of the polymerization.

Most commodity grade LLDPE is made on supported catalysts in a gas phase fluidized bed reactors (FBR). In such polymerizations highly porous supported catalyst particles are injected into the reactor. Polymer rapidly forms in the pores of the support, leading to a buildup of hydraulic stress inside the catalyst particles. This build-up of stress causes the initial support material to fragment, but if this is done correctly one catalyst particle leads to one polymer particle exhibiting morphology similar to the precursor catalyst carrier, with the fragments of the initial support being finely dispersed inside the expanding polymer phase. During the course of the polymerization, monomers and other species diffuse from the gas phase, dissolve and diffuse through the polymer to the active sites, thus forming more polymer and causing the particles to grow by expansion. Thus any process that influences the dissolution and diffusion of active species in the polymer will potentially have an impact on the rate of production and of incorporation of the different species present in the reaction.

In addition, ethylene polymerization is so exothermic that the heat removal rate often limits productivity more than any other single factor. In order to overcome this limitation and to improve the space time yield of the process, manufacturers often employ a number of techniques referred to collectively as condensed mode cooling.^[1] This involves adding a chemically inert species, often called induced condensing agents (ICA) if they can be liquefied with normal cooling water, to the recycle stream. Optionally one can introduce lighter components such as ethane or propane. While strictly speaking not really true ICA, we will use the term ICA to englobe all alkanes added to the recycle stream. ICA have a

higher heat capacity than other process fluids, so if they are fed into the reactor in vapor form, they help increase the heat capacity of the continuously flowing gas stream and help evacuate extra energy. If they are fed into the reactor in the form of liquid droplets, these can rapidly heat up and evaporate, further adding to the heat removal capacity.

It is well-known that the solubility (and diffusivity) of penetrants in a semi-crystalline polymer like LLDPE is non-ideal. Some groups have looked at the impact of mixtures of species on their mutual solubility in PE in the absence of polymerization and shown that heavier compounds, like ICA or 1-alkenes can increase the solubility of lighter ones, and conversely lighter compounds can decrease the solubility of heavier ones (the so-called co-solubility effect).^[2,3,4] Previous papers from our research group have discussed the impact of the solubility effect of a number of ICA for high density polyethylene (HDPE) on reaction rate^[5], the molecular weight distribution and particle morphology^[6], crystallization rate^[7] and reactor behavior^[8]. On the other hand, very little experimental work has been done to understand the impact of adding ICA on ethylene polymerization in the presence of an α -olefin. Alizadeh et al.^[9] performed a limited number of experiments on the copolymerization of ethylene and 1-hexene, and showed that adding hexane as an ICA increased the rate of copolymerization, but they did not investigate the impact of n-hexane on the comonomer uptake. These results suggest that the complex interactions between the different components in an LLDPE system in the presence of ethane or an ICA might have an impact on the incorporation of the comonomer. An experimental study of the impact of some industrially pertinent ICA on copolymerization reaction rates and polymer properties is presented in the current study.

2 Experimental

Materials

Argon, hydrogen, ethane, ethylene and propane, all with a minimum purity of 99.5%, were obtained from Air Liquide (Paris, France). Ethylene and ethane were passed over purifying columns of zeolite and active carbon before use. 1-butene having a minimum purity of 99% was obtained from Air Liquide and 1-hexene with a minimum purity of 97% was obtained from Sigma-Aldrich ICN (Germany). Anhydrous n-pentane (n-C5) with a minimum purity 99% was obtained from Sigma-Aldrich ICN - Germany), and propane and ethane with a

minimum purity of 99.5 % received from Air Liquide. Triethylaluminium (TEA) co-catalyst was obtained from Witco (Germany). A commercial TiCl_4 supported on MgCl_2 Zeigler-Natta catalyst was used for all polymerizations. Sodium chloride (NaCl) with a minimum purity of 99.8%, and used as a seedbed to disperse the catalyst particles.

Polymerization

The gas phase polymerization experiments were performed in a spherical stirred-bed semi-batch reactor described elsewhere^[5,9]. The reactor uses a special anchor type stirrer to maintain uniform the reacting conditions. Unlike the FBR, where there is a constant flow of all reactants through the reactor, this stirred-bed reactor is run in semi-batch mode, so (with the exception of ethylene) all components involved in the formation of the polymer are added to the reactor in one short (ICA, salt, catalyst, comonomer, hydrogen). Ethylene is fed continuously to maintain a constant pressure, and the polymerization rate is calculated by following the pressure drop in the ethylene feed ballast.

The experimental limits for the ethylene pressure, and the partial pressures of 1-butene as a comonomer, and n-pentane as ICA (in the range from 0 to 0.29 for $1\text{-C}_4 / \text{C}_2$ and $n\text{-C}_5 / \text{C}_2$) were defined based on a range of values found in several patents.^[10,11,12,13,14] When 1-hexene was used as the comonomer, the pressure of this species was set at 0.8 bars, just below the dew point at 80°C. The range of pressures used for ethane and propane was 0-15 bars. The ethylene pressure (7 bar), hydrogen pressure (1 bar) and reactor temperature (80 °C) were kept constant for all experimental conditions.

Characterization

DSC analysis was performed using Mettler Toledo DSC 3+ model. Polyethylene was weighed (typical sample size 5-10 mg) and placed in an aluminum capsule with a volume of 40 uL. The sample was first cooled to - 20 °C, giving start the analysis being heated to 180 °C at a rate of 10 °C/min, held for 10 min and then cooled down to - 20 °C at a rate of 10 °C/min. This temperature was maintained for 10 minutes, and the sample was reheated to 10 °C/min to 180 °C. The melting behavior of the samples was studied in the second heating run from room temperature up to 180 °C at the same rate of cooling to detect the melting point (T_m) and the determination of the melting enthalpy (ΔH_f) of the samples. The degree of crystallinity (χ_c) of the samples was calculated by considering the percentage by weight of

the crystalline phase obtained from the polyethylene fraction and the heat of melting from 293 J.g⁻¹ to 100% crystalline polyethylene. The crystallization temperature (T_c) is obtained in the cooling run.

CEF analysis was performed using Agilent Technologies 7890B Gas Chromatograph. A sample of approximately 4 mg of LLDPE is dissolved in 8 mL of 1,2,4-trichlorobenzene (TCB) at 160 °C in the automatic sampler. Dilution continues for 60 min. The polymer solution was stabilized at 95 °C before being injected into the CEF column. The dynamic crystallization step starts by lowering the column temperature from 95 to 35 °C at a cooling rate of 2 °C.m⁻¹ and a solvent flow of 0.065 mL.min⁻¹. After the crystallization cycle is complete, the column temperature is maintained at 35 °C for a few minutes under fresh solvent flow at a constant elution flow rate of 1 mL.min⁻¹. The dynamic elution step begins when the temperature begins to increase at a constant heating rate of 4 °C.min⁻¹, from 35 to 130 °C. The concentration of the polymer fractions in the eluent is monitored by an infrared detector placed at the outlet of the column. The behavior of dynamic crystallization allows the evaluation of the peak temperature and the dynamic elution of the amount of methyl (-CH₃) per thousand carbon atoms, which is considered the comonomer content of the analyzed polymer.

The ASTM D1238 test was used to determine the melt flow index (MFI) of the polymer powders using an extrusion MFI tester (Zwick Roell, ulm, Germany). The procedure includes melting the polymer powder samples at 190 °C with a mass of 21.6 kg followed by extrusion. The measurement required about 5 g of the powder polymer samples to be loaded in the melt flow apparatus. A precision scale of 0.001 g was used to measure the extruded plastic mass and the melt flow time was 10 min.

3 Results and discussion

It is well known that ethylene polymerization on Ziegler-Natta or metallocene catalysts exhibits a “comonomer effect”, where adding small quantities of an α -olefin comonomer leads to an increase in the overall rate of polymerization despite the fact that the homopolymerization rate of higher α -olefins is generally lower than that of ethylene under similar conditions of temperature and pressure. This can explain a portion of the results seen in Figures 1-3, but not all. This has been demonstrated in a previous paper, and interested

readers are referred to reference [9] for more information. It is clear that there are other phenomena that need to be taken into consideration. Both alkanes and α -olefins also exhibit what is referred to as the cosolubility effect, where heavier compounds increase the solubility of lighter ones in the amorphous phase of PE; i.e. are cosolvents for ethylene. It should also be noted that lighter compounds decrease the solubility of heavier ones; e.g. ethylene is actually an anti-solvent for the ICAs and α -olefins used in this study, so we could expect that a compound like ethane would be as well.^[3,15,16] However, no studies have really concentrated on the impact of more than 2 absorbing species on the actual rate of copolymerization and the impact of this on polymer properties. In the following sections we will look at the impact of different types of ICA (heavier or lighter than the comonomers) on the rates of homo- and copolymerization of ethylene with either 1-butene or 1-hexene, and on the final polymer properties of the polymer produced in the different experiments.

3.1 Effect of ethane

The patent literature often cites the use of ethane as a regulator of partial pressure, and one patent from Braskem talks of using upwards of 16 bars of ethane in a gas phase process.^[11] Very little experimental work appears to have been done in the open literature, so we decided first to investigate the impact of the lightest component, ethane, on the polymerization of ethylene. It can be seen from Figure 1(a) that increasing the pressure of ethane from 0 to 15 bars has very little observable impact on the observed polymerization rate. The curves on this graph are each the average of 2 runs, so the small differences between the kinetic curves shown in this figure can easily be attributed to experimental error. However, the influence of ethane on the copolymerization of 1-butene and ethylene is quite different. First of all, the comonomer effect is visible in Figure 1(b). There is a notable increase in the rate of polymerization of the copolymer system with respect to that of the homopolymer at 0 bars of ethane. However, the situation begins to evolve as the ethane content in the copolymerization system increases. As the ethane pressure increases from 0 to 15 bars, the initial rate of copolymerization decreases markedly. After approximately 15 minutes, the rate curves cross (interestingly at the same point), and the system with the highest pressure shows the highest rate of polymerization, and virtually no deactivation for the remaining 45 minutes of the experiment. There is some deactivation for 10 bars and 5 bars, and the experiments with low ethane concentrations behave not too differently from the polymerization with 0 bars of

ethane. The explanation for the evolution of the rates of polymerization in the copolymerization experiments is not obvious.

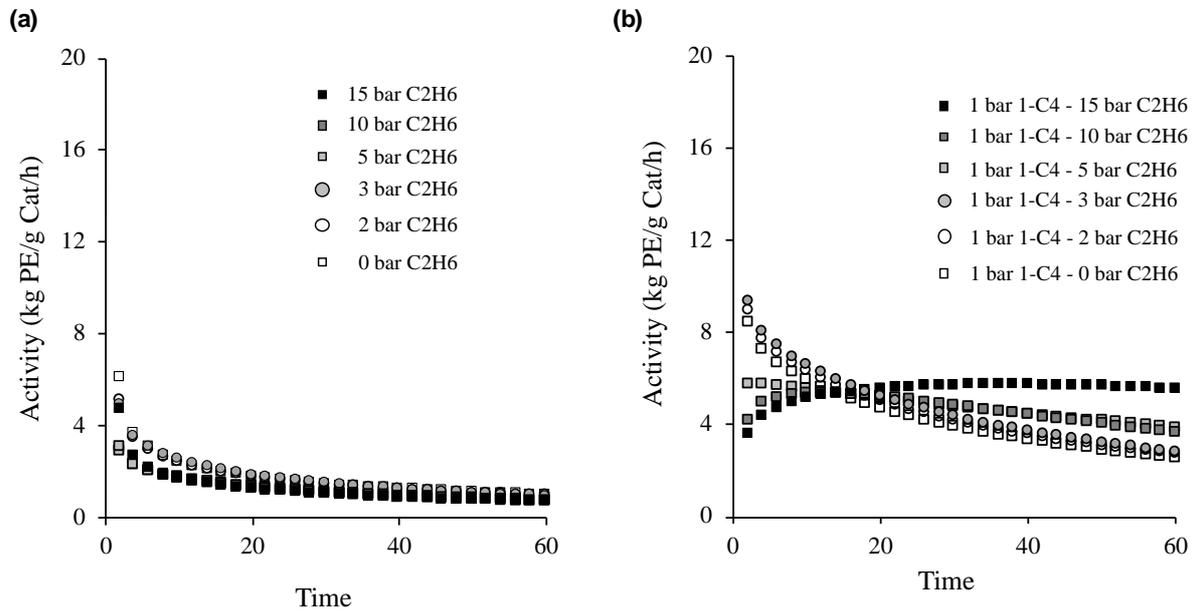


Figure 1. Impact of different partial pressures of ethane on the rate of polymerization of 7 bars of ethylene at 80°C: (a) homopolymer; (b) 1 bar 1-C₄.

Figure 2 shows that there is some difference in the gas phase (and therefore particle) temperatures in the copolymerization runs. It is possible that an increase in the gas phase heat capacity from 52 kJ/mol/K at 0 bars of ethane to 63 kJ/mol/K could be responsible for the differences in the initial reaction rates. However, if this were the case one would expect the 15 bar experiment to remain at a lower activity and lower gas phase temperature than the 0 bar ethane experiments, which is clearly not the case. Modelling studies by Kittilsen et al.^[17] and Parasu Veera et al.^[18] suggest that it is possible that the higher ethane levels lead to lower concentrations of monomer in the particles. These authors showed that if high levels of inert materials are present in the gas phase, they could be drawn into the particles by convection and lead to an overall decrease in the observed rate of polymerization, and that these convective transport effects will disappear as the reaction progresses. At 10 and 15 bars of ethane, the initial copolymerization rates are very close to those of the homopolymerization. This is not seen for the lower ethane concentrations, nor for the homopolymerization. All of this together suggests that there is a convective effect at high ethane levels that reduces the amount of butene actually entering the particles. This disappears as the polymerization progresses.

Finally Figure 3 shows the impact of changing ethane pressures on the physical properties of the final polymer. As one might expect, the influence of the ethane levels on the crystallinity and on the MFI is relatively insignificant. The crystallinity of the homopolymers remains essentially unchanged to within an estimated reproducibility of plus or minus 2 percent. The results of the MFI are similar; changing ethane levels changes the MFI imperceptibly except at 15 bars, where the MFI drops a little. On the one hand this is not inconsistent with the expected antisolvent effects of light components on heavier ones. In this case 15 bars of ethane might diminish a little bit the concentration of 1-butene in the amorphous phase of the polymer, and thus at the active sites (little information on the cosolubility of these components in PE is available, so it is not possible to predict the exact impact of this). A lower butene content could conceivably cause the MFI to decrease (i.e. the molecular weight to increase) clearly including ethane has zero impact on the solubility of ethylene. However, one would expect a corresponding increase in the crystallinity of the polymer since this would mean a higher ethylene to comonomer ratio at the active sites, and this is not evident from the crystallinity measurements

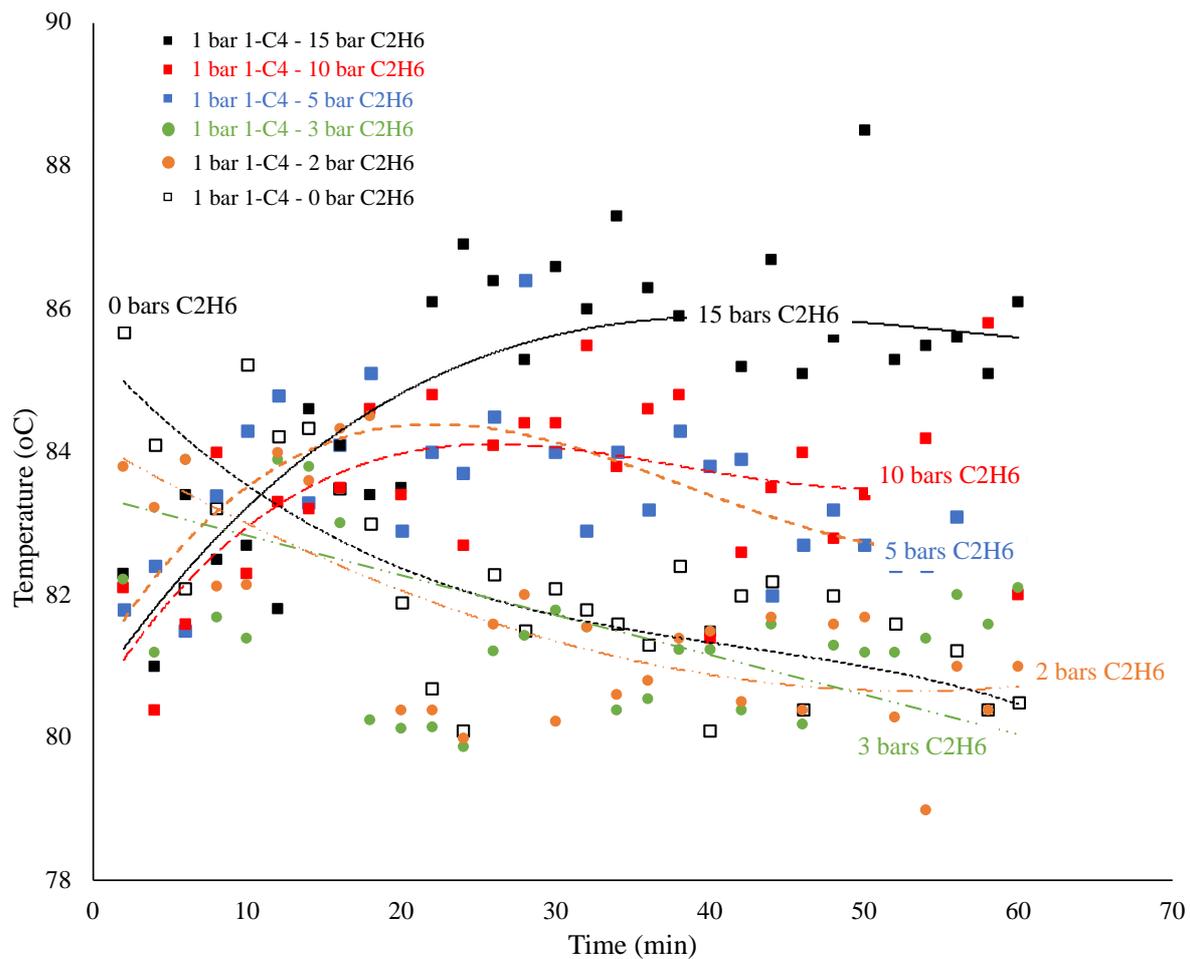


Figure 2. Gas phase temperatures for the copolymerization experiments shown in Figure 1(b). The points are the raw data and the lines (3rd order polynomial fit) are simply there to guide the eye.

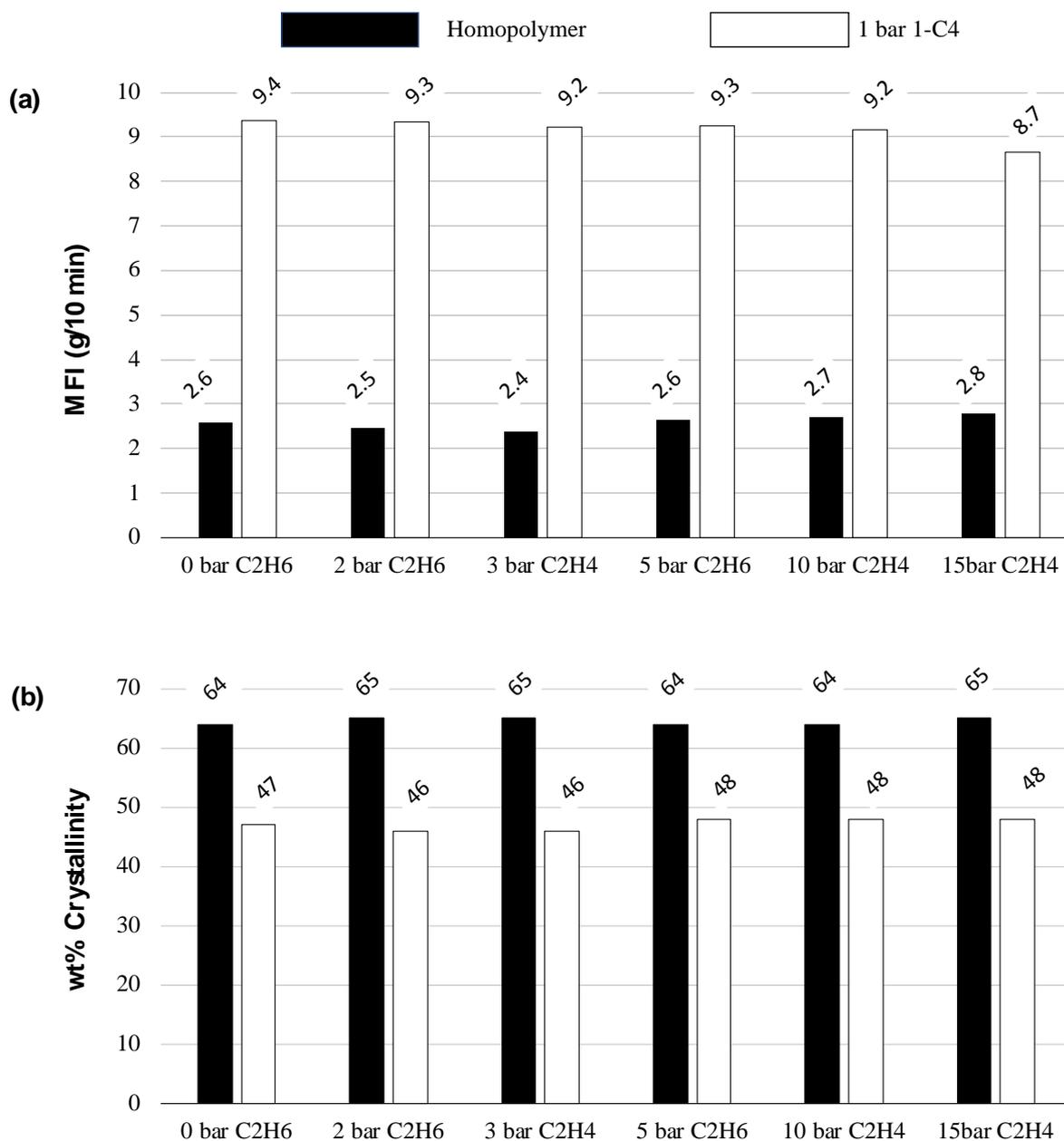


Figure 3. Physical properties of homo- and copolymers (1 bar 1-C4) of ethylene for different pressures of ethane. (a) Melt Flow Index (21.6 kg, g/10 min); (b) Crystallinity (weight per cent).

In order to explore this point in more detail, CEF analyses were done on each of the resultant polymer from the experiments shown in Figure 1(b). An example of the analyses is shown in Figure 4, and the number of branches per 1000C for each ethane level in the experiments of Figure 1(b) are shown in Table 1. For the CEF analyses we did not include the ambient temperature peak. It can be seen from Figure 4 that there are two non-ambient temperature peaks, often characteristic of Ziegler-Natta polymerizations. The small peak, extending from approximately 40-80°C most likely consists of low molecular weight polymer, and the

narrower large peak of more crystalline, higher molecular weight polymer. Table 1 shows that as the ethane concentration is increased from 0 to 15 bars during the copolymerization experiments, there is a slight, but constant decrease in the number of branch points in both peaks. This result suggests that in fact the ethane is acting as a (very weak) antisolvent for 1-butene in these experiments. Given the level of change in the number of branch points, it is not unexpected that the differences in composition cannot be picked up accurately by a technique like DSC.

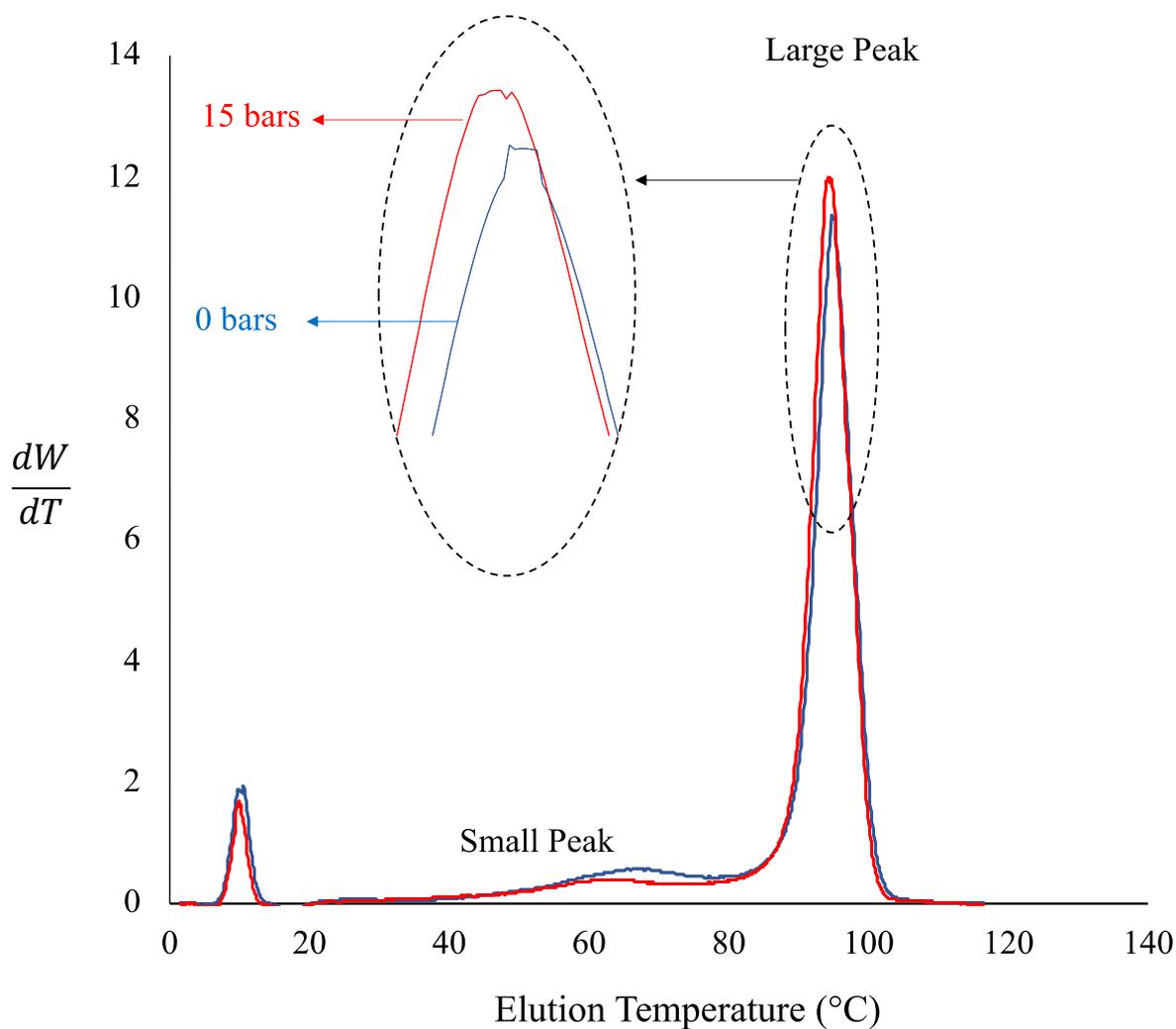


Figure 4. CEF elution curves for 0 and 15 bars of ethane during the copolymerization of ethylene and 1-butene. Area under each curve is proportional to the crystallinity of the polymer fraction.

Table 1. CEF analyses for copolymerizations in Figure 1(b).

Bars Ethane	CH3/1000C Small Peak	CH3/1000C Large Peak
0	48.9	6.4
2	46.6	5.2
3	46.0	5.3
5	43.3	4.9
10	42.2	4.8
15	43.2	3.9

In conclusion, when 7 bars of ethylene is copolymerized with 1 bar of 1-butene, in the presence of 1 bar of hydrogen at a nominal reactor temperature of 80°C, it appears that the ethane acts as a weak antisolvent for 1-butene, but has no visible effect on the solubility of ethylene during the experiments. Ethane also has a noticeable, reproducible effect on the initial rates of polymerization (and effect that we can also see for propane in the following section), with higher ethylene concentrations corresponding to a significantly lower observable rate of copolymerization (an effect not seen in homopolymerization). It is possible that this rate reduction at high ethane concentrations is due to a convective mass transfer resistance. However, this rate reduction does not have an observable effect on the MFI of the final polymer. And although the CEF results suggest that higher ethane concentrations lead to a lowering of the number of branches in the main polymer chains, this effect is not particularly strong for ethane, and very high ethane pressures in the reactor would be needed to see a significantly influence during a full-scale polymerization.

3.2 Effect of Propane and Pentane

In terms of the impact of propane, commonly used as a process gas for certain commercial applications, it is interesting to note that similar trends in terms of the overall impact of increasing the propane partial pressures on ethylene copolymerization can be seen in Figure 5, where higher propane levels correspond to a longer time reaching the maximum activity. There is a comonomer effect of both 1-butene (Figure 5a) and 1-hexene (Figure 5b) which can be seen by comparing the zero propane curves in Figure 5 with the zero ethane curves in Figure 1(a). Furthermore, in both cases we see the cosolubility effect in evidence for both monomers as the propane pressure increases; clearly increasing the propane levels leads to higher copolymerization rates. As expected^[19] this is also true of pentane. It can be seen

from Figure 6 that increasing the amount of pentane in the reactor increases the rates of the homopolymerization of ethylene, and its copolymerization with 1-butene and with 1-hexene. In other words, both a comonomer effect, and an additional cosolubility effect due to the presence of n-pentane are observed. If we compare Figure 1(b), Figure 5(a) and Figure 6(b), it can be seen that the heavier the ICA, the greater its impact on the rate of polymerization will be because the heavier the ICA, the greater its cosolubility effect will be for a given pressure.

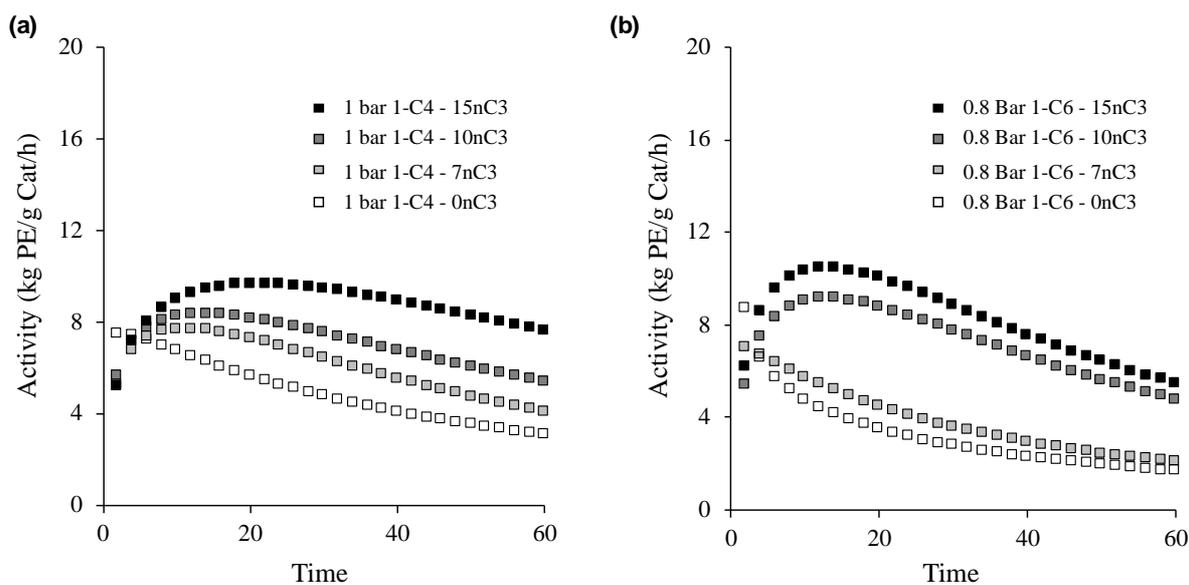


Figure 5. Impact of different partial pressures of propane on the rate of polymerization of 7 bars of ethylene at 80°C: (a) 1 bar of 1-butene; (b) 0.8 bars of 1-hexene.

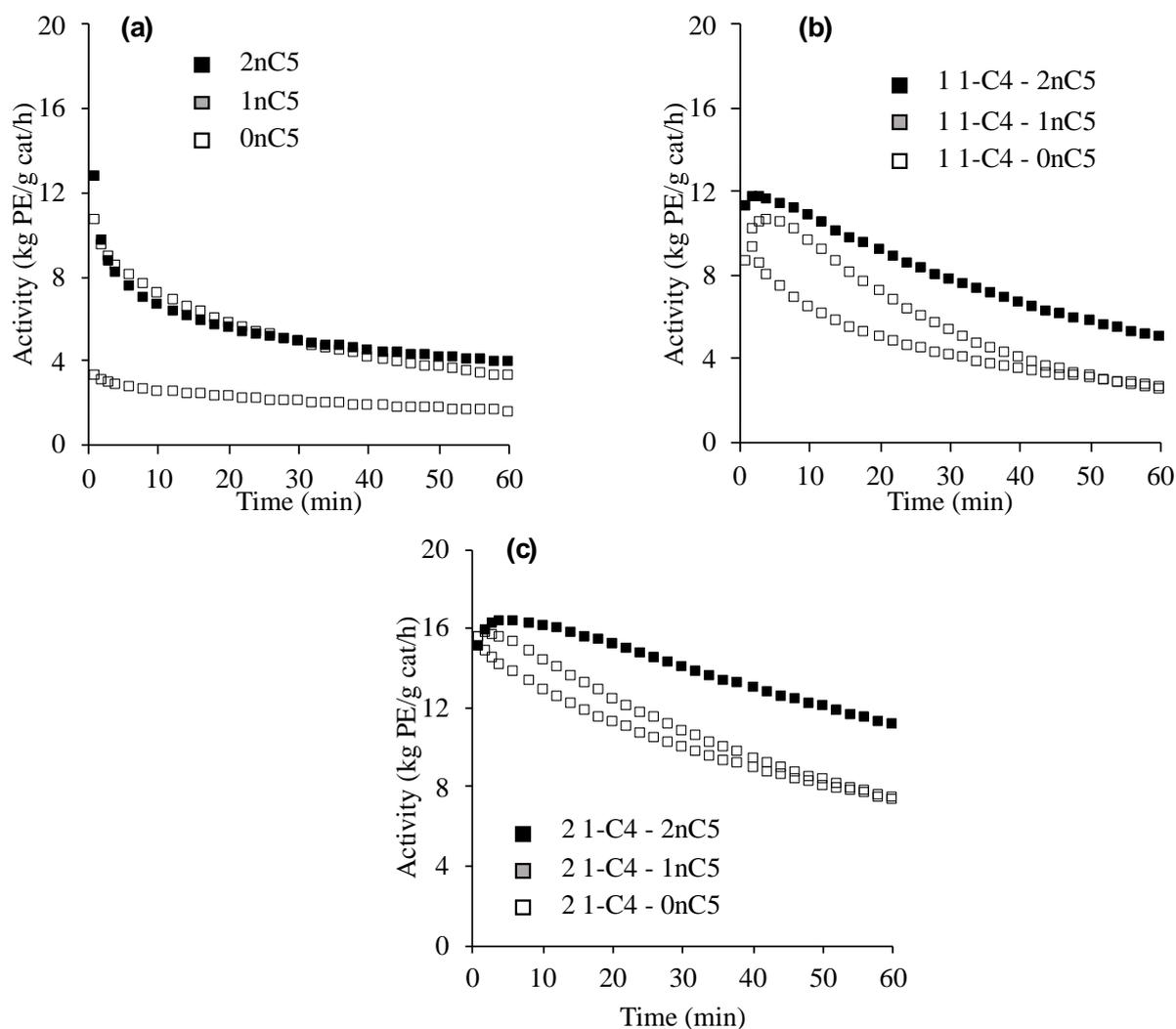


Figure 6. Impact of different partial pressures of n-pentane on the rate of polymerization of 7 bars of ethylene at 80°C: (a) without comonomer; (b) 1 bar of 1-butene; (c) 2 bars of 1-butene.

An analysis of the powders from the previous section reveals a clearer picture of the impact of the ICA on polymer properties. It can be seen from Figure 7 as one increases the quantity of propane in the gas phase mixture, the crystallinity clearly increases for both 1-butene (Figure 7a) and 1-hexene (Figure 7b). Similar results are seen in Figure 7(c) for 1-butene and different quantities of n-pentane. Figure 8 shows us that increasing levels of ICA cause noticeable drops in the MFI for both propane and pentane as ICA. As with the rates of polymerization above, small increases in pentane pressures lead to more significant changes in polymer properties than much larger changes of propane pressure. As an aside, the same experiments (1-butene in the presence of n-pentane) were run again, but for only 15 minutes

instead of 1 hour. The results of the analyses of the crystallinity of the copolymers from these runs can be seen in Figure 9 and compared to those of Figure 7 (c). It can be seen that the trend in terms of the impact of the amount of pentane present in the reactor on the crystallinity is virtually the same in both cases. This implies that while composition drift is certainly important in certain systems, it does not appear to be the case in the current set of experiments. This comparison was not performed for the other blends of ICA and comonomers tested here, but there is no reason to think that this would be substantially different.

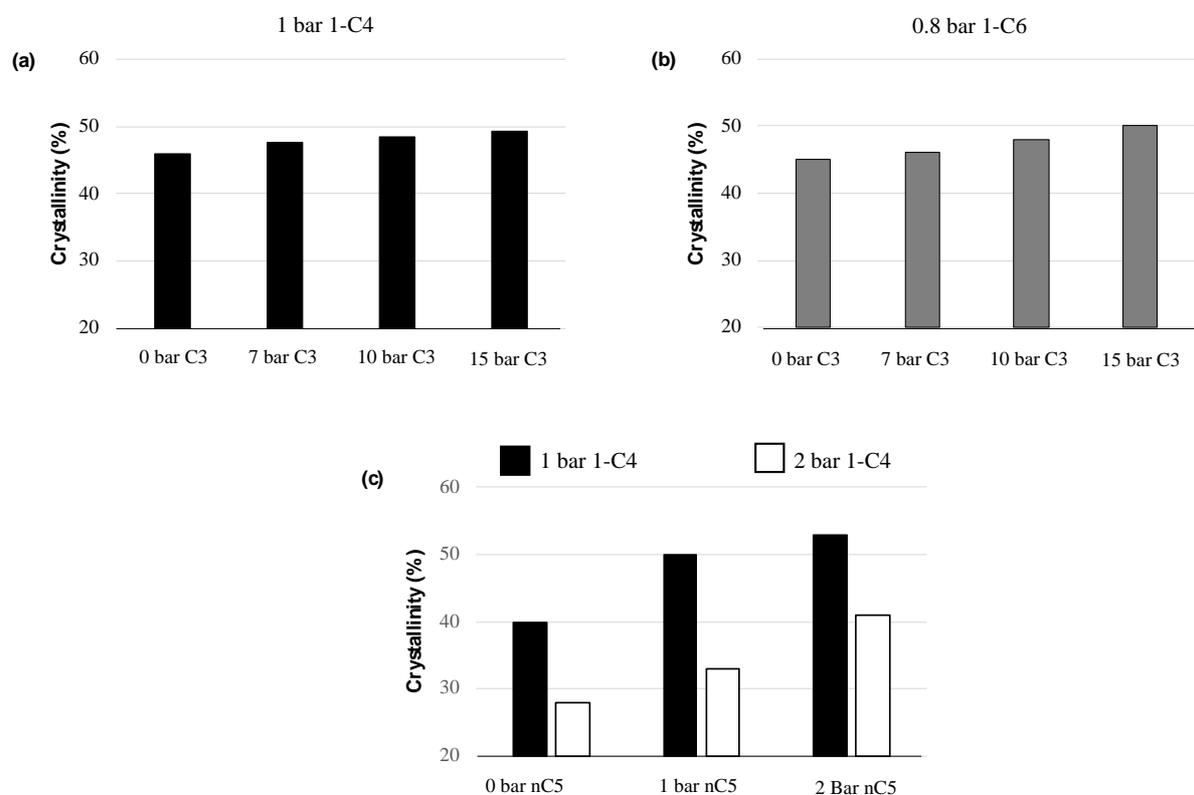


Figure 7. The crystalline weight fraction for copolymers made from 1 bar of hydrogen, 7 bars of ethylene and: (a) 1 bar of 1-butene for different pressures of propane; (b) 0.8 bar of 1-hexene for different pressures of propane; (c) 1 and 2 bars of 1-butene for different pressures of pentane.

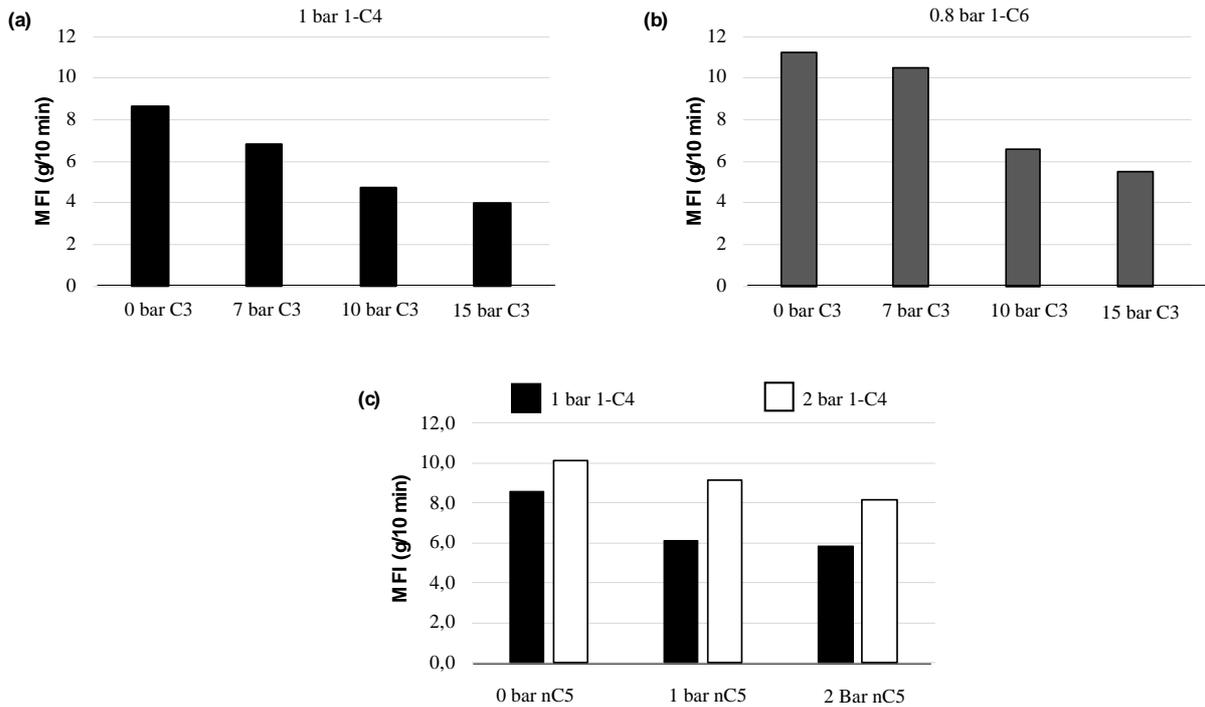


Figure 8. The MFI (g/10 min) for copolymers made from 1 bar of hydrogen, 7 bars of ethylene and: (a) 1 bar of 1-butene for different pressures of propane; (b) 0.8 bar of 1-hexene for different pressures of propane; (c) 1 and 2 bars of 1-butene for different pressures of pentane.

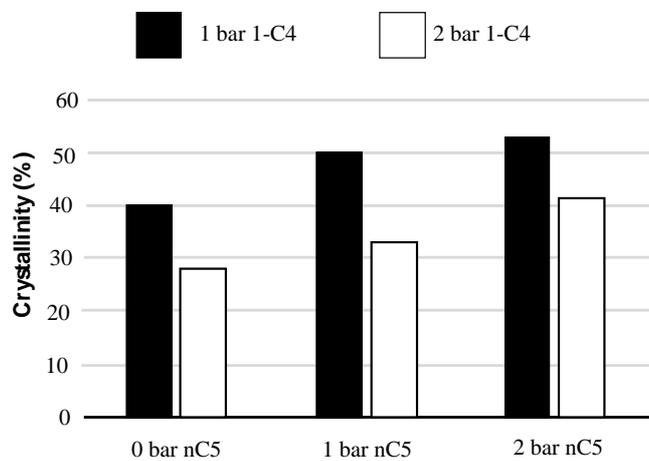


Figure 9. The crystallinity (%) for copolymers obtained after 15 minutes of polymerization made from 1 bar of hydrogen, 7 bars of ethylene and 1 and 2 bars of 1-butene for different pressures of pentane.

Table 2. CEF analyses for copolymerizations in propane

Bars Propane	1 bar 1-butene		0.8 bar 1-hexene	
	CH3/1000C Small Peak	CH3/1000C Large Peak	CH3/1000C Small Peak	CH3/1000C Large Peak
0	48.9	6.4	86.9	8.1
5	44.1	6.2	70.7	7.5
10	35.9	5.1	63.9	7.3
15	34.1	4.4	56.9	6.7

Table 3. CEF analyses for copolymerizations of ethylene and 1-butene in pentane

Bars Pentane	1 bar 1-butene		2 bar 1-butene	
	CH3/1000C Small Peak	CH3/1000C Large Peak	CH3/1000C Small Peak	CH3/1000C Large Peak
0	48.9	6.4	58.5	11.7
1	46.7	4.7	56.2	10.2
2	44.8	3.4	52.1	9.5

4 Conclusion

In this study we present a study focused on identifying certain physical phenomena that occur during the copolymerization of ethylene with either 1-butene or 1-hexene in the presence of ethane, propane and n-pentane as ICA.

When ethane is present in the reactor, it appears to have virtually no impact on the molecular weight and crystallinity of ethylene-1-butene copolymers. Nor does up to 15 bars of ethane influence the observed rate of homopolymerization. However, the initial rates of copolymerization actually decrease as the ethane partial pressure increases. This was unexpected, and the reason for this is not at all clear. The reactor temperature of the copolymerizations is slightly lower for 10 and 15 bars of ethane than for the lower partial pressures, but since this effect is not seen in homopolymerization we do not think it is due to an increased heat capacity at the higher pressures (if it were, we would expect the same trends in the homopolymerization). A possible explanation for this would be mass transfer resistance. It has been shown in the literature that very high concentrations of inert compounds in the gas phase might actually hinder the arrival of slowly reacting species to

the interior of the particles.^[17] It is therefore not impossible that higher ethylene pressures cause the transfer of butene to be much slower than in the case of less dilute systems. One can see that the initial rates for 10 and 15 bars of ethane are very close to the homopolymerization rates at short times. In addition, analogous behaviour is seen when propane is used as the ICA. Short time experiments would be very useful in determining whether or not this is the case, as one would be able to see differently levels of comonomer incorporation (and eventually molecular weights). Nevertheless, the fact remains that ethane seems to have virtually no impact on ethylene solubility. It has been observed that the copolymer is slightly more crystalline in the presence of 15 bars of ethane, suggesting that perhaps the ethane acts as a (weak) antisolvent for butene. However even if this is true, the impact remains very small, and it is not likely that commercial processes run with such high ethane levels.

The effect of propane is more pronounced. As expected, it appears to have a positive cosolubility effect on ethylene with the polymerization rate increasing and the MFI decreasing as the propane pressure increases. On the other hand, the crystallinity of the copolymer clearly increases as the propane pressure increases. All of the observations can be explained by the fact that increasing propane pressure increases the ethylene concentration in the amorphous phase of the polymer, and thus at the active sites, and decreases (or has little influence on) the butene concentration in the polymer. Finally, for heavier ICA, the effect is even more pronounced, and the variations in rate, MFI and crystallinity follow similar trends for the same reason. 15 minute polymerizations with the ethylene-1C5-nC5 system show that it is unlikely that composition drift could explain these results.

Of course, one needs to pay particular attention to the ability of the catalyst to incorporate comonomer, and the residence time distribution of the reactor being used before trying to blindly extend these results to any polymerization processes. However the overall point here remains independent of the system under consideration: it is extremely important to account for solubility-related phenomena and their impact on polymer properties. Ignoring the contribution of chemically inert alkanes in the reactor (not to mention the type of comonomer) will lead to an inaccurate assessment of the impact of reaction conditions on final polymer properties.

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