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2
3 **Full Paper**

4
5 **Condensed Mode Cooling for Ethylene Polymerization: Part V. Reduction**
6 **of the crystallization rate of HDPE in the presence of Induced Condensing**
7 **Agents**

8
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18

19 **ABSTRACT**

20
21 The crystallization of high-density polyethylene (HDPE) alone, and in the presence of n-
22 hexane (a common induced condensing agent – ICA) was studied using Differential Scanning
23 Calorimetry (DSC). The presence of a non-crystallizable ICA which is partially soluble in the
24 amorphous phase of HDPE reduces the rate of crystallization. This was reflected by a shifting
25 of the crystallization and melting peaks of HDPE to lower temperatures when the ICA
26 concentration in the medium increases. It is also observed that the rate of crystallization of
27 HDPE can be very slow when the ratio of ICA to HDPE increases from zero. This behavior is
28 useful to better understand the physical effects that can potentially occur at the beginning of
29 the gas phase polymerization of ethylene, and suggests that the crystallization of the nascent
30 polymer, and thus the properties of the polymer in the reactor will be quite different from
31 those of the powder at later stages of the reaction when running in condensed mode.

32
33 **Keywords:** induced condensing agents (ICA); isothermal crystallization; high density
34 polyethylene; kinetic of crystallization.

35

1 Introduction

High density polyethylene (HDPE) can be produced on an industrial scale using different types of processes, the two most widely used being in diluent slurry and a gas phase. In a gas phase process, the polymerization takes place in a continuous fluidized bed reactor (FBR), where a gas mixture is brought into contact with a supported catalyst. The mixture typically is composed of ethylene, hydrogen, variable amounts of comonomers such as 1-butene or 1-hexene, inert gases to regulate partial pressures, and eventually alkanes to help with heat transfer. These last compounds are often referred to as induced condensing agents (ICA), and are often isomers of butane, pentane, and hexane¹⁻³.

The monomer(s) diffuse from the continuous phase into the pores of the solid catalyst particles, where they then polymerize at the active sites situated therein. As polymer builds up, it creates hydraulic tensions that provoke the rupture or fragmentation of the original support⁴⁻⁶. The morphology of the final particles will depend strongly on this fragmentation step because the way in which the particles rupture represents a trade-off between the rate of generation of stress caused by the polymerization on the one hand, and the ability of the particle to dissipate the mechanical energy on the other⁷⁻⁹. Thus, the physical properties of the polymer during this part of the polymerization, and in particular the crystallinity¹⁰ can have a strong influence on fragmentation. In addition, the crystallinity can influence monomer solubility¹¹, as well as the rates of diffusion¹² through the growing polymer particle¹³⁻¹⁵. These last two quantities (solubility and diffusivity of penetrants) will also be a function of the type and quantity of ICA added to the reactor. For instance, it has recently been shown that adding up to 0.8 bars of n-hexane to a gas phase polymerization of ethylene can lead to a significant enhancement of both monomer diffusivity and reaction rate with respect to what is observed for a polymerization in the absence of ICA¹⁶. The authors of this last work noted

62 that the greatest deviation between experiment and model predictions was at the beginning of
63 the reaction, where the free-volume based model apparently underestimated the effective
64 diffusivity of ethylene in the amorphous polymer in the presence of n-hexane. It is entirely
65 possible that this is because the fraction of amorphous material is underestimated during this
66 phase of the polymerization. This in turns begs the question about how fast the formation of
67 crystals is with respect to the formation of polymer chains – in other words, can we assume
68 that the crystallinity of the nascent polymer is similar to that of the final reactor powder?

69

70 Note also that laboratory scale polymerization of ethylene in the presence of an ICA (pentant
71 or hexane) revealed that adding the ICA led to the formation of an HDPE that had a higher
72 degree of crystallinity than a polymer made with ethylene alone under otherwise identical
73 conditions. In addition, adding the ICA also led to significant increases in the average
74 molecular weight of HDPE.¹⁶ The increase in the average molecular weight can be (at least in
75 large part) attributed to an increase in the ethylene concentration at the active sites due to the
76 comonomer effect, and the higher crystallinity in the presence of an ICA was mainly
77 attributed to the mechanism of crystallization of polymer chains in the presence of solubilized
78 ICA which can act to promote solvent vapor annealing¹⁷. It is possible that this combination
79 of rapidly forming chains and higher molecular weight leads to a slowing down of the
80 crystallization process, allowing the chains more time to reorganize and form more crystalline
81 polymers.

82

83 The crystallization of the polymer is governed by the extent and type of branching, the
84 comonomer composition, and external factors such as the presence of plasticizers like ICA. In
85 general, the crystallization of polymers is a kinetic phenomenon: in the molten state, all of the
86 polymer chains are disordered (amorphous), and they need time to organize in an ordered

87 structure (crystalline polymer). There will **therefore be a characteristic** time for chain
88 crystallization, just as there is a characteristic time for chain formation.

89

90 All of these points suggest that it would be useful for us to understand what, if any, influence
91 the presence of an ICA has the rate of crystallization during PE production – is it rapid with
92 respect to the fraction of a second that the polymer chains grow? Or is it a slower process?

93

94 *Polymer crystallization theory*

95 Whenever particles crystallize out of solution, two fundamental processes are involved:
96 crystal nucleation and growth. A unified theory of crystallization does not exist, but a set of
97 complementary theories have been developed that can help us to understand the impact of
98 sorbed alkanes on PE crystallization. Morphological theories generally calculate an
99 equilibrium morphology based on the energetic interactions of different crystal faces in order
100 to estimate its final form, and thus do not take into consideration the nucleation phase, which
101 is in fact useful **to understand the role that ICA might play in crystallization** ^{18–20}. All
102 **morphological theories consider two barriers to crystal growth: one that accounts for the**
103 **thermodynamic barrier to include a crystalline stem on the growing lamella, and another that**
104 **accounts for the diffusion of a molecule towards the lamella. Inclusion of a stem into a**
105 **growing crystal is enhanced by decreasing temperatures whereas the second barrier becomes**
106 **more significant.** The purpose here is not to discuss the differences between the theories, but
107 rather to understand the points they have in common to assess what affects the rate of
108 crystallization. Moreover, for temperatures far above the glass transition temperature (T_g),
109 which is the case in the present work, polymer diffusion is fast enough that it is not the
110 limiting mechanism. Therefore, only the crystalline stem deposit mechanism has to be
111 considered.

112

113 In this case, the crystallization rate is controlled by the free energy difference between the
114 liquid and the solid phases. This difference is commonly considered proportional to the
115 degree of supercooling, represented by the difference between the equilibrium melting
116 temperature (T_m^0) and the temperature at which we are observing the system. T_m^0 is the
117 temperature at which the crystal would melt if it was of infinite dimensions,²¹ and it is thus
118 the limiting temperature for the crystallization process. More rarely, a “zero growth”
119 temperature instead of T_m^0 is considered as the limit²². Regardless of the definition chosen,
120 crystallization kinetics are governed by the temperature difference between this limiting
121 temperature and the actual crystallization temperature, and this degree of supercooling is in
122 the denominator of a negative exponential function. This means that a small variation of the
123 supercooling drastically modifies the crystallization kinetics. In addition to the crystallization
124 temperature, the crystallization kinetics can be alternatively modified by the concentration of
125 a diluent that alters the equilibrium melting temperature.²³

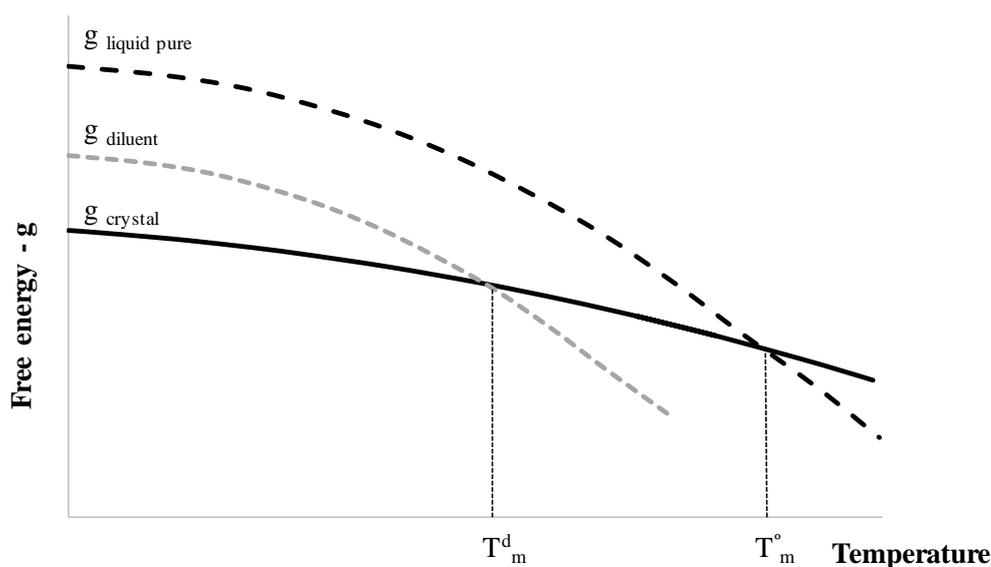
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127 This last point can be illustrated using Flory-Huggins theory to calculate the free energy of the
128 fringed micelle model, in which the crystallization processes occur only when the system is
129 supersaturated. In general, supersaturation can be imposed on a system by cooling, solvent
130 evaporation, the addition of an anti-solvent or by chemical reaction²⁴. Supersaturation is the
131 driving force of the crystallization process, meaning that crystallization occurs only if the
132 system is supersaturated. This implies that in order for a crystallization process to occur
133 spontaneously, it needs to be accompanied by decrease in the free energy. Thus the increase
134 of entropy due to presence of a diluent means that T_m^0 decreases, and this must be
135 compensated for by a decrease in the crystallization temperature. The Flory-Huggins

136 equation describes this dependence of the equilibrium melt temperature on the concentration
137 of a diluent ²⁵.

138

139 Figure 1 shows the relationship of the free energy with temperature, where it compares the
140 effect of the presence of the diluent on the free energy. The equilibrium melt temperature will
141 be lower for a dilute system, and this has been observed in the case of polyethylene in the
142 presence of heavier alkanes ²⁶, xylenes and o-dichlorobenzene ²⁷⁻²⁹, and other diluents ^{25,30,31}.
143 Teymouri et. al. ³² evaluated LDPE and n-hexane thermograms with different swelling times
144 and observed that although there were no major changes in equilibrium melt temperature,
145 there was a significant shift in the lowest melt peak in the presence of the solvent (from 90 °C
146 for pure LDPE to 70 °C for LDPE swollen by Hexane). It was observed that the rate of
147 crystallization decreased at temperatures near the melting point, and was kinetically
148 controlled under thermodynamic conditions far from equilibrium ³³. Some kinetic studies of
149 polyethylene with xylene ³⁴ and o-dichlorobenzene ³⁵, show that the rate of crystallization
150 decreases as we approach the melting point.



151

152 Figure 1 - Relation between free energy and temperature for pure polymer and diluent systems.

153

154 If one considers crystallization caused by cooling, it can be assumed that crystallization in the
155 presence of a diluent will occur for an equivalent degree of supercooling with respect to the
156 crystallization temperature of pure polymer.

157

158 In conclusion, since the presence of alkanes in of polyethylene causes a decrease in the
159 equilibrium melting temperature, it must also lead to a depression of the crystallization
160 temperature and rate. It is therefore possible that the crystallization rate of polyethylene is
161 slower in the presence of an ICA (with respect of a system without ICA) at temperatures
162 between 90 - 115 °C.

163

164 **2 Experimental section**

165

166 **2.1 Materials**

167

168 The high-density polyethylene (HDPE) used in this work was produced in gas phase
169 polymerization experiments performed in the spherical stirred-bed semi batch reactor, as
170 described elsewhere¹⁵. Polymerizations were run at a pressure of 7 bars of ethylene at 70 °C
171 without hydrogen and 80 °C in presence of 1 and 3 bar hydrogen. Molecular weight data are
172 shown in Table 1. N-Hexane was used as the induced condensing agent (minimum purity
173 99%, from Sigma-Aldrich ICN - Germany). The ICA properties are shown in Table 2.

174

175 Table 1. HDPE types

Samples ^{a)}	T_{reactor} °C	P_{Ethylene} bar g	P_{Hydrogen} bar g	Yield g _{pol} ·g _{cat} ⁻¹	M_n kg·mol ⁻¹	M_w kg·mol ⁻¹	M_z kg·mol ⁻¹
HDPE70	70	7	0	1,575	114	751	2,936
HDPE-1H ₂	80	7	1	2,158	59	278	955
HDPE-3H ₂	80	7	3	1,312	33	145	448

176 a) The sample name is identified by HDPE + polymerization temperature [°C]
177

178 Table 2. ICA proprieties

ICA	P^{vap} bar 70 – 120 °C	BP °C at 1 atm	M_w kg. mol ⁻¹
<i>n</i> -Hexane	1.034 – 3.987	69	86.18

179

180

181 2.2 Preparation of sample blends

182

183 In order to evaluate the impact of ICA on the crystallization process, HDPE and blends of
184 HDPE plus different levels of ICA were placed in 120 μ L medium pressure steel capsules,
185 and analyzed by DSC. In the case of the blends, a given mass (5 - 20 mg) of HDPE was
186 weighed and placed in the medium pressure capsule. Then a specific volume (varying from 10
187 - 60 μ L) of *n*-hexane (ICA) was added to the capsule using a micropipette. Due to the volatile
188 nature of *n*-hexane, the amount of ICA finally enclosed in the capsule was determined
189 gravimetrically. The capsules were weighed before and after the DSC analyses to verify if any
190 ICA had evaporated during the procedure, thus correcting the ICA mass. These limits of
191 polymer weight plus ICA concentration were chosen to represent different moments in the
192 semi-batch, lab scale polymerization process. Note that in a semi-batch reactor the ratio of ICA
193 to polymer is actually quite high during the very early stages of polymerization (zero polymer
194 in a salt seed bed at the beginning of polymerization), and decreases as polymer is formed.

195

196 2.3 Differential Scanning Calorimetry (DSC)

197

198 The DSC analyses were carried out using a Mettler Toledo DSC 3+ model in two different
199 ways: i) an non-isothermal evaluation of the impact of different blend composition on the

200 crystallization temperatures and degree of crystallinity of the polymer samples; ii) a study of
 201 the isothermal crystallization kinetics to assess the crystallization times at different values of
 202 T_c . The ICA concentration in the blends for each study phase is shown in Table 3.

203

204 Table 3. ICA:HDPE blends (weight percent ICA:HDPE)

Samples	Non-isothermal	Isothermal
HDPE70	0 – 22 – 87 – 99 – 99.8 %	0 – 17 – 25 – 85 %
HDPE-1H ₂	-	0 – 15 – 28 – 86 %
HDPE-3H ₂	-	0 – 15 – 28 – 86 %

205

206 All analyses were performed under a nitrogen atmosphere - 30 mL/min. The following
 207 procedure was used for the non-isothermal analyses:

- 208 (i) Cooling of the sample from room temperature to -20 °C at a rate of 10 °C / min;
- 209 (ii) Heating from -20 °C to 180 °C at a rate of 2 °C / min;
- 210 (iii) Isothermal hold at 180 °C for 120 min;
- 211 (iv) Cooling from 180 °C to -20 °C with rates of 2 °C / min;
- 212 (v) Isothermal hold at -20 °C for 120 min;
- 213 (vi) Heating from -20 °C to 180 °C at a rate of 2 °C / min.

214

215 The parameters of interest in the first non-isothermal studies are the range of crystallization
 216 temperatures (T_c), melting temperatures (T_m - corresponding to the second heating), total heat
 217 of crystallization (Q_c - measurement of the area under the endotherm divided by the polymer
 218 mass in the blend), total heat of fusion (Q_m - measurement of the area under the exotherm also
 219 divided by the polymer mass in the blend), and degree of crystallinity (w_c - calculated in
 220 relation to 100% crystalline HDPE).

221 The isothermal crystallization of the ICA+HDPE mixtures was performed at different
222 crystallization temperatures (T_c). The procedure starts by cooling the sample from room
223 temperature to -20 °C at a rate of 10 °C / min and continues with a cycle of five sequential
224 steps:

225 (i) Heating from -20 °C to 180 °C at a rate of 2 °C / min;

226 (ii) Cooling from 180 °C to T_c at rates of 50 °C / min;

227 (iii) Isothermal hold at T_c for 120 min;

228 (iv) T_c cooling to -20 °C with rates of 10 °C / min;

229 (v) Heating from -20 °C to 180 °C at a rate of 2 °C / min.

230

231 T_c values of 91, 94, 97, 100 and 115 °C were employed in this study. The thermograms were
232 analyzed to obtain the time and degree of crystallization for a given T_c isotherm, and the
233 melting temperature.

234

235 All data obtained in the analysis were from the thermograms treated using STARe Software
236 Evaluation, version 14.00. The enthalpy of 100% crystalline polymer was taken as $\Delta H^\circ = 293$
237 J / g³⁶. For validation, the method was repeated for different concentrations of the blend, such
238 as HDPE70-85% for the non-isothermal and HDPE70-1%, HDPE70-80% for the isothermal.

239 All runs showed a standard deviation of less than 10%.

240

241 **3 Results and discussions**

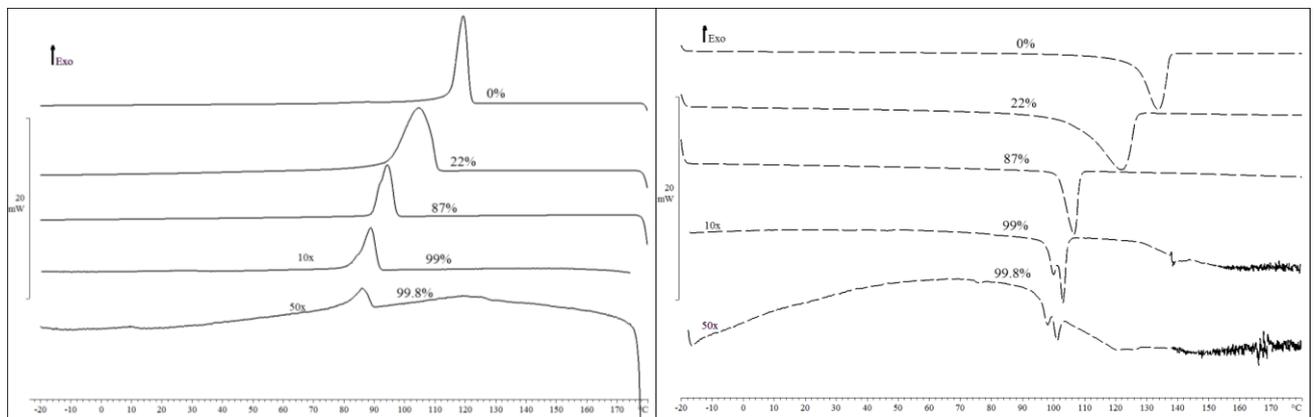
242

243 *Non-isothermal analyses*

244 In the first series of experiments, the non-isothermal evolution of the crystallization and
245 melting points of the different mixtures of HDPE and ICA are shown in Figure 2, and a

246 summary of the properties of these same runs are presented in Table 4. If one considers the
 247 thermograms in Figure 2, it is immediately (and perhaps intuitively) obvious that the
 248 crystallization temperature of mixtures of HDPE and ICA decrease as the relative
 249 concentration of the latter increases. As pointed out by Yamamoto ³³, the rate of
 250 crystallization decreases as the system approaches its melting point. In other words, one might
 251 suspect from these results that the characteristic time for crystallization would be different in
 252 the samples with different ICA:HDPE ratios.

253



254

255 Figure 2 - Non-isothermal thermograms from HDPE70 samples: Left are the peaks of the exothermic
 256 crystallization curves (T_c) and right are the peaks of the endothermic melting curves (2a heating - (T_m)).
 257 The curve size of the 99% blend is multiplied by ten, and for the blend 99.8% is multiplied by fifty.

258

259 In addition, and as shown in Table 4, all the samples show the same (expected) tendencies
 260 with the increase of ICA concentration in the blends:

- 261 • T_c and T_m , estimated by the peak of the exothermic and endothermic curves
 262 respectively, decrease. T_m decreases by 33 °C over the range of compositions studied,
 263 and T_c by 34°C in the case of HDPE70;

264 • There is an increase in the total heat of crystallization (Q_c), of melting (Q_m), and of the
 265 degree of crystallinity (w_c). At high ICA to polymer ratios, the polymer is almost
 266 entirely crystalline at the end of the cooling step.

267

268 Note that in case of very diluted system, it can be reasonably assumed that there is no longer
 269 entanglement between polymer chains, entanglements which would be trapped and excluded
 270 from the crystallizable entities. Hence, the final attainable crystallinity is higher.

271

272 The difference between Q_c and Q_m remained approximately invariant, which shows that the
 273 presence of ICA has a very strong influence on the total amount of crystalline phase in the
 274 polymer, the HDPE that recrystallizes from dilute solutions having a higher overall
 275 crystallinity than those recrystallizing from solutions more concentrated in polymer.

276

277 Table 4. Parameters obtained from the thermograms

Samples	Parameters	ICA:HDPE blends				
		0%	22%	87%	99%	99.8%
HDPE70	y_{ICA}	0%	22%	87%	99%	99.8%
	$y_{polymer}$	100%	78%	13%	1%	0.2%
	w_c (%)	55.7	56.2	67.5	86.3	97.3
	T_c on (°C)	122	111	97	92	90
	T_c peak (°C)	120	105	95	89	86
	T_c end (°C)	115	95	90	84	82
	T_m (°C)	134	122	106	103	101
	Q_c (J / g)	163	165	198	253	285
	Q_m (J / g)	-165	-165	-197	-250	-282
	ΔQ_{m-c}	1.2%	0.3%	0.5%	1.1%	1.1%

278

279 Figure 3a shows that the melting point depression is more pronounced when there is more
 280 ICA in the capsule, as expected³⁷. Figure 3b shows the peak of the crystallization temperature
 281 and the crystallization range. It can be seen from this figure that crystallization can be seen at

282 temperatures below 100 °C for blends containing more than 20% ICA. For levels of less than
283 20% ICA by weight, the range is around 115 - 122 °C.

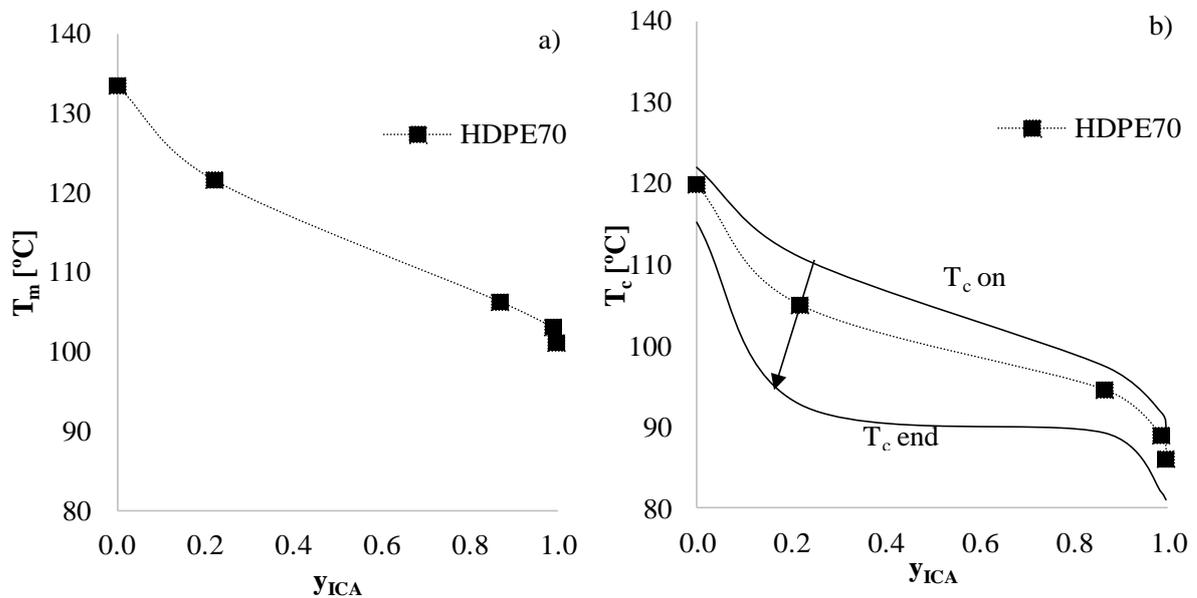
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285 These initial observations support the idea that when ICA are present during the nascent stage
286 of polymerization in a semi batch reactor, they can promote a decrease in rate of
287 crystallization during the first instants of the polymerization before significant levels of
288 polymer begin to accumulate, and the equilibrium melt temperature can eventually approach
289 the temperature of the reactor.

290

291 In order to better understand the behavior of the crystallization rate, the isotherms were
292 evaluated in the range 90 - 115 °C for comparison of the different blends. An isotherm at 130
293 °C (chosen as no crystallization is expected at this temperature) was also measured and used
294 to subtract any imperfections from the curves analyzed.

295



296

297 Figure 3 - a) Melt temperature and b) Crystallization temperature as a function of the mass fraction of
298 ICA in an ICA-HDPE mixture

299

300 *Isothermal analyses*

301 The isotherms used in this part of the study began after abrupt cooling. According to Zhang et
302 al.³⁶ if the cooling is rapid enough under the right conditions, there is not sufficient time for
303 crystal nucleation and growth. We therefore considered that the quantity of crystallization that
304 occurred during the cooling phase was negligible, and that the vast majority crystallization
305 occurred during the isothermal phase. Nevertheless, when the degree of supercooling is high
306 enough, the crystallization can be quite rapid. Even though we used the cooling rate of 50 °C /
307 min, a preliminary study showed that some of the samples might begin to crystallize during
308 the initial phase cooling before the temperature is stabilized. Thus we will only present results
309 for the pure polymer and 17% ICA:HDPE at $T_c = 115$ °C, 25% ICA:HDPE at $T_c = 100$ °C and
310 85% ICA:HDPE at $T_c = 94$ °C, and for samples of polymers with hydrogen (lower molecular
311 weight) at $T_c = 115$ °C. The ICA in each blend can be solubilized in the amorphous phase of
312 the available polymer mass and also present as a vapor. If enough ICA is present, it can be
313 also be present as a separate liquid phase.

314

315 From the data obtained by DSC, the study of crystallization kinetics was carried out using the
316 classical model of Avrami^{38,39} and an evaluation of the equilibrium melt temperature (T_m^0)
317 with the procedure of Hoffman and Weeks⁴⁰.

318

319 The Avrami approach aims at calculating the volume of material that crystallizes as a function
320 of time. The model states that the crystallinity developed by a heated isothermal material for a
321 time t can be correlated with the type and kinetics of nucleation and crystalline growth. The
322 main assumptions on which the Avrami equation is based are that the sample is large enough
323 to neglect the edge effects, the nuclei distribution is spatially random, and the activation of the
324 nuclei and the growth rate of the crystalline lamellae are independent of time (the last two

325 assumptions being verified in isothermal mode). This model, described by equation 1,
326 provides parameters for the kinetics of total crystallization under isothermal conditions^{36,41}.

327

$$328 \quad \alpha(t) = 1 - \exp(-kt^n) \quad \text{Equation 1}$$

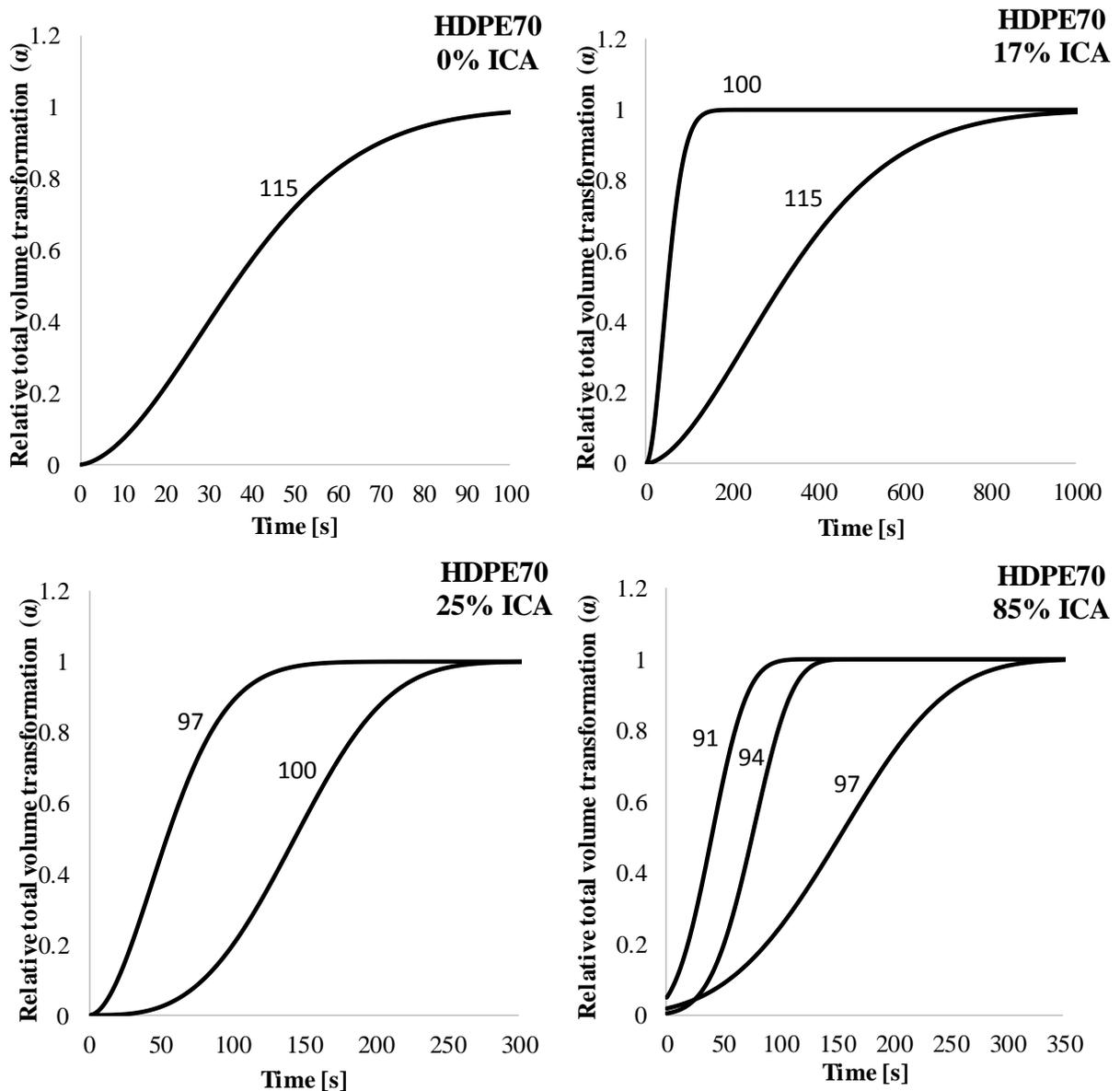
329

330 Where $\alpha(t)$ is the relative (fractional) crystallinity as a function of time, and n and k are the
331 Avrami parameters. n is related to the type of nucleation, morphology, and size of crystals
332 developed during crystallization, and k is related to the nucleation rate and growth of the
333 crystalline phase. The evaluation of the relative crystallinity as a function of time is carried
334 out from the ratio between the partial (at time t) and total areas of the crystallization isotherm
335 (in relation to the baseline, which represents the zero-heat flux), generating a typical
336 sigmoidal curve. By plotting equation 1 in double log form, we obtain a straight line whose
337 slope gives the values of n , and the intercept (at $\log(t) = 0$) gives the values of k .

338

339 All isotherms shown in Figures 4 and 5 have a sigmoid shape characteristic of a phase
340 transformation process. The results show that an increase of T_c corresponded to a shift to
341 longer crystallization times, indicating a decrease in the rate of crystallization for all of the
342 blends studied with respect to pure polymer. This is a consequence of reducing the
343 supercooling, thus reducing the driving force of the crystallization process. Analyzing the
344 specific behavior of the mixtures (Figure 4) at 0 and 17% of ICA at $T_c = 115$ °C (all ICA
345 absorbed in the polymer), and as the ICA concentration in the capsule increases
346 (corresponding to the presence of a liquid phase) it was found that the presence of ICA affects
347 the crystallization behavior of the polymer, both in terms of the temperature and the time of
348 crystallization. It is clear that the blends have a much slower crystallization relative to the
349 pure polymer. The hexane molecules act as a diluent, slowing down the crystallization process

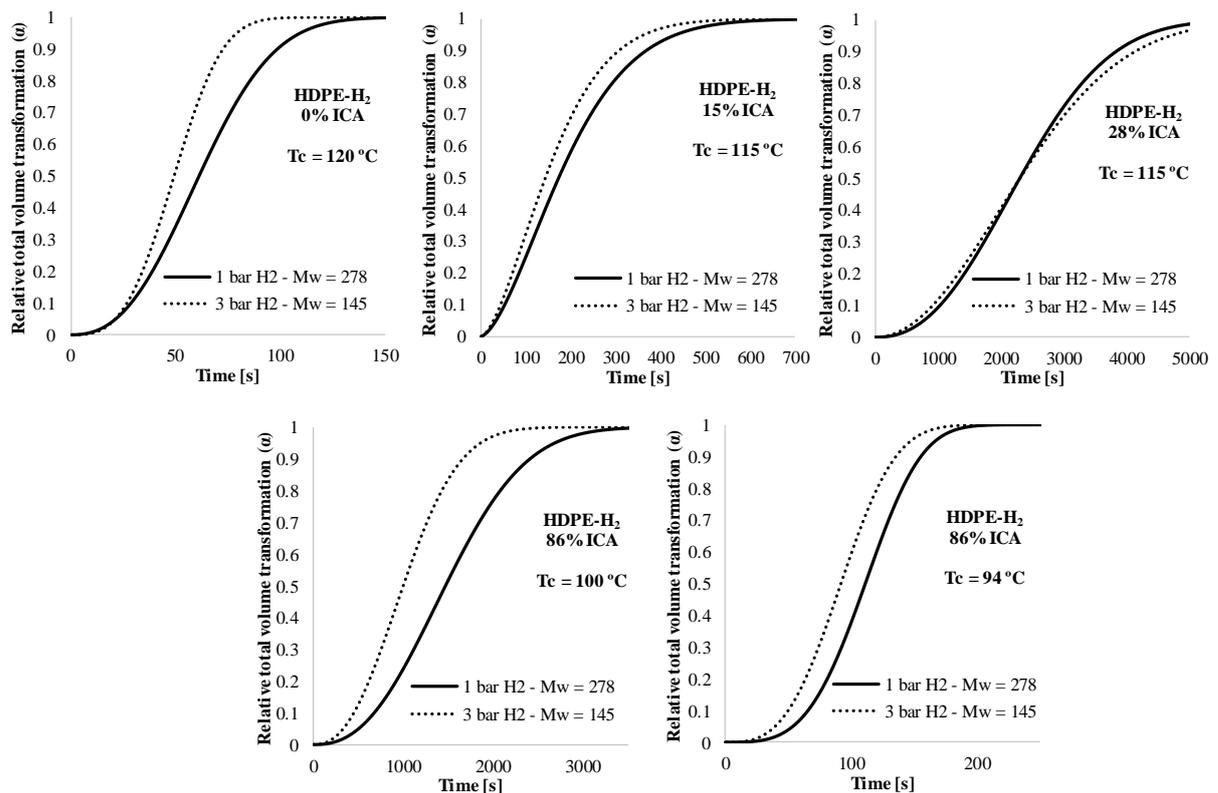
350 by modifying the liquid free energy (see Figure 1) and consequently reducing the
 351 supercooling for a given crystallization temperature. Table 6 shows a significant increase of
 352 the $t_{1/2}$ values observe (the time it takes to reach 50% of the total crystallization for a given
 353 sample blend) in the presence of ICA.



354 Figure 4 - Relative crystallinity curves for HDPE70 blends samples at different T_c [°C]
 355

356
 357 When we evaluate the impact of the molecular weight on the rate of crystallization, we see
 358 that the crystallization time increases as the molecular weight increases. HDPE-1H₂ (278 kDa)
 359 and HDPE-3H₂ (145 kDa) pure, 15% ICA:HDPE-H₂ and 86% ICA:HDPE-H₂, the

360 crystallization time is faster for the lower molecular weight polymer. However, 28%
 361 ICA:HDPE-H₂ exhibit almost the same behavior (Figure 5). Indeed, for such dilution, the
 362 decrease in molecular mobility caused by an increase of molecular weight is negligible. The
 363 variation of $t_{1/2}$ as a function of molecular weight is displayed in Table 6.
 364



365
 366 Figure 5 - Relative crystallinity curves for HDPE70 blends samples at different T_c [$^\circ\text{C}$]

367
 368 A study of the melting behavior of the samples in the presence of ICA was then performed on
 369 the samples that were isothermally crystallized at different temperatures. The melting occurs
 370 over a wide range of temperatures because of different sizes and degrees of perfection of the
 371 crystals present. If T_m is defined as the peak of the curve, its value does not truly represent an
 372 intrinsic property of the material. For this reason, T_m^o , which represents the melting
 373 temperature of infinitely large crystals, constitutes a more appropriate parameter for
 374 evaluating the differences in thermal stability of the various compositions ³⁹.

375

376 The calculation of T_m^o was performed according to the Hoffman-Weeks procedure, in which
377 the measured melting temperature T_m (obtained in the last step of the thermal characterization
378 procedure) of each isothermally crystallized sample is plotted against its T_c . The line of
379 equation $T_m = T_c$ is also plotted and the intersection of the two lines gives the value of T_m^o .

380

381 Table 5. Time of half crystallization - $t/2$.

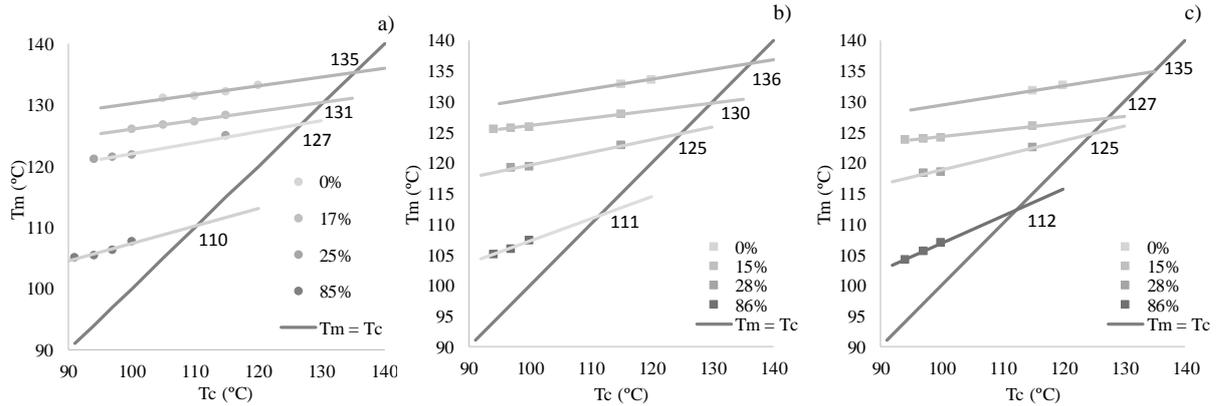
T_c [°C]	HDPE70				HDPE-1H ₂				HDPE-3H ₂			
	0%	17%	25%	85%	0%	15%	28%	86%	0%	15%	28%	86%
91				73								
94				108				112				92
97			54	240				322				212
100		49	143					1470				998
115	36	313				174	2.303			143	2.303	
120					62					49		

382

383

384 The evaluation of T_m^o according to the Hoffman-Weeks method (Figure 5.5), allows one to
385 compare T_m^o of the pure HDPE with that of the blends. For pure HDPE average value of T_m^o is
386 approximately 135.5 °C. While this value it is lower than the theoretical melting point for
387 HDPE ($T_m^o \approx 142$ °C⁴⁰), this value lies within the range 133 - 138 °C typically observed for
388 real HDPE⁴². These differences are due to possible experimental error, but all points present
389 errors less than 5%. T_m^o for blends of ICA and HDPE is lower than that of pure HDPE,
390 typically near 130 °C for 15-17% ICA:HDPE, and 110 °C for 85% ICA:HDPE. A decrease in
391 the equilibrium melting temperature is observed for both two samples. This shows that there
392 is miscibility between HDPE and ICA.

393



394
 395 Figura 6 - Determination of T_m^0 by the Hoffman-Weeks method. a) HDPE70 - fraction ICA. b)
 396 HDPE-1H2 - fraction ICA. c) HDPE-3H2 - fraction ICA.
 397

398 Considering the Flory-Huggins theory, the equilibrium melting temperature variation with the
 399 diluent concentration can be expressed by:

400

$$401 \quad \frac{1}{T_m^0} - \frac{1}{T_{m,melt}^0} = \frac{RV_u}{\Delta h_u V_d} (\phi_d - \chi \phi_d^2) \quad \text{Equation 2}$$

402

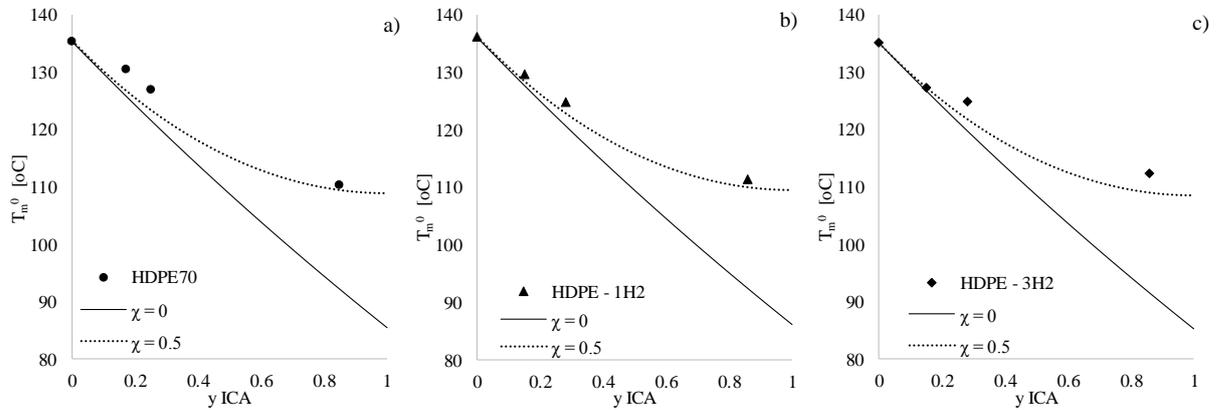
403 where T_m^0 and $T_{m,melt}^0$ are the equilibrium melting temperatures of respectively the polymer in
 404 solution and the bulk polymer $T_{m,melt}^0 = 414.6\text{K}$ and V_d is the molar volume of the diluent (for
 405 hexane this is 113 \AA^3), V_u is the molar volume of the repeat unit (for ethylene 38 \AA^3)⁴³, ΔH_u
 406 is the heat of fusion of the repeat unit ($4,096 \text{ J.mol}^{-1}$), ϕ_d is the volume fraction of the diluent
 407 in the blend and χ is the Flory-Huggins interaction parameter. An interaction parameter value
 408 lower than 0.5 indicates a total miscibility while the miscibility is only partial for χ greater
 409 than 0.5. The experimental equilibrium melting temperature was considered in equation.

410

411 Figure 7, the obtained values of T_m^0 are plotted against the volume fraction of ICA. Clearly
 412 (especially for HDPE 70), a value of χ lower than 0.5 leads to a theoretical description of the
 413 equilibrium melting temperature for all ICA fractions. This leads to the conclusion that (as

414 one would expect) the PE and ICA are totally miscible over range of ICA fractions
415 investigated here.

416



417

418 Figura 7 - Evaluation Flory equation. a) HDPE70 - fraction ICA. b) HDPE-1H₂ - fraction ICA. c)
419 HDPE-3H₂ - fraction ICA.

420

421 4 Conclusions

422

423 In the current study, the isothermal crystallization kinetics of blends of n-hexane and HDPE
424 were analyzed by differential scanning calorimetry. The main conclusions are summarized
425 below:

426

- ICA:HDPE ratios form **miscible** blends

427

- An equilibrium melt temperature depression (i.e. lower T_m), and an increase in the
428 attainable crystallinity of HDPE **were observed with increasing quantities of ICA;**

429

- The crystallization time is significantly higher for the blends compared to the pure
430 polymer.

431

432 **The impact on the crystallization time could have a significant impact on several process-**
433 **related issues. First of all, if a virgin catalyst particle is injected into the reactor without**
434 **prepolymerization, the ratio of ICA to polymer on the particle will be very high as the initial**
435 **chains are formed. This means that the diffusivity and solubility of ethylene will be higher**

436 during the initial instants, and thus the concentration of monomer at the active sites and rate of
437 polymerization will also be higher with respect to polymer formed on “mature” particles.
438 This is important, especially if we wish to interpret lab-scale data in terms of a kinetic model,
439 since it is essential to be able to distinguish between physical phenomena (e.g. sorption or
440 diffusion) and intrinsic catalyst kinetics.

441

442 In addition, the slower crystallization rate in the presence of ICA implies that the polymer
443 particles can, in some instances undergo a fragmentation step where the polymer is essentially
444 all amorphous in the presence of ICA, whereas in dry mode, it is possible that the polymer
445 crystallizes much more quickly and the particle fragmentation (and transport processes) is
446 quite different in dry mode. One also suspects the melting point depression caused by the
447 ICA would lead the fresh particles to be much stickier than the “older” ones, and perhaps
448 increase the possibility of agglomeration in the reactor.

449

450 Finally, while slurry phase polymerization has not been discussed in the current paper, it
451 should be clear from the results presented here that polymer swelling, crystallization and
452 morphogenesis will all probably be quite different if one compares slurry to gas phase
453 processes.

454

455

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475 **TOC**

476

477 The crystallization rate of high-density polyethylene (HDPE) was studied using Differential
478 Scanning Calorimetry (DSC), and it was shown that the presence of an alkane (or induced
479 condensing agent) **reduces the rate of polymer crystallization, in some cases to time scales on**
480 **the order of minutes under conditions characteristic of lab-scale experiments.**

481

482 **References**

483

484 (1) J. R. Parrish, G. A. Lambert, D. N. Thomas, "Gas Phase Polymerization and Method
485 of Controlling Same," Patent US 7625987 B2, **2009**.

486 (2) R. Y. Banat, F. Al-Obaidi, A. K. Malek, "Olefin Gas Phase Polymerisation," US
487 2013/0066027 A1, **2013**.

488 (3) R. Y. Banat, F. Al-Obaidi, A. K. Malek, "Olefin Gas Phase Polymerisation," US
489 2014/0148563 A1, **2014**.

490 (4) W. L. Carrick; G. L. Karapinka; R. J. Millington. Polymerization Process. US
491 3324095, **1967**.

492 (5) H. B. Irvin; F. T. Sherk. Polyolefin Reactor System. US 4121029, **1978**.

493 (6) A. R. Miller. Fluidized Bed Reactor. US 4003712, **1977**.

494 (7) T. F. L. McKenna, A. Di Martino, G. Weickert, J. B. P. Soares. Particle Growth during
495 the Polymerisation of Olefins on Supported Catalysts, 1 - Nascent Polymer Structures.
496 *Macromol. React. Eng.* 4 (1), 40–64, **2010**.

497 (8) A. Di Martino, G. Weickert, F. Sidoroff, T. F. L. McKenna. Modelling Induced
498 Tension in a Growing Catalyst/Polyolefin Particle: A Multi-Scale Approach for
499 Simplified Morphology Modelling. *Macromol. React. Eng.* 1 (3), 338–352, **2007**.

500 (9) B. Horáčková, Z. Grof, J. Kosek. Dynamics of Fragmentation of Catalyst Carriers in
501 Catalytic Polymerization of Olefins. *Chem. Eng. Sci.* 62 (18–20), 5264–5270, **2007**.

502 (10) A. Alizadeh, T. F. L. McKenna. Particle Growth during the Polymerization of Olefins
503 on Supported Catalysts. Part 2: Current Experimental Understanding and Modeling
504 Progresses on Particle Fragmentation, Growth, and Morphology Development.
505 *Macromol. React. Eng.* 12 (1), **2018**.

506 (11) V. Kanellopoulos, D. Mouratides, P. Pladis, C. Kiparissides. Prediction of Solubility of
507 α -Olefins in Polyolefins Using a Combined Equation of State - Molecular Dynamics
508 Approach. *Ind. Eng. Chem. Res.* 45 (17), 5870–5878, **2006**.

509 (12) A. G. Fisch, J. H. Z. dos Santos, N. S. M. Cardozo, A. R. Secchi. Mass Transfer in
510 Olefin Polymerization: Estimative of Macro- and Microscale Diffusion Coefficients
511 through the Swollen Polymer. *Chem. Eng. Sci.* 63 (14), 3727–3739, **2008**.

512 (13) M. Namkajorn, A. Alizadeh, E. Somsook, T. F. L. McKenna. Condensed Mode
513 Cooling for Ethylene Polymerisation : The Influence of Inert Condensing Agent on the
514 Polymerisation Rate. *Macromol. Chem. Phys.* 1918 (215), 873–878, **2014**.

515 (14) A. Alizadeh, M. Namkajorn, E. Somsook, T. F. L. McKenna. Condensed Mode

- 516 Cooling for Ethylene Polymerization: Part II. From Cosolubility to Comonomer and
517 Hydrogen Effects. *Macromol. Chem. Phys.* No. 216, 985–995, **2015**.
- 518 (15) F. N. Andrade, T. F. L. McKenna. Condensed Mode Cooling for Ethylene
519 Polymerization: Part IV. The Effect of Temperature in the Presence of Induced
520 Condensing Agents. *Macromol. Chem. Phys.* 218 (20), 1–8, **2017**.
- 521 (16) M. Namkajorn, A. Alizadeh, D. Romano, S. Rastogi, T. F. L. McKenna. Condensed
522 Mode Cooling for Ethylene Polymerization: Part III. The Impact of Induced
523 Condensing Agents on Particle Morphology and Polymer Properties. *Macromol. Chem.*
524 *Phys.* 217 (13), 1521–1528, **2016**.
- 525 (17) J. Mark, K. Ngai, W. Graessley, L. Mandelkern, E. Samulski, J. Koenig and G.
526 Wignall. *Physical Properties of Polymers*, Third Ed.; Cambridge University Press,
527 **2003**.
- 528 (18) R. Boistelle, J. P. Astier. Crystallization Mechanisms in Solution. *J. Cryst. Growth* 90
529 (1–3), 14–30, **1988**.
- 530 (19) R. J. Kirkpatrick, Crystal Growth from the Melt: A Review. *Am. Miner.* 60, 798–814,
531 **1975**.
- 532 (20) M. Zhang, B.-H. Guo, J. Xu. A Review on Polymer Crystallization Theories. *Crystals*;
533 Vol. 7, 4, **2017**.
- 534 (21) J. D. Hoffman, R. L. Miller. Kinetic of Crystallization from the Melt and Chain
535 Folding in Polyethylene Fractions Revisited: Theory and Experiment. *Polymer.* 38
536 (13), 3151–3212, **1997**.
- 537 (22) G. Strobl, T. Y. Cho. Growth Kinetics of Polymer Crystals in Bulk. *Eur. Phys. J. E* 23
538 (1), 55–65, **2007**.
- 539 (23) L. Mandelkern, A. L. Allou Jr. The fusion of polyethylene single crystals. Academic
540 Press, *Polymers*, 4 447-452, **1973**.
- 541 (24) A. G. Jones, Crystallization Process Systems. *Cryst. Process Syst.* 341, **2002**.
- 542 (25) F. Toquet, L. Guy, B. Schlegel, P. Cassagnau, R. Fulchiron. Effect of the Naphthenic
543 Oil and Precipitated Silica on the Crystallization of Ultrahigh-Molecular-Weight
544 Polyethylene. *Polym. (United Kingdom)* 97, 63–68, **2016**.
- 545 (26) A. Nalcajima, F. Hamada. Estimation of Thermodynamic Interactions between
546 Polyethylene and N-Alkanes by Means of Melting Point Measurements. *Kolloid-*
547 *Zeitschrift und Zeitschrift für Polymere, Band 205* 82, 55- 61, **1965**.
- 548 (27) G. Valdecasas, The Crystallization of Polymer-Diluent Mixtures. *J. Polym. Sci. Phys*

- 549 13, 2103–2115 **1975**.
- 550 (28) E. Riande, J. M. G. Fatou. Effect of Solvent on the Crystallization from Dilute
551 Polyethylene Solutions. *Polymer*. 17 (9), 795–801, **1976**.
- 552 (29) E. Riande, J. M. G. Fatou. Crystallization of Dilute Polyethylene Solutions: Influence of
553 Molecular Weight. *Polymer*. 17, 99–104, **1976**.
- 554 (30) E. Riande, J. M. G. Fatou. Crystallization Kinetics of Polyethylene Paraffin Mixtures.
555 19, 1295–1299, **1978**.
- 556 (31) W. Cobbs Jr, R. Burton. Crystallization of Polyethylene Terephthalate. *J. Polym. Sci.*
557 10 (3), 275–290, **1953**.
- 558 (32) Y. Teymouri, A. Adams, B. Blümich. Compact Low-Field NMR: Unmasking
559 Morphological Changes from Solvent-Induced Crystallization in Polyethylene. *Eur.*
560 *Polym. J.* 80, 48–57, **2016**.
- 561 (33) T. Yamamoto. Computer Modeling of Polymer Crystallization - Toward Computer-
562 Assisted Materials' Design. *Polymer* 50 (9), 1975–1985, **2009**.
- 563 (34) A. J. McHugh, W. R. Burghardt, D. A. Holland. The Kinetics and Morphology of
564 Polyethylene Solution Crystallization. *Polymer*. 27 (10), 1585–1594, **1986**.
- 565 (35) S. Chew, J. R. Griffiths, Z. H. Starchurski. The Crystallization Kinetics of Polyethylene
566 under Isothermal and Non-Isothermal Conditions. *Polymer* 30 (5), 874–881, **1989**.
- 567 (36) J. Zhang, S. Chen, J. Su, X. Shi, J. Jin, X. Wang, Z. Xu. Non-Isothermal
568 Crystallization Kinetics and Melting Behavior of EAA with Different Acrylic Acid
569 Content. *J. Therm. Anal. Calorim.* 97 (3), 959–967, **2009**.
- 570 (37) T. F. L. McKenna. Condensed Mode Cooling of Ethylene Polymerization in Fluidized
571 Bed Reactors. *Macromol. React. Eng.* 1800026, **2018**.
- 572 (38) Z. Zhang, F. Yu, H. Zhang. Isothermal and Non-Isothermal Crystallization Studies of
573 Long Chain Branched Polypropylene Containing Poly(Ethylene-Co-Octene) under
574 Quiescent and Shear Conditions. *Polymers (Basel)*. 9 (6), **2017**.
- 575 (39) H. Marand, J. Xu, S. Srinivas. Determination of the Equilibrium Melting Temperature
576 of Polymer Crystals: Linear and Nonlinear Hoffman-Weeks Extrapolations.
577 *Macromolecules* 31 (23), 8219–8229, **1998**.
- 578 (40) J. D. Hoffman, J. J. Weeks. Melting Process and the Equilibrium Melting Temperature
579 of Polychlorotrifluoroethylene. *J. Res. Natl. Bur. Stand. Sect. A Phys. Chem.* 66A (1),
580 13–28, **1962**.
- 581 (41) E. Koscher, R. Fulchiron. Influence of Shear on Polypropylene Crystallization:

582 Morphology Development and Kinetics. *Polymer* 43 (25), 6931–6942, **2002**.
583 (42) E. Benham, M. McDaniel. Polyethylene, High Density; 2004; Vol. **1936**.
584 (43) Anesthetic Structure Database | Ethene (Ethylene)
585 http://asd.molfield.org/php/view_details.php?id=45&java=false (accessed Nov 23, **2018**).
586
