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# Challenges in the emulsion co- and terpolymerization of vinylidene fluoride

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## **Abstract**

The feasibility of co- and terpolymerizing vinylidene fluoride (VDF) with ethylene (C2) and/or vinyl acetate in an emulsion polymerization process was studied for different C2 pressures, initiator concentration, surfactant concentration, pH, C2 injection protocols and the influence of vinyl acetate (VAc) in the reaction medium. Pressure drop and temperature profiles, as well as gravimetry were used to follow the rate of polymerization. The microstructure of the synthesized products was assessed fluorine and hydrogen nuclear magnetic resonance spectroscopy ( $^{19}\text{F}$  and  $^1\text{H}$  NMR). C2 was found to cause an inhibition/retardation effect on the copolymerization with VDF (and with VDF/VAc). However, statistical copolymers containing VAc and VDF were synthesized by reducing as far as possible the homogeneous nucleation of the VAc in water phase. This was done by adding VAc into the reaction after the homogeneous-coagulative nucleation of VDF takes place (around 5 minutes after initiator injection).

## 1 Introduction

Polyvinylidene fluoride (PVDF) homo and copolymers are usually synthesized commercially using free-radical suspension or emulsion polymerization process<sup>1</sup>. Copolymerization of vinylidene fluoride (VDF) can of course be performed to modify the properties of the final product (melting point, glass transition temperature, crystallinity, stability, elasticity, permeability, chemical reactivity, etc.)<sup>2,3</sup>. Most studies in the open literature dealing with the copolymerization of VDF examine its reaction fluorinated or perfluorinated monomer<sup>4,14,15</sup>, but very little information is available involving copolymers of VDF and only non-fluorinated monomers. Reports of copolymers of perfluorinated monomers with ethylene can be found in the literature in the literature<sup>5-8</sup>, and some patents suggest that terpolymers of VDF, halogenated monomers and ethylene are possible<sup>6,8-10</sup>. Adding ethylene (C2) might increase the ability to “shape” the final polymer product, and, if it were possible to do so, using ethylene as a comonomer could also introduce certain cost-reduction benefits<sup>11</sup>. C2 conversion in these reactions is generally high, but they tend to slow down polymerization since radicals ending in olefin units are relatively unreactive toward propagation<sup>3</sup>.

Returning to the possibility of copolymerizing VDF with relatively inexpensive molecules such as vinyl acetate or  $\alpha$ -olefins, little work seems to have been published. Some studies have shown that VDF copolymerization with ethylene is possible using different types of catalysts<sup>12</sup> or via free radical polymerization at pressures of several hundred bars and temperatures over 200°C<sup>13</sup>. However, no indications are given that attempts at copolymerizing ethylene and vinylidene fluoride in an emulsion system have been made.

It has been shown in the literature that polymers with good high piezoelectric properties have been made by the copolymerization of vinylidene cyanide (VDCN) and vinyl acetate (VAc)<sup>14,15</sup>, attributed to assistance of dipolar orientation of the cyanide group by VAc units in the copolymer chain, so it might be interesting to see if similar polymers can be made via the copolymerization of VDF, C2 and VAc. The radical copolymerization of VDF with VAc has been investigated through various polymerizations procedures in supercritical CO<sub>2</sub> (200-230 bar, 45 °C), suspension (145 bar, 82 °C) and solution (20 bar, at 110 °C, 130 °C and 80 °C)<sup>16-18</sup> in which it has been showed that VAc units are preferentially incorporated into the copolymer chains ( $r_{VDF} = -0.40$ ;  $r_{VAc} = 1.67$ )<sup>16</sup>. Furthermore, VAc, when copolymerized with VDF can act as a chain transfer agent<sup>19-22</sup>, so it is not clear how best to incorporate it into copolymers with VDF and C2 in an emulsion system.

In this work, we will investigate the feasibility of the emulsion copolymerization of VDF with C2 and VAc under conditions similar to those used for VDF homopolymerization.

## **2 Methodology**

### **2.1 Materials**

Vinylidene fluoride monomer (VDF, 99%) was kindly supplied by Arkema (Pierre Bénite, France). Ethylene (C2, 99.5%) was purchased from Air Liquide. Vinyl Acetate (VAc, 99%, Sigma Aldrich). All monomers were used without further purification. Polymerization was initiated with Potassium Persulfate (99 %, Sigma Aldrich); the emulsion was stabilized by a proprietary surfactant. Ethyl Acetate (ACS grade, Carlo Erba Reagent) was used as Chain Transfer Agent (CTA). Sodium acetate (99 %, Sigma Aldrich) was used as pH regulator

(NaOAc). Deuterated dimethylsulphoxide (d<sub>6</sub>-DMSO – 99%, Sigma Aldrich) was utilised as Nuclear Magnetic Resonance (NMR) solvent. All reagents were employed as received.

## 2.2 Autoclave and Polymerization Procedure

Experiments were carried in a 4 L high pressure jacketed autoclave (Stainless Steel type 316), equipped with an impeller-type mixer. The reactor temperature was measured by a thermocouple J Atex. Oil (Ultra 350, Lauda) circulating in the jacket was used to control the reactor temperature. The temperature of the circulating oil in the reactor jacket was measured with a platinum resistance Pt100. The reactor pressure was monitored with a pressure sensor Atex (type PA-23EB, Keller).

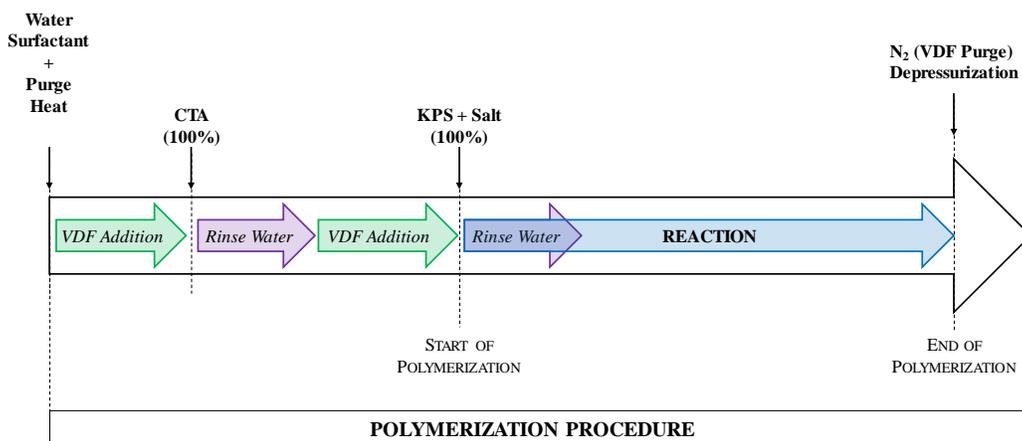
Vinylidene fluoride monomer was introduced into the reactor via a jacketed line refrigerated by a heat transfer liquid (Kryo 60, Lauda) that circulated in crosscurrent at -25°C. The head of the dual diaphragm pump (Metering pump Novados H1, Axflow) was also refrigerated by the cryogenic bath to guarantee that the monomer stayed in liquid phase through the pumping. The upstream pressure was set-up to 30bar and was adjusted by a pressure regulating valve located just after the gas bottle. The mass flow of monomer was monitored with a Coriolis flowmeter (Optimass 3000, Khrone). The aqueous solutions (i.e CTA, mixture of initiator + sodium acetate and VAc) were introduced via a syringe pump (500HL Syringe Pump, Isco). The inlet lines of the reactor are equipped with check valves. Nitrogen was used to remove the residual oxygen contained in the additives aqueous solutions and in the initial reactor charge.

Deionized water and surfactant were added to the reactor, the reactor was sealed and agitation speed was set at the desired rate. The temperature of reactor was increased using the circulation bath until the desired temperature was reached (typically 83 °C).

Aqueous solutions and specific amounts of vinyl acetate were prepared and the oxygen contained was removed by purging with nitrogen. VDF was added to the reactor via a diaphragm pump, and the inlet mass was monitored via a Coriolis mass-flowmeter. When the desired pressure was attained (typically 88 bar), VAc was introduced via a syringe pump (when noted). After the pressure was stabilized following the VAc injection (since VDF is soluble in VAc), the injection protocol was started. Aqueous solutions of chain transfer agent and initiator (oxygen-free) were introduced with the help of a syringe pump. The reaction was left to proceed without monomer feed. At the end of the polymerization the agitation speed was slowed down to 150 rpm, the reactor was cooled down, and the remaining VDF monomer mixture was gently degassed. The reactor contents were purged with nitrogen, and then the polymer was recovered from the reactor via a bottom valve.

### **2.2.1 Injection Protocol:**

The *reference injection protocol* utilised in the polymerisation procedures are illustrated in Figure 1. Once a certain VDF pressure was reached (typically 69 bar), the total amount of CTA was added and VDF was fed again. After the VDF pressure reached its desired value (88 bar) the total amount of the solution of initiator and salt were injected into the reactor. A small (known) amount of water was added at the end of each injection to ensure the entire amount of each species is inside the reactor, and to rinse the feed line.



**Figure 1.** Illustration of the reference injection protocol.

### 2.3 Latex and Polymer Characterization

Gravimetric analysis was utilised to measure the solids content of the latexes. A certain amount of sample ( $m_{\text{Latex}}$ ) in an aluminium dish was placed inside an oven at 100 °C over 4 hours. After all the water evaporation, the dried latex was weighted ( $m_{\text{Dried Latex}}$ ). Finally, the Polymer Content (PC) was calculated considering the solid fraction of the other species ( $m_{\text{Solid Reactants}}$ ) utilised in the polymerization process (Surfactant, Potassium Persulfate and pH Regulator). Particle Diameter ( $D_P$ ) in Volume was measured with a Mastersizer 3000® from Malvern Instruments, and subsequent Number of Particles ( $N_P$ ) was computed according to Ecoscia-Mendez methodology<sup>1</sup>.

A Mettler-Toledo DSC 3+/700 was used to measure the melt temperature ( $T_m$ ), glass transition temperature ( $T_g$ ) and crystallization temperature ( $T_c$ ) via differential scanning calorimetry (DSC). DSC samples were cooled-down at -80 °C and maintained at that temperature for 10 minutes, then heated up until 200 °C, at a rate of 10 °C·min<sup>-1</sup>, and kept at that temperature for 10 minutes.

Functionality, copolymer sequences, copolymer composition and type of VDF addition were evaluated by  $^{19}\text{F}$  and  $^1\text{H}$  Nuclear Magnetic Resonance (NMR), recorded on a Bruker Avance III (400 Hz) in deuterated Dimethyl Sulfoxide (d6-DMSO) in 5mm tubes at 25 °C with a BBFO<sup>+</sup> 5mm probe at the NMR Polymer Center of the Institut de Chimie de Lyon (ICL). The dried product of the latexes were dissolved on d6-DMSO at 16.7 g.L<sup>-1</sup>. The  $^1\text{H}$  NMR spectra obtained were calibrated with the aid of d6-DMSO peak (2.5 ppm).  $^{19}\text{F}$  NMR were calibrated utilising a CF<sub>3</sub> peak from the fluorinated surfactant.  $^{19}\text{F}$  NMR was used to determine the types of VDF additions in the polymer chain (i.e. Head-to-Tail – Conventional Addition or Head-to-Head Addition – Reverse addition) and  $^1\text{H}$  NMR was also used in combination with  $^{19}\text{F}$  NMR to determine functionality, copolymer sequences and copolymer composition.

$^1\text{H}$  NMR peak assignments (400 MHz DMSO, chemical shift [ppm]): 0.85 (t, -CF<sub>2</sub>-CH<sub>3</sub>, VDF Reverse Termination), 0.95 (VDF-CH<sub>2</sub>-CH<sub>3</sub>, VDF-C2 Termination), 1.22-1.25 (-CF<sub>2</sub>-CH<sub>2</sub>-CF<sub>2</sub>-CH<sub>3</sub>, Reverse VDF-C2 Termination), 1.44 (CH<sub>2</sub>-CH(OAc)-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH(OAc)-, VAc-C2-VAc) 1.56-1.61 (VDF-CH<sub>2</sub>-CH<sub>3</sub>, VDF-C2 Termination), 1.72-1.79 (CH<sub>2</sub>-CH(OAc)-CH<sub>2</sub>-CH(OAc)-CH<sub>2</sub>-CH(OAc)-, VAc-VAc-VAc Monomer Sequence), 1.92-2.03 (m, -CH(OAc)-), 2.28-2.43 (m, -CF<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CF<sub>2</sub>-, VDF-VDF Head-to-Head Addition), 2.70-3.19 (t, -CH<sub>2</sub>-CF<sub>2</sub>-CH<sub>2</sub>-CF<sub>2</sub>-, VDF-VDF Head-to-Tail Addition), 4.60-4.90 (-CH<sub>2</sub>-CH(OAc)-CH<sub>2</sub>-CH(OAc)-CH<sub>2</sub>-CH(OAc)-, VAc-VAc-VAc Monomer Sequence), 4.90-5.30 (-CH<sub>2</sub>-CH(OAc)-CF<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH(OAc)-, VAc-VDF-VAc Monomer Sequence), 5.30-5.70 (CF<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CH(OAc)-CF<sub>2</sub>-CH<sub>2</sub>, VDF-VAc-VDF Monomer Sequence).

$^{19}\text{F}$  NMR peak assignments (400 MHz DMSO, chemical shift [ppm]): -91.70 (-CH<sub>2</sub>-CF<sub>2</sub>-CH<sub>2</sub>-CF<sub>2</sub>-, VDF-VDF Head-to-Tail Addition), -91.90 (-CH<sub>2</sub>-CH<sub>2</sub>-CF<sub>2</sub>-CH<sub>2</sub>-CF<sub>2</sub>-CH<sub>2</sub>-CF<sub>2</sub>-, VDF-VDF Head-to-Tail Addition) -92.40 (-CH<sub>2</sub>-CF<sub>2</sub>-CH<sub>2</sub>-CF<sub>2</sub>H, VDF Regular Termination), -92.70

(-CH<sub>2</sub>-CF<sub>2</sub>-CH<sub>2</sub>-CF<sub>2</sub>-, VDF-VDF Head-to-Tail Addition), -93.15 (PVAc-CH<sub>2</sub>-CH(OAc)-CH<sub>2</sub>-CF<sub>2</sub>-PVDF), -93.50 (-CH<sub>2</sub>-CF<sub>2</sub>-CH<sub>2</sub>-CH(OAc)-), -93.90 (-CH<sub>2</sub>-CF<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>, VDF-C2 Termination), -94.70 (-CH<sub>2</sub>-CH<sub>2</sub>-CF<sub>2</sub>-CH<sub>2</sub>- VDF-VDF Tail-to-Tail Addition), -113.80 (-CH<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CH<sub>2</sub>-, VDF-VDF Head-to-Head Addition), -115.50 (-CF<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CF<sub>2</sub>-, VDF-VDF Head-to-Head Addition), -115.60 (-CF<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-CF<sub>2</sub>-, VDF-VDF Head-to-Head Addition), -116.00 (-CH<sub>2</sub>-CF<sub>2</sub>-CF<sub>2</sub>-CH<sub>2</sub>-, VDF-VDF Head-to-Head Addition).

### 3 Results and Discussion

#### 3.1 Influence of Ethylene Pressure and Initiator Concentration

For the first experiments, it was decided to keep VDF Emulsion Polymerization reference recipe (Table 1) and perform variations of VDF Pressure (P<sub>VDF</sub>) and C2 Pressure (P<sub>C2</sub>), whilst maintaining overall pressure inside the reactor at 88 bar.

**Table 1.** Reference experimental conditions

	P <sub>VDF</sub>	[Surf]	[KPS]	[NaOAc]	[EA]
	bar	g/Lw	g/Lw	g/Lw	g/Lw
<i>Reference</i>	88	1.5	0.1	0.06	13.40

Table 2 shows conditions and results of experiments varying P<sub>C2</sub> and Initiator Concentration ([KPS]). **The only observable polymerization occurred only in Run 5, evidenced by the PC of 24.35%, with 1 %mol of C2 in the monomer feed mixture and an initiator**

concentration of  $10[\text{KPS}]_{\text{Reference}}$ . Even at 5% of C2, with an initiator concentration of  $15[\text{KPS}]_{\text{Reference}}$  (Run 7) no polymerization was noticed. Degradative effect of proton transfer reaction (PTR) of the gaseous monomers throughout initiation was the postulated cause. Given that the CTA can have a degradative proton transfer reaction in VDF polymerization, it was removed from future experiments to ensure that it did not hinder the emulsion polymerization process<sup>22</sup>.

**Table 2.** Experimental conditions and gravimetry results of emulsion polymerizations carried under varied ethylene pressures ( $P_{\text{C2}}$ ) and KPS concentrations.

	$P_{\text{VDF}}$	$P_{\text{C2}}$	$\text{VDF C2}$		$[\text{Surf}]$	$[\text{KPS}]$	$[\text{NaOAc}]$	$[\text{EA}]$	$\text{PC}$
	<i>bar</i>		<i>%mol</i>		<i>g/Lw</i>	<i>g/Lw</i>	<i>g/Lw</i>	<i>g/Lw</i>	<i>%</i>
<i>Run 1</i>	60	28	85	15	1.5	0.09	0.06	13.40	-
<i>Run 2</i>	80	8	85	15	1.5	0.09	0.06	13.41	-
<i>Run 3</i>	80	8	95	5	1.5	0.55	0.36	13.37	0.03
<i>Run 4</i>	80	8	95	5	1.5	0.91	0.61	0.00	0.16
<i>Run 5</i>	86	2	99	1	1.5	0.90	0.60	0.00	24.35
<i>Run 6</i>	84	4	98	2	1.5	0.90	0.60	0.00	0.82
<i>Run 7</i>	78	10	95	5	1.5	4.44	2.96	0.00	1.41

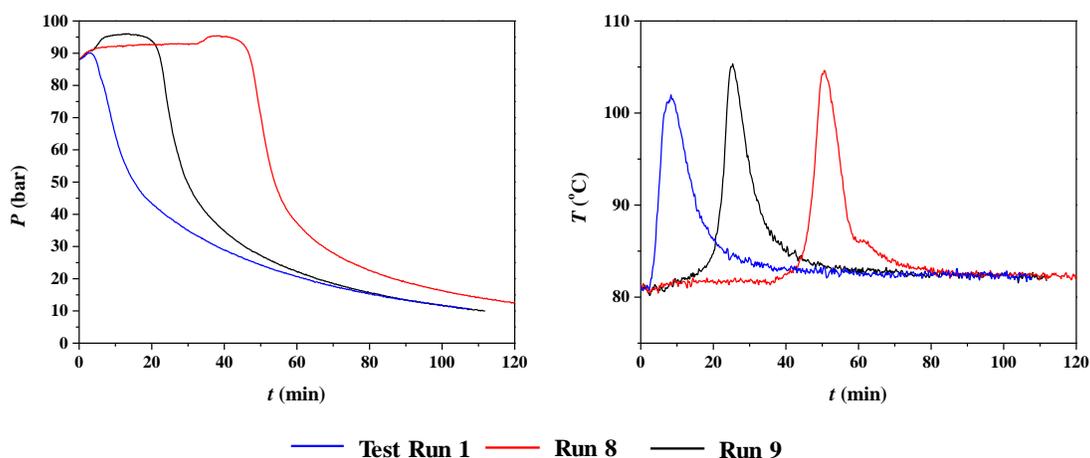
Further investigation (Table 3) was carried by comparing a VDF homopolymerization procedure (Test Run 1) and two reactions under Run 5 conditions with different KPS injection. In Run 8, two shots, each containing half of  $[\text{KPS}]=0.9 \text{ g/L}_w$  were added at  $t=0$  and then  $t=30$  min (Figure 2). The start of the reaction was noticed as soon as the second KPS shot was given. Run 9 was carried with a full shot of KPS containing the full amount to achieve  $0.9 \text{ g/L}_w$ .

Figure 3 suggests that adding as little as 1%mol of C2 into the monomer feed mixture (Run 9) slows down the reaction by preventing the nucleation process from beginning. The

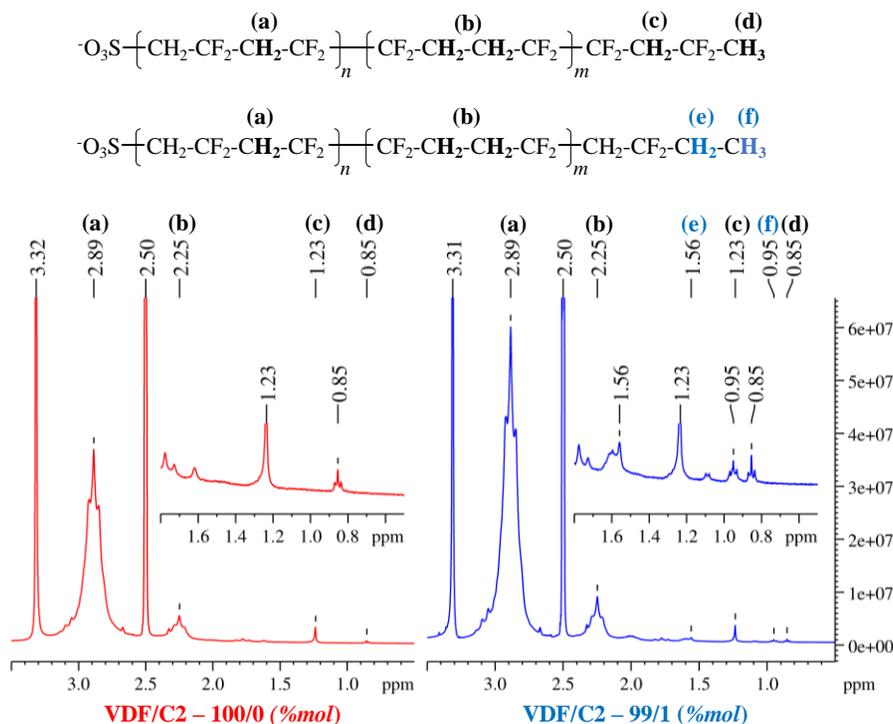
homopolymerization of PVDF begins almost immediately, whereas the onset of a measurable reaction rate depends on the amount of KPS added. When KPS is added divided into 2 shots it is likely that any radicals produced by the decomposition of the initiator react with C2 monomer units, which immediately halt propagation before they can participate in the formation of polymer chains. The stagnant values of  $T_m$ , Crystallinity,  $D_p$  and  $N_p$  (Table 3) also show that once the C2 radicals are consumed, the reaction carries on as an usual PVDF emulsion polymerization.  $^1\text{H}$  (Figure 3) and  $^{19}\text{F}$  (Figure 4) NMR spectra confirmed the previously postulated PTR, due to the termination of polymer chains were in fact, due to C2 units being added to VDF units and not being reactive enough in these conditions to further polymerize. Peaks around 0.95 and 1.60 ppm in the  $^1\text{H}$  NMR spectra and -93.90 ppm in the  $^{19}\text{F}$  NMR spectra were assigned to polymer chains finalized with C2 units. It is likely that this inhibition/retardation effect is caused by PTR to ethylene, and that under the conditions typically used to make PVDF industrially, the reactivity of a radical formed from the reaction of VDF and an olefin is too low for chain growth to occur<sup>3</sup>.

**Table 3.** Experimental conditions, gravimetry,  $D_p$ ,  $N_p$  and DSC scans results of emulsion polymerizations carried under low ethylene pressures ( $P_{C2}$ ).

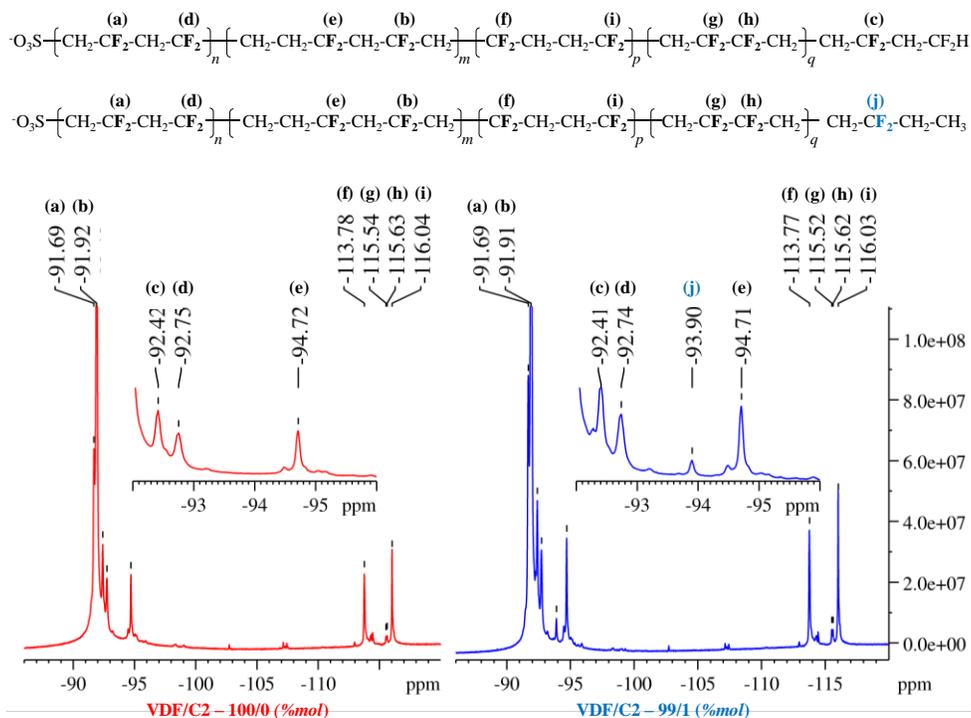
	$P_{\text{VDF}}$ (bar)	$P_{\text{C2}}$ (bar)	VDF %mol	C2	[Surf] g/Lw	[KPS] g/Lw	[NaOAc] g/Lw	[EA] g/Lw	PC %	$D_p$ nm	$N_p$ $\times 10^{19}$	$T_m$ °C	Crystallinity %
<b>Test Run 1</b>	88	0	100	0	1.5	0.90	0.60	0.00	24.22	200.1	5.9	158.9	32.6
<b>Run 8</b>	86	2	99	1	1.5	0.90*	0.60*	0.00	24.19	205.2	5.4	159.2	33.4
<b>Run 9</b>	86	2	99	1	1.5	0.90	0.60	0.00	24.35	203.7	5.6	159.5	32.4



**Figure 2.** Pressure (left) and temperature profile (right) of VDF and C2 emulsion polymerizations carried under low ethylene pressures ( $P_{C2}$ ).



**Figure 3.** Expansion of the 0.5-3.5 ppm of the  $^1\text{H}$  NMR spectra of Test Run 1 and Run 9 from Table 3 recorded in  $\text{d}_6\text{-DMSO}$ .



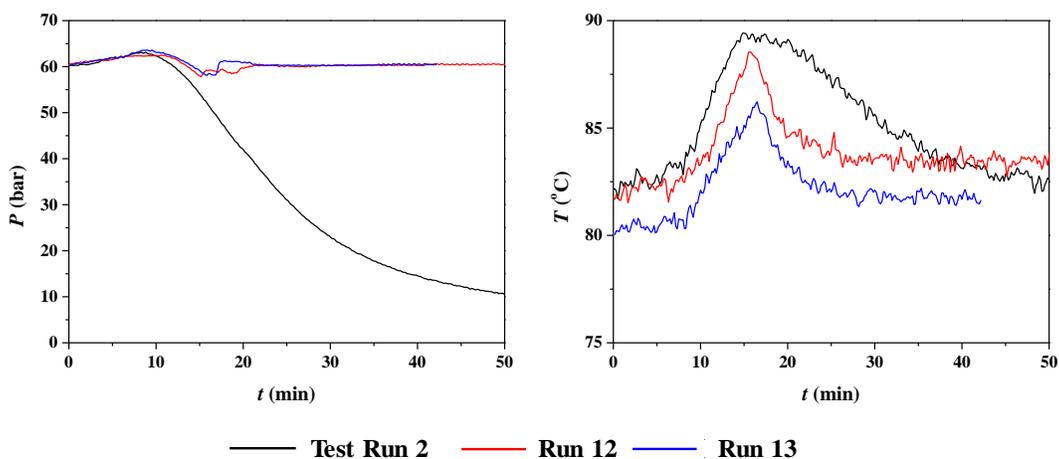
**Figure 4.** Expansion of the -118.0  $\rightarrow$  -89.0 ppm region of the  $^{19}\text{F}$  NMR spectra of Test Run 1 and Run 9 from Table 3 recorded in d6-DMSO.

An additional investigation was carried under semi-batch conditions. C2 was injected throughout the reaction of conventional VDF emulsion homopolymerization. Reactions at  $P_{\text{VDF}}=60$  bar were carried in order to guarantee polymerization under supercritical conditions for both monomers<sup>22</sup>. Shortly after noticeable pressure drop, indicative of nucleation/propagation of PVDF polymerization, C2 was injected at  $P_{\text{C}_2}=60$  bar. These experiments would confirm if the addition of C2 in a growing PVDF chain truly halts the polymerization process. Conditions and results are listed in Table 4. Indeed, the addition of C2 during VDF emulsion polymerization lead to the same inhibition/retardation effect previously seen in the batch experiments. After C2 injection at  $t=15$  min, a clear decrease of temperature followed by the increase and stagnation of pressure (Figure 5) implied that the growing VDF-radicals were consumed by C2 units and no

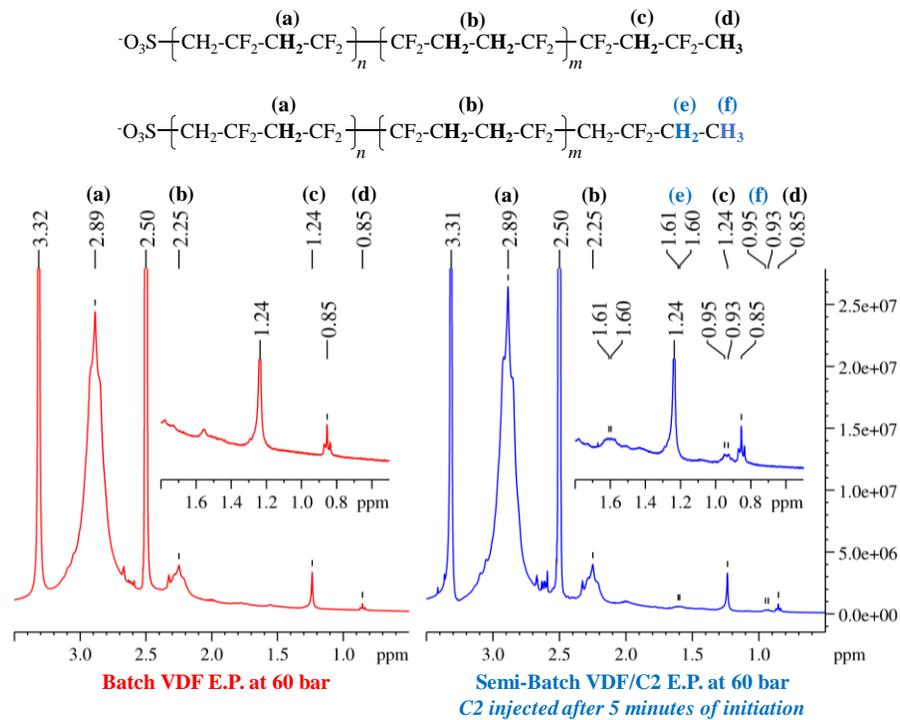
further propagation occurred. This is further confirmed by alike  $^1\text{H}$  (Figure 6) and  $^{19}\text{F}$  (Figure 7) NMR spectra chemical shifts.

**Table 4.** Experimental conditions and gravimetry results of VDF and C2 emulsion polymerizations carried under different C2 injection protocol conditions.

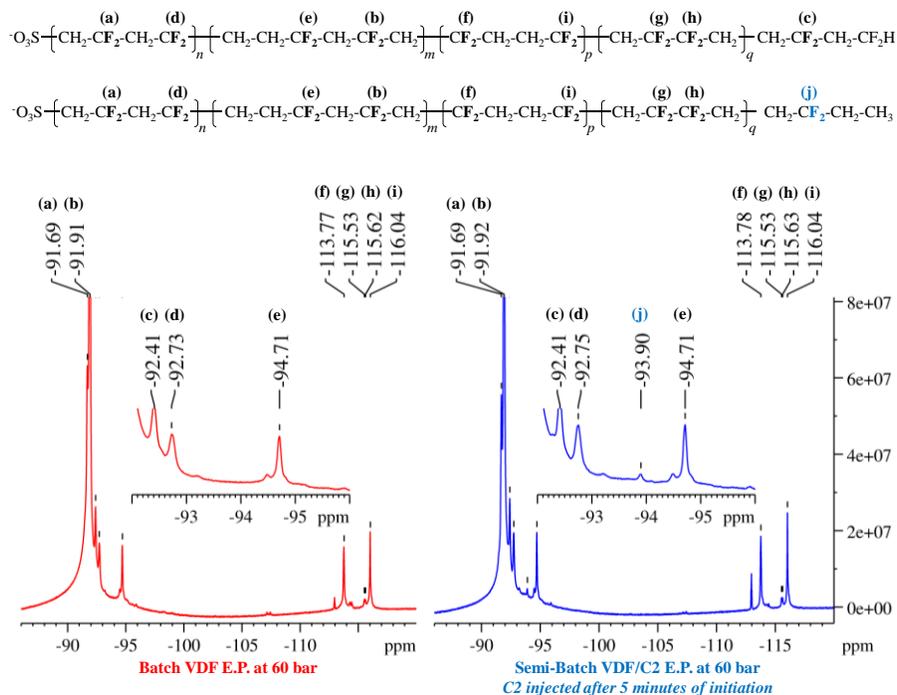
	$P_{\text{VDF}}$	$P_{\text{C2}}$	VDF	C2	[Surf]	[KPS]	[NaOAc]	[EA]	PC
	bar		%mol		g/Lw	g/Lw	g/Lw	g/Lw	%
<i>Test Run 2</i>	60	0	100	0	1.5	0.09	0.07	0.00	14.51
<i>Run 10</i>	60	2*	99	1	1.5	0.09	0.06	0.00	4.30
<i>Run 11</i>	60	2*	99	1	1.6	0.10	0.06	0.00	3.92



**Figure 5.** Pressure (left) and temperature profile (right) of VDF and C2 emulsion polymerizations carried under different C2 injection protocol conditions.



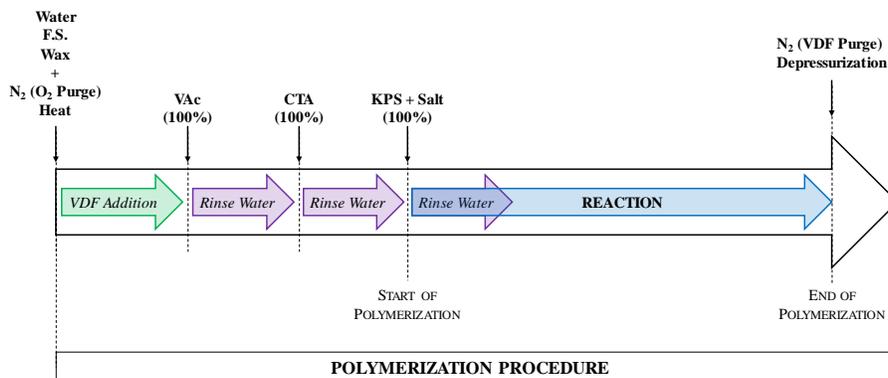
**Figure 6.** Expansion of the 0.8-5.0 ppm (top) and 0.6-2.0 ppm (bottom) region of the  $^1\text{H}$  NMR spectra of Test Run 2 and Run 11 from Table 4 recorded in  $d_6$ -DMSO.



**Figure 7.** Expansion of the -118.0  $\rightarrow$  -89.0 ppm region of the  $^{19}\text{F}$  NMR spectra of Test Run 2 and Run 11 from Table 4 recorded in  $d_6$ -DMSO.

### 3.2 Influence of Vinyl Acetate in the reaction media

Since it is clear that C2 cannot be incorporated into VDF polymer chains under standard industrial production conditions, it was decided to add Vinyl Acetate (VAc) into the reaction media. It is known that VAc can react with C2 in emulsion polymerization conditions comparable to those used here<sup>23</sup>. Thus, if VAc can react with VDF, it is possible that terpolymers containing VDF, C2 and VAc could be produced. The polymerization procedure is given in Figure 8. Reactions conditions and results are given in Table 5.



**Figure 8.** Illustration of the VAc injection protocol of the polymerization procedures containing VDF, C2 and VAc.

**Table 5.** Conditions, gravimetry,  $D_p$ ,  $N_p$  and DSC scans results of VDF, C2 and VAc emulsion polymerization.

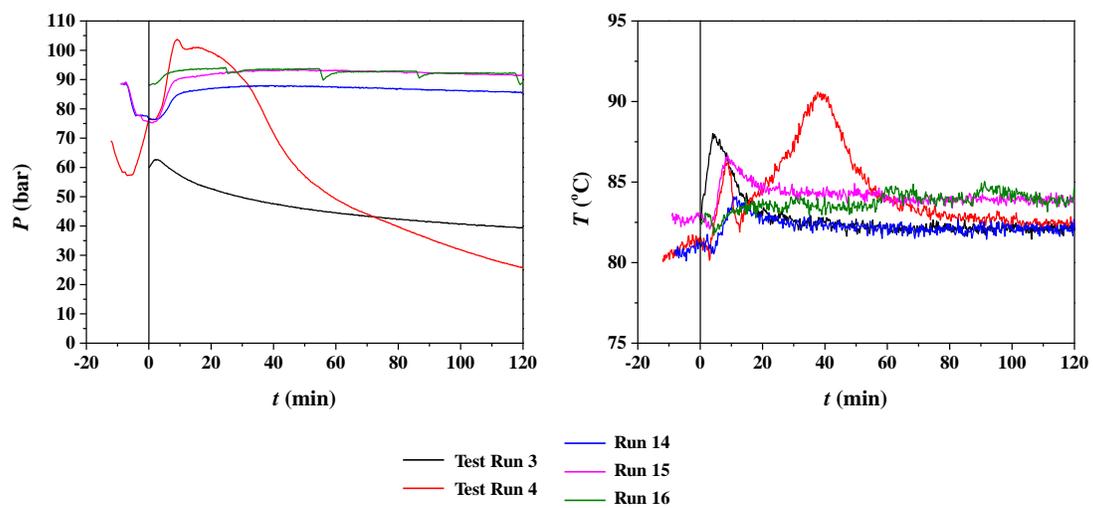
	$P_{VDF}$	$P_{C2}$	[VAc]	VDF	C2	VAc	[Surf]	[KPS]	[NaOAc]	[EA]	PC	$D_p$	$N_p$	$T_g$	$T_c$	$T_m$
	bar	bar	wt%	%mol			g/Lw	g/Lw	g/Lw	g/Lw	%	nm	$\times 10^{19}$	$^{\circ}C$	$^{\circ}C$	$^{\circ}C$
<b>Test Run 3</b>	0.0	60.00	10.0	0.0	60.00	40.0	1.6	1.00	0.74	0.00	12.24	121.5	13.6	-9.2	-	-
<b>Test Run 4</b>	88.0	0.00	10.0	85.0	0.00	15.0	1.5	0.90	0.61	0.00	29.16	180.1	9.7	-20.3	100.4	143.5
<b>Run 12</b>	44.0	44.00	10.0	63.0	22.00	15.0	1.5	0.91	0.62	0.00	9.34	113.0	13.0	-4.9	-	-
<b>Run 13</b>	77.0	11.00	10.0	80.0	5.00	15.0	1.5	0.91	0.62	0.00	12.39	125.2	12.3	9.1	-	-
<b>Run 14</b>	77.0	11.00	10.0	80.0	5.00	15.0	1.5	0.91	0.60	0.00	11.58	99.1	23.4	11.2	-	-

Firstly, two test runs were carried to guarantee that VAc reacts under the experimental conditions in this work with VDF and C2, separately (Test Runs 3 and 4 - Figure 9). Subsequently, runs containing all three monomers (VDF, C2 and VAc) were carried out under similar conditions. Runs 12 through Run 14 showed no significant conversion of the gaseous monomers, identified by the stagnant pressure and temperature profiles (Figure 9). An additional run in which VAc shots were gradually added throughout the reaction (Run 14), did not affect the consumption of VDF and C2. All reactions containing both VDF and VAc presented a

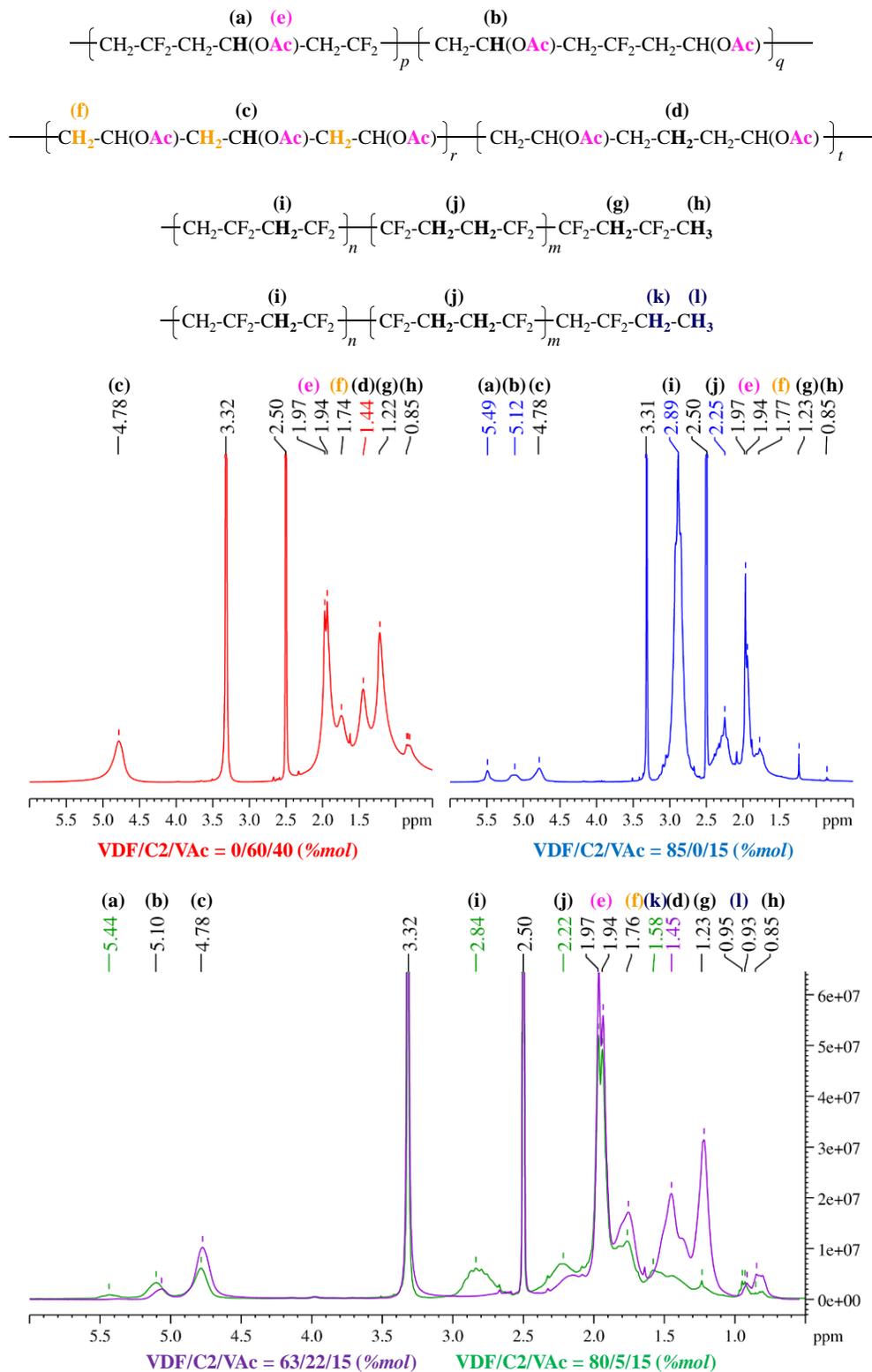
decrease of pressure after VAc injection ( $t < 0$ ), indicating the solubilization of VDF into VAc. Despite the lack of noticeable conversion from the gaseous monomers, a film-like polymer was obtained which was attributed to the homopolymerization of VAc. The obtained latexes showed that the gradual addition of VAc increases  $N_p$ , indicative of a VAc-centric nucleation process.

DSC analysis show no signs of a combined C2 and VDF incorporation into the polymer chain due to no clear appearance of  $T_c$  and  $T_m$ ; However, the increase of  $T_g$  is indicative of VDF and VAc copolymerization.  $^1H$  (Figure 10) and  $^{19}F$  (Figure 11) NMR spectra of Run 12 and Run 13 demonstrate the same previously seen inhibition/retardation effect when C2, identifiable by peaks at 0.95, 1.60 and -93.90, despite the presence of VAc. There were no signs of C2 incorporation, but VAc+VDF polymerization was noticed, identifiable by the peaks between 4.60 and 5.70 ppm on  $^1H$  NMR spectra as well as -93.10 and 93.50 ppm on the  $^{19}F$  NMR spectra.

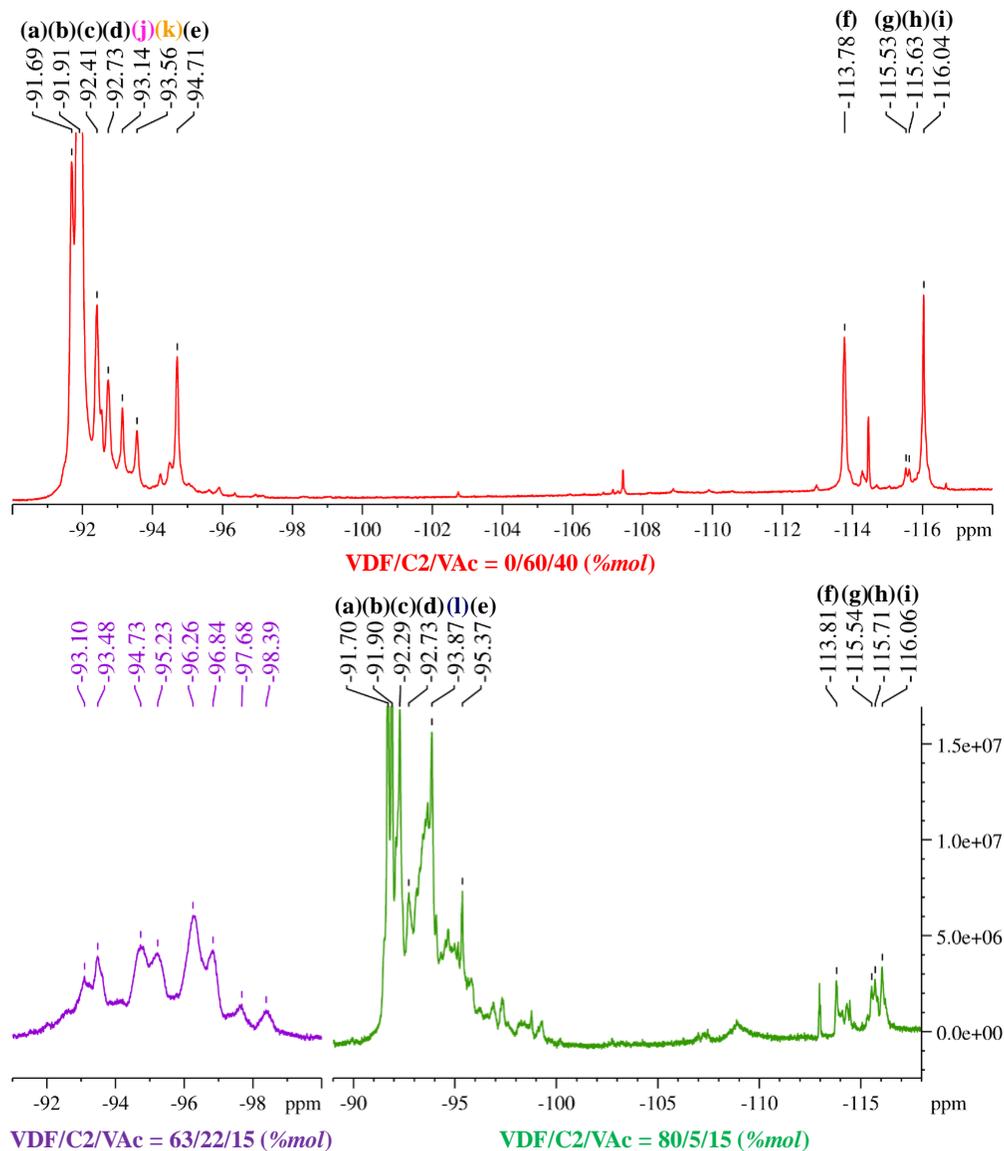
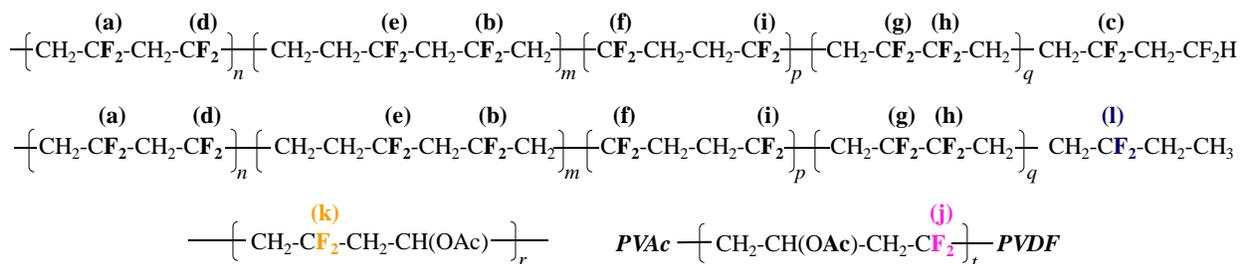
The copolymerization of C2+VAc (Test Run 3) and VDF+VAc (Test Run 4) was confirmed by  $^1H$  NMR and  $^{19}F$  NMR spectra, in which assignments were made of the monomer sequences: VAc-C2-VAc, VDF-VAc-VDF, VAc-VDF-VAc and VAc-VAc-VAc (Figure 10 and Figure 11) <sup>17,24</sup>. Regarding the VDF+VAc emulsion polymerization, little information is available in the open literature. Plenty of studies investigated VDF+VAc polymerization in scCO<sub>2</sub>, suspension, and solution processes <sup>16,17,25</sup>. Since the results acquired from Test Run 4 seemed promising, it was decided to further investigate the emulsion polymerization of VDF with VAc under the reference conditions which are used for VDF homopolymerization.



**Figure 9.** Pressure profile (left), temperature profile (right) of VDF, C2 and VAc emulsion polymerization.



**Figure 10.** Expansion of the 0.5-6.0 ppm region of the  $^1\text{H}$  NMR spectra of Test Run 3, Test Run 4, Run 12 and Run 13 from Table 5 recorded in  $d_6$ -DMSO.



**Figure 11.** Expansion of the -118.0 → -89.0 ppm region of the  $^{19}\text{F}$  NMR spectra of Test Run 4, Run 12 and Run 13 from Table 5 recorded in  $d_6$ -DMSO..

### 3.3 Influence of VDF/VAc Ratio in Feed

The influence of VDF/VAc ratio in feed was investigated in batch emulsion polymerizations. Reference recipe of reactant concentrations and conditions were kept (Table 6), and VDF/VAc Ratio in Feed were varied whilst maintaining overall pressure inside the reactor at 88 bar. The full amount of VAc was injected before the initiator. The polymerization was stopped after 4 hours of reaction.

**Table 6.** Reference experimental conditions

	$P_{VDF}$	[Surf]	[KPS]	[NaOAc]	[EA]
	<i>bar</i>	<i>g/Lw</i>	<i>g/Lw</i>	<i>g/Lw</i>	<i>g/Lw</i>
<i>Reference</i>	88	1.5	0.1	0.06	13.40

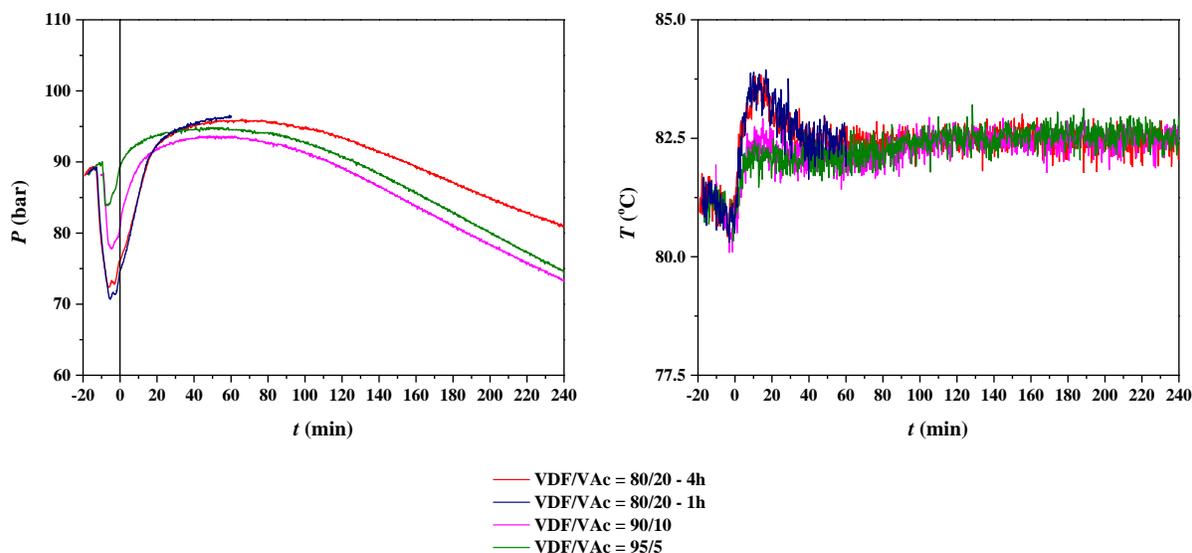
Table 7 shows the conditions and gravimetry results of the experiments performed varying VDF/VAc ratio in feed. As expected from previous experiments, VDF was solubilized into VAc at  $t < 0$  (Figure 12) leading to a small drop in the reactor pressure. Furthermore, Runs 15, 16 and 17 demonstrated a gradual increase followed by stagnation of the pressure throughout the first 60 to 90 minutes of reaction. This was followed by the decrease of pressure. The increase of % VAc into feed indicated a decrease of VDF consumption rate due to the degradative chain transfer provided from VAc<sup>26</sup> and an increase in  $N_P$  indicative of VAc homogeneous nucleation governs the reaction media. Additionally the presence of crystallinity, similar  $T_m$  values of PVDF produced under the same conditions<sup>22</sup> and gradual increase of  $T_g$  as

VAc fraction increases are indicative of higher incorporation of VAc into the polymer chain (Table 7).

The pressure increase followed by stagnation during the first 60-90 minutes of reaction indicates the preferential polymerization of VAc instead of VDF. Run 15b, identical to Run 15 was stopped at the maximum value of the plateau for proof. The polymer content of Run 15b was almost equal to the amount of VAc added to the system (approximately 10 wt%<sub>H2O</sub>) and the physical appearance of the dried matter was transparent pellets (Run 15) and film-like (Run 15b), and the measured value of  $T_g$  is very close to that expected for PVAc. All these points are indicative of VAc homopolymerization<sup>4</sup>.

**Table 7.** Experimental conditions, gravimetry and DSC scans results of emulsion polymerizations carried under varied VDF/VAc ratio in reaction feed.

	$P_{VDF}$	VDF	VAc	[Surf]	[KPS]	[NaOAc]	[EA]	PC	$D_p$	$N_p$	$T_g$	$T_c$	$T_m$	Crystallinity
	bar	%mol		g/Lw	g/Lw	g/Lw	g/Lw	%	nm	$\times 10^{19}$	$^{\circ}C$	$^{\circ}C$	$^{\circ}C$	%
<b>Run 15</b>	88	80	20	1.50	0.09	0.06	13.36	17.20	141.10	11.81	22.4	88.3	147.5	13.7
<b>Run 16</b>	88	90	10	1.50	0.09	0.07	13.36	15.57	145.60	9.86	11.0	119.7	158.7	24.5
<b>Run 17</b>	88	95	5	1.50	0.09	0.07	13.36	13.88	155.20	7.27	2.6	127.4	162.8	30.4
<b>Run 15b</b>	88	80	20	1.50	0.09	0.06	13.36	9.78	110.40	14.15	35.1	-	-	-



**Figure 12.** Pressure (left) and temperature (right) profiles of emulsion polymerizations carried under varied VDF/VAc ratio in reaction feed.

$^1\text{H}$  and  $^{19}\text{F}$  NMR chemical shifts in the copolymer synthesized have shown clear characteristic signals of both VDF and VAc final latex. As expected from copolymerization synthesis composition drift, since  $r_{\text{VAc}} > r_{\text{VDF}}$ <sup>4</sup>, the fraction of VAc incorporated into the copolymer chain is higher than VAc added in the feed. Also, as the amount of VAc injected into the reaction decreases, the amount of incorporated VDF units into the copolymer increases (Table 8). On the other hand, the monomer sequencing confirmed the tendency of VAc to preferentially polymerize at the first 60-90 minutes of reaction time, evidenced by the higher amounts of VAc-VAc sequences (60% and 58%, respectively) for Runs 15 and 16. The comparative runs varying polymerization time (Table 8) have confirmed that throughout the first 60-90 minutes of polymerization time, mainly VAc homopolymerization occurs (64% for VAc-VAc-VAc monomer sequencing). However, it was postulated that the 40% of VDF incorporated into the copolymer for Run 15b occurred due the initially solubilized VDF into the VAc droplets, which

are then transferred inside the particles that initially carry the copolymerization until it reached low enough concentration, followed by the start of VDF in gas phase being consumed.

**Table 8.** Integration results from  $^1\text{H}$  NMR spectra in **Erreur ! Source du renvoi introuvable.**

	Polymerization Time	Monomer in Feed		Monomer in Polymer		Monomer Sequencing		
		VDF (A)	VAc (B)	VDF (A)	VAc (B)	ABA	BAB	BBB
	hours	% mol		% mol		%		
<i>Run 15</i>	4	80	20	67	33	13	31	56
<i>Run 16</i>	4	90	10	77	23	18	36	45
<i>Run 15b</i>	1	80	20	40	60	7	29	64

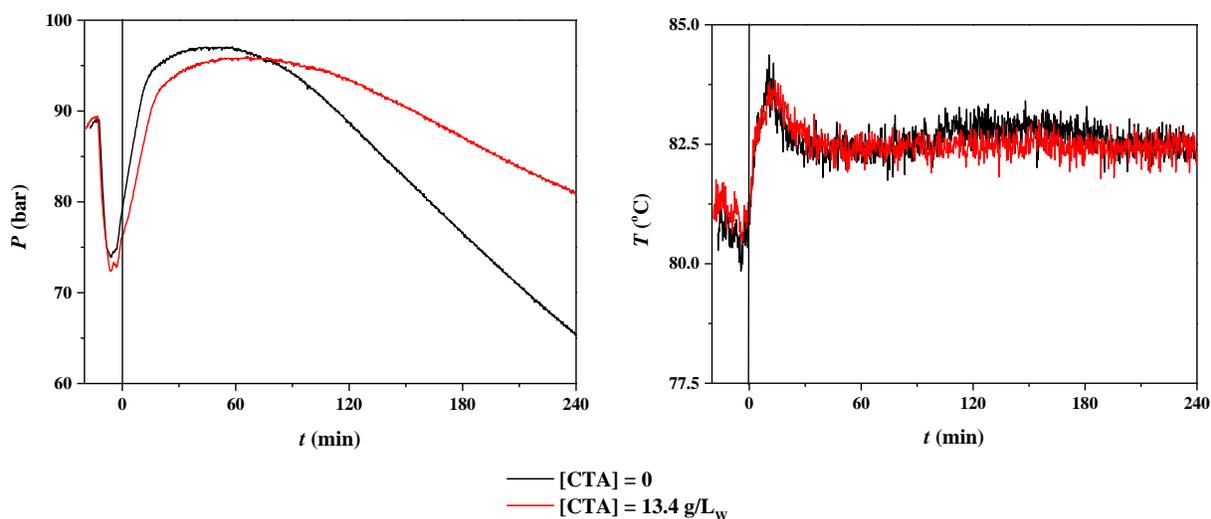
### 3.4 Influence of CTA

The influence of CTA was investigated by conducting batch emulsion polymerizations, varying CTA (Ethyl Acetate - EA) concentration (Table 9), with constant molar ratio of monomers in feed (VDF/VAc = 80/20). The full amount of VAc was injected together with CTA before the start of the reaction. The polymerization was stopped after 4 hours.

**Table 9.** Experimental conditions, gravimetry and DSC scans results of emulsion polymerizations carried under different CTA concentration conditions.

	$P_{\text{VDF}}$	VDF	VAc	[Surf]	[KPS]	[NaOAc]	[EA]	PC	$D_P$	$N_P$	$T_g$	$T_c$	$T_m$	Crystallinity
	bar	%mol		g/Lw	g/Lw	g/Lw	g/Lw	%	nm	$\times 10^{19}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$	%
<i>Run 15</i>	88	80	20	1.50	0.09	0.06	13.36	17.20	141.10	11.81	22.41	88.33	147.47	13.68
<i>Run 18</i>	88	80	20	1.50	0.09	0.06	0.00	24.15	156.10	12.32	15.10	104.93	153.92	19.32

Similar to the previous runs, a decrease of pressure after VAc injection, and a gradual increase followed by stagnation of pressure throughout the first 60-90 minutes of reaction was noticed (Figure 13). The presence of EA decreases VDF consumption rate due to degradative chain transfer<sup>26</sup>. Lower VDF incorporation was noticed by the decrease of PC and crystallinity, increase of  $T_g$ , despite similar  $N_p$  values (Table 9). Indeed,  $^1\text{H}$  and  $^{19}\text{F}$  NMR chemical shifts in the copolymer synthesized further confirms lower VDF incorporation despite similar monomer sequencing (Table 10).



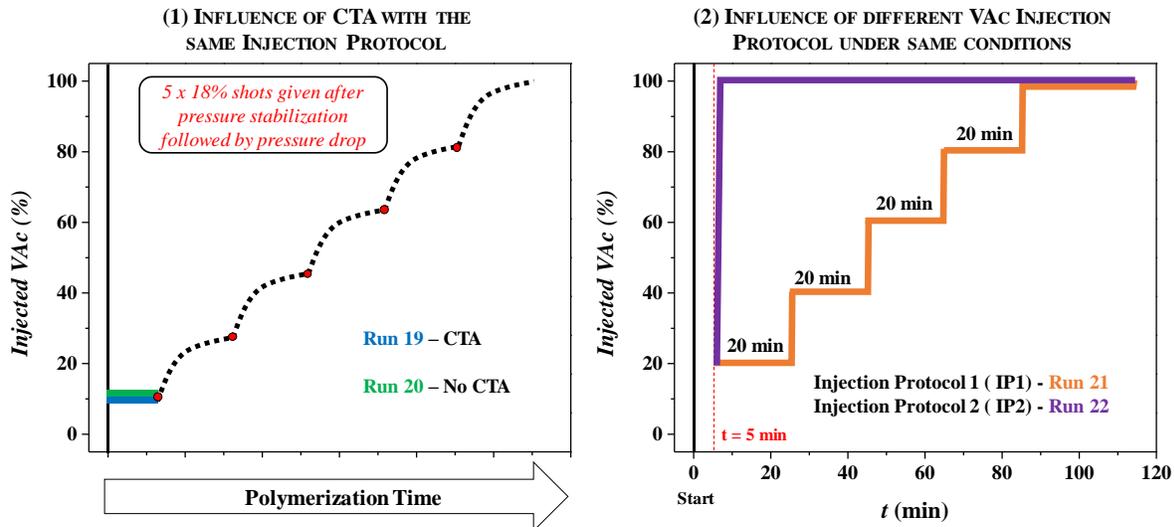
**Figure 13.** Pressure (left) and temperature (right) profiles of VDF and VAc emulsion polymerizations carried under different CTA concentration conditions.

**Table 10.** Integration results from  $^1\text{H}$  NMR spectra of Runs 15 and 18.

	[Ethyl Acetate]	Monomer in Feed		Monomer in Polymer		Monomer Sequencing		
		VDF (A)	VAc (B)	VDF (A)	VAc (B)	ABA	BAB	BBB
	$g/L_w$	% mol		% mol		%		
<b>Run 15</b>	13.36	80	20	67	33	13	31	56
<b>Run 18</b>	0.00	80	20	76	24	15	33	52

### 3.5 Influence of VAc Injection Protocol

The influence of VAc injection protocol (IP) was investigated through batch emulsion polymerizations of VDF and VAc with same monomer molar ratio (VDF/VAc = 90/10). This investigation was divided into two sections: (1) Influence of CTA with the same IP and (2) Influence of different VAc IP under the same conditions. Figure 14. is a schematic of the IPs utilized. The reactions conditions are presented in Table 11.



**Figure 14.** IP utilized in: (1) Influence of CTA with the same IP and (2) Influence of different VAc IP under the same conditions

**Table 11.** Experimental conditions of VDF and VAc emulsion polymerizations carried under different VAc injection protocol conditions.

	$P_{VDF}$ bar	VDF %mol	VAc %mol	[Surf] g/Lw	[KPS] g/Lw	[NaOAc] g/Lw	[EA] g/Lw
<i>Run 19</i>	88	90	10	1.50	0.09	0.06	13.37
<i>Run 20</i>	88	90	10	1.49	0.09	0.06	0.00
<i>Run 21</i>	88	90	10	1.50	0.09	0.06	0.00
<i>Run 22</i>	88	90	10	1.50	0.09	0.06	0.00

### 3.5.1 Influence of CTA with the same IP

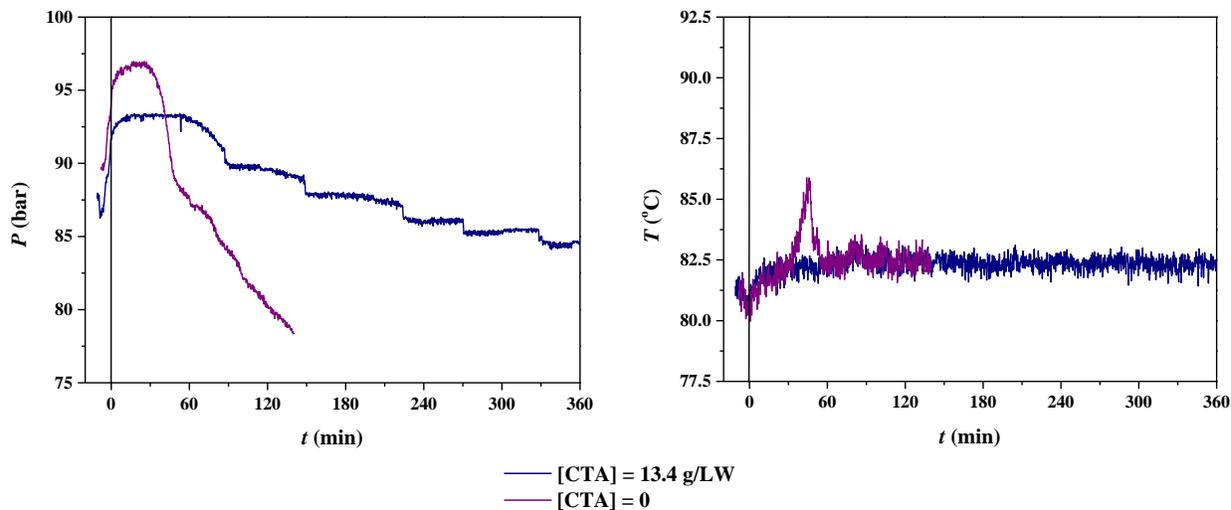
Pressure and temperature profiles of batch emulsion polymerizations with same IP and varying EA concentrations are given in Figure 15. The initial shot (10% of total VAc mass) caused the pressure stagnation time (VAc homopolymerization), this period was nearly doubled in presence of EA. Furthermore, in accordance with CTA (VAc and EA) causing degradative

chain transfer<sup>26</sup>, the absence of EA lead to rapid nucleation (peak in temperature profile) and increased VDF uptake, evidenced by presence of crystallinity, higher PC value and the specific IP administered in these experiments (Run 19 had shots added every hour, Run 20 had shots added every 20 minutes).

Changing the IP of VAc lead to differences into the copolymer structure evidenced by <sup>1</sup>H and <sup>19</sup>F NMR. Indeed, integration results (Table 13) confirmed that the copolymers presented higher percentages of VAc into the copolymer chain when in presence of EA (Table 8). Furthermore, similarly to section 3.4, monomer sequencing was similar but VDF consumption was lower. However, monomer sequencing showed that VAc homopolymerization (BBB Sequence) has decreased compared to Run 16 (Table 8), indicative that the gradual addition of VAc throughout the polymerization process better controls the initial homopolymerization of VAc.

**Table 12.** Experimental conditions, gravimetry and DSC scans results of VDF and VAc emulsion polymerizations carried under same VAc IP and varying CTA concentrations.

	<b>P<sub>VDF</sub></b>	<b>VDF VAc</b>		<b>[Surf]</b>	<b>[KPS]</b>	<b>[NaOAc]</b>	<b>[EA]</b>	<b>PC</b>	<b>D<sub>P</sub></b>	<b>N<sub>P</sub></b>	<b>T<sub>g</sub></b>	<b>T<sub>c</sub></b>	<b>T<sub>m</sub></b>	<b>Crystallinity</b>
	<i>bar</i>	<i>%mol</i>		<i>g/Lw</i>	<i>g/Lw</i>	<i>g/Lw</i>	<i>g/Lw</i>	<i>%</i>	<i>nm</i>	<i>x10<sup>19</sup></i>	<i>°C</i>	<i>°C</i>	<i>°C</i>	<i>%</i>
<b>Run 19</b>	88	90	10	1.50	0.09	0.06	13.37	9.25	186.20	2.81	6.44	-	-	-
<b>Run 20</b>	88	90	10	1.49	0.09	0.06	0.00	15.22	227.90	2.52	6.57	97.54	149.66	12.21



**Figure 15.** Pressure (left) and temperature (right) profiles of VDF and VAc emulsion polymerizations carried under same VAc IP and varying CTA concentrations.

**Table 13.** Integration results from  $^1\text{H}$  NMR spectra Runs 19 and 20.

	[Ethyl Acetate]	Monomer in Feed		Monomer in Polymer		Monomer Sequencing		
		VDF (A)	VAc (B)	VDF (A)	VAc (B)	ABA	BAB	BBB
	$\text{g/L}_w$	% mol		% mol		%		
<b>Run 19</b>	13.36	90	10	67	33	23	44	33
<b>Run 20</b>	0.00	90	10	73	27	29	41	30

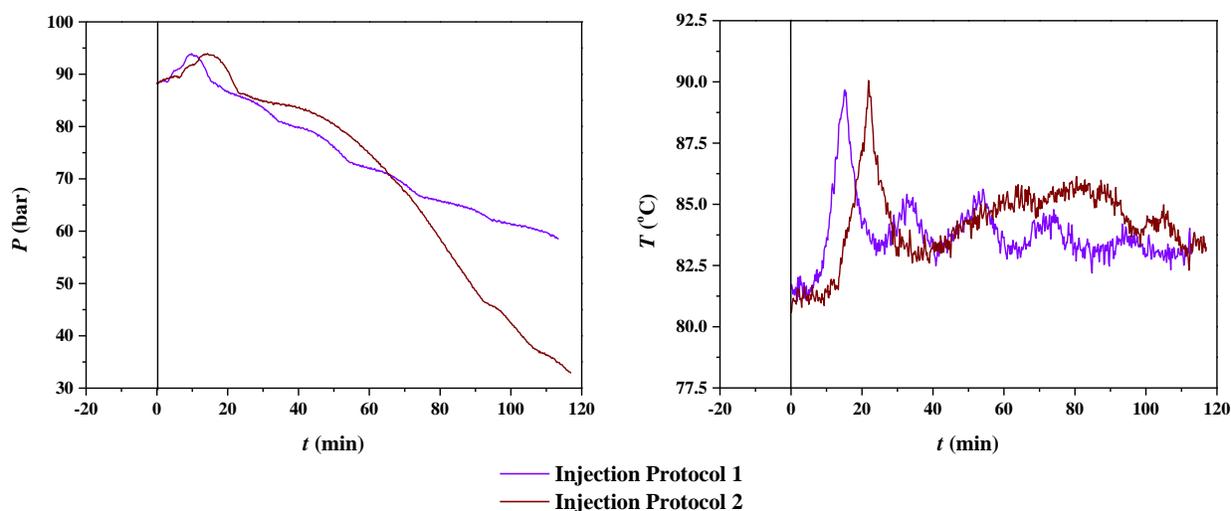
### 3.5.2 Influence of different VAc IP under the same conditions

Section 3.5.1 explicitly showed improvement in the VDF uptake by gradually injection VAc into the reaction media. Therefore, semi-batch emulsion polymerizations under the same conditions and two IP of VAc, in which VAc is injected 5 minutes after the initiation of the VDF polymerization, then carried for 2 hours (Table 14, Figure 14).

**Table 14.** Experimental conditions and gravimetry results of VDF and VAc emulsion polymerizations carried under same conditions and different VAc injection protocol.

	P <sub>VDF</sub>	VDF	VAc	[Surf]	[KPS]	[NaOAc]	[EA]	PC	D <sub>P</sub>	N <sub>P</sub>	T <sub>g</sub>	T <sub>c</sub>	T <sub>m</sub>	Crystallinity
	bar	%mol		g/Lw	g/Lw	g/Lw	g/Lw	%	nm	x10 <sup>19</sup>	°C	°C	°C	%
<i>Run 21</i>	88	90	10	1.50	0.09	0.06	0.00	20.45	181.80	6.59	2.88	111.64	152.12	18.90
<i>Run 22</i>	88	90	10	1.50	0.09	0.06	0.00	23.84	183.50	7.43	-23.55	124.45	159.06	31.00

Higher overall VDF consumption was noticed if VAc is added at t = 5 minutes (after initiation of VDF homopolymerization) (Figure 16). Furthermore, greater VDF uptake was noticed, if VAc is added in one-shot (IP2) instead of gradually (IP1), especially evidenced by lower values of T<sub>g</sub> and higher values of crystallinity. Additionally, the N<sub>P</sub> have shown to be similar values in which the homogeneous-coagulative nucleation mechanism governs the reaction<sup>26</sup>. The homogeneous-coagulative nucleation mechanism of PVDF emulsion homopolymerization provides an initial preferential addition of VDF units on polymer chain to a point at which, when VAc is added to the reaction media, the expected favored addition of VAc units is hindered, whilst the copolymerization for VDF and VAc is facilitated. Indeed, the lowest composition drift was noticed (Table 15), indicated by similar values acquired <sup>1</sup>H NMR integration, and the monomer sequencing integration results presented the highest percentages of VDF-VAc-VDF and VAc-VDF-VAc sequences.



**Figure 16.** Pressure (left) and temperature (right) profiles of VDF and VAc emulsion polymerizations carried under same conditions and different VAc injection protocol.

**Table 15.** Integration results from  $^1\text{H}$  NMR spectra of Runs 21 and 22.

	Injection Protocol	Monomer in Feed		Monomer in Polymer		Monomer Sequencing		
		VDF (A)	VAc (B)	VDF (A)	VAc (B)	ABA	BAB	BBB
		% mol		% mol		%		
<i>Run 21</i>	IP1	90	10	74	26	32	37	31
<i>Run 22</i>	IP2	90	10	86	14	37	29	34

## 4 Conclusion

In this work the feasibility of the emulsion copolymerization of VDF and C2 was studied through various experimental conditions. An initial batch experiments varying C2 and VDF pressures inside the reactor media showed no conversion unless injected C2 in the reactor was approximately 1 %mol in the monomer feed mixture and 10-fold multiplied reference KPS concentration. Further investigation suggested that initiator-decomposition-born radicals are

immediately consumed before polymer chain propagation. Semi-batch experiments in which C2 was injected into the reaction media once initiation of VDF homopolymerization was noticed showed halt in the polymerization process as soon as C2 was injected. Therefore, the presence of C2 in the reaction media caused an inhibition/retardation effect due to proton transfer reaction and C2 being less reactive in propagation. DSC analysis confirmed no integration of C2 units into the polymer chain,  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis confirmed the presence of C2-terminated chains.

Another set of experiments containing vinyl acetate (VAc) as third monomer, believed to increase the reactivity of both C2 and VDF was utilized. Indeed, VAc did react with VDF and C2 separately. However, in reactions containing all three monomers, pressure and temperature profiles showed no significant consumption of the gaseous monomers (C2 and VDF), even if VAc was added throughout the reaction. Due to the presence C2 in the reaction media, inhibition/retardation effect occurred for the gaseous monomers. DSC,  $^1\text{H}$  and  $^{19}\text{F}$  NMR analysis confirmed formation of PVAc, small amounts of P(VAc+VDF) copolymer, little to no incorporation of C2 into the polymer chain and C2-terminated polymer chains.

Despite not being able to synthesize the copolymer, the area of exploration in which that the copolymerization is feasible has been narrowed. Ultimately, the increase of C2-radical reactivity and propagation with VDF might rely on chemical and physical conditions such as catalysts, incorporation of new monomers, agitation rates, the implementation of new agitators and/or baffles into the reactor.

Further investigation was carried due to promising results of the emulsion polymerization of VDF with VAc under scale-down industrial VDF homopolymerization conditions. A series of

stable latexes of VDF/VAc copolymers were synthesized that circumvent the VAc limitations in solution and suspension copolymerization with VDF, which include the need for lower reaction volumes and yields, higher temperatures and pressures which particularly affect the industrial process. Initial tests showed a priority of VAc incorporation into the copolymer chain despite higher percentages of VDF present in the monomer feed, caused by the homogeneous nucleation of VAc. Albeit VAc also acts as a CTA throughout the copolymerization process, the presence of EA into the reaction media mainly benefited incorporation of VAc, due to the degradative chain transfer EA causes in VDF homopolymerization.

Experiments utilizing various VAc injection protocols have showed that administering VAc throughout the reaction provides control on the preferential polymerization of VAc, identified by the decrease in VAc-VAc-VAc monomer sequence units. Preferable copolymer compositions and structure containing VAc and VDF, in which the monomer sequencing is statistic and with great thermal stability (when compared to PVDF) were found to be synthesized if no amounts of VAc are added before initiation, followed by the injection of VAc after the homogeneous-coagulative nucleation process of PVDF homopolymerization has taken place.

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