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# INVESTIGATION OF CHAIN TRANSFER AGENTS EFFECT ON THE POLYMERIZATION OF VINYLIDENE FLUORIDE

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**Keywords:** vinylidene fluoride, free radical polymerization, chain transfer, kinetics

## ABSTRACT

The effect of chain transfer agents (CTA) ethyl acetate (EA), octyl acetate (OA) and isopropyl alcohol (IPA) on the rate of polymerization of vinylidene fluoride (VDF) in an emulsion polymerization and in solution polymerization in dimethyl carbonate (DMC) initiated by Tert-butyl Peroxypivalate was investigated. Pressure profiles of the polymerizations were recorded. Solids content and rate of polymerization were calculated by gravimetry, size exclusion chromatography was utilized to evaluate CTA activity and the produced polymers microstructure were characterized by  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectroscopies. It is proposed that the observed reduction in polymerization rate in both systems is due to degradative chain transfer reactions.

## 1 INTRODUCTION

Polyvinylidene fluoride (PVDF) shows a unique set of physical and thermal properties, making it a very attractive material for a number of applications that require low coefficients of friction, inertness, good resistance to flame and to ultraviolet light, just to name a few. It can also be thermos-formed, extruded, injected, and welded. According to technobleak.com, the world market for PVDF was valued at just under a billion dollars in 2017, and expected to grow by approximately 7% per year between 2018-2025<sup>1</sup>. Clearly a better understanding of the polymerization mechanism would be useful to help improve PVDF properties and production processes. However, a recent review from our group highlighted the fact that there is only a limited amount of information on the kinetics and processes of the emulsion polymerization of vinylidene fluoride (VDF) in the open literature<sup>2</sup>.

Apostolo et al.<sup>3</sup> proposed a kinetic mechanism to describe the rate and molar mass distribution of a VDF-hexafluoropropylene copolymer made in an emulsion polymerization process. The mechanism included radical initiation, four different possible propagation reactions, termination by disproportionation, back-biting reactions, as well as chain transfer to monomer, to chain transfer agent (CTA), and to polymer. They used experimental data to estimate different rate constants, including radical transfer to a CTA. However, they do not make any mention of the impact of the CTA (type or quantity) on the kinetics. In fact, most of the modelling studies discussed by Mendez-Ecoscia include the important transfer to CTA step, but neglect to consider the impact of the transfer to CTA step on the reaction, assuming that it is an ideal step that leads to the generation of new radicals that reinitiate chains instantaneously.

However, it is clear from certain patents<sup>4-7</sup> that when the CTA levels are increased, it is necessary to increase the amount of initiator. In other words, certain types of CTA lead to a reduction in the polymerization rate<sup>6,8-11</sup>. Additional patents speak of the possibility of “degradative chain transfer” to certain  $\alpha$ -olefins<sup>12</sup>, implying that the chain transfer reaction slows down the polymerization. In a similar vein, another patent states that the use of certain chain transfer agents such as acetates can lead to the

formation of water-soluble fluorinated substances, implying that the resulting reaction between a transferred radical and monomer unit can lead to an un- or very poorly-reactive species<sup>11</sup>. Finally, it is also thought that chain transfer reactions to certain surfactants or solvents<sup>13</sup> with labile hydrogen atoms can also inhibit emulsion polymerization processes. In conclusion, there is a substantial body of evidence in the patent literature suggesting that chain transfer reactions, both to CTA and other species in the reactor can be important.

However, and as mentioned above, very few studies in the literature attempt to account for the impact of the CTA on the rate of emulsion polymerization of VDF. The only study in the literature that seems to attempt to account for this is the paper of Pladis et al.<sup>14</sup>, where the authors postulated that the presence of a highly water-soluble chain transfer agent (ethyl acetate – EA) increased the probability of radical desorption from the particles in an emulsion polymerization system, and that this desorption of radicals led to a reduction in the rate of polymerization. While it is likely that radical desorption does indeed occur, there seems to be no reason to discount re-entry of the desorbed radicals. Furthermore, the patent literature points toward the fact that transfer reactions to species other than just the CTA (including surfactants) suggest that some form of degradative chain transfer reaction, i.e. one where the transfer-generated radicals are far less reactive than initiator-born radicals. A study has therefore been carried out using both solution and emulsion polymerizations to demonstrate that the degradative chain transfer mechanism is the reason that the rate of emulsion polymerization of VDF decreases as the CTA concentration increases.

## **2 METHODOLOGY**

### **2.1 Materials**

Vinylidene fluoride monomer (VDF) and surfactant for emulsion polymerization were kindly supplied by Arkema (Pierre Bénite, France) and used without further purification. Dimethyl Carbonate (DMC – ReagentPlus®, 99%, Sigma Aldrich) was used as received. The solution polymerizations were initiated

using Tert-butyl Peroxypivalate (TBPP, trade name Luperox<sup>®</sup> 11M75), graciously supplied by Arkema (Günzburg, Germany); Ethyl Acetate (ACS grade, Carlo Erba Reagent), Octyl Acetate (99%, Sigma Aldrich) and Isopropyl Alcohol (>99%, Sigma Aldrich) were used as Chain Transfer Agents (CTA). Deuterated dimethylsulphoxide (d6-DMSO – Sigma Aldrich) was utilised as Nuclear Magnetic Resonance (NMR) solvent. Sodium acetate (99 %, Sigma Aldrich) was used as buffer in the emulsion polymerization experiments. All reagents were employed as received. Dimethyl sulfoxide (DMSO) was purified by addition of 2.13g of NaNO<sub>3</sub> in 2.5L of solvent, then vacuum filtrated at high temperature. The purified DMSO was utilised for Size Exclusion Chromatography (SEC) analysis.

## **2.2 Autoclave and Polymerization Procedure**

### **2.2.1 Solution Polymerization**

A 50 mL autoclave equipped with a stirring and temperature Parr Reactor Controller (PARR4848) and a SPY<sup>RF</sup> (JRI) Pressure Recorder in combination with a Sirius Stockage Software (v.1.5.10) was used for small scale experiments. In the batch polymerization procedure, a liquid mixture containing specific amounts of DMC and TBPP was charged into the autoclave. The autoclave was then sealed, and the liquid mixture was deoxygenized by purging nitrogen under constant stirring (175 rpm) for 30 minutes under an ice bath. Stirring was set to 350 rpm and the temperature of the autoclave was controlled via an electric heating mantel. Reactor temperature was raised to 55 °C and stabilized for 3 minutes. VDF was added continuously until a pressure of 15 bars was reached at 70 °C. The start of the reaction (t=0) was set once 70 °C is reached. At the end of the polymerization, agitation was decreased (175 rpm), the electric heater was removed, and the autoclave was put into an ice bath. At room temperature, the product was removed.

### 2.2.2 Emulsion Polymerization

The reaction vessel was a 4 L jacketed autoclave (Stainless Steel type 316) equipped with a rupture disc rated at 110 bars, and an impeller-type agitator. The reactor temperature was measured by a thermocouple J, protected by a metal tube and placed inside the reactor. This temperature probe as well as dip tube can be considered to serve as baffle. Oil (Ultra 350, Lauda) circulating in the jacket was used to control the reactor temperature. The inlet and outlet 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 the jacketed feedline line, which was refrigerated by a heat transfer liquid (Kryo 60, Lauda) that circulated countercurrently at  $-25^{\circ}\text{C}$ . The head of the dual diaphragm pump (Metering pump Novados H1, Axflow) was also refrigerated to guarantee that the monomer stayed in liquid phase through the pumping. The upstream pressure was set-up to 30bar, and it was adjusted by a pressure regulating valve located just after the gas bottle. The mass flow of cooled inlet monomer was monitored with a Coriolis flowmeter (Optimass 3000, Khrone). The aqueous solutions were introduced with the help of a syringe pump (500HL Syringe Pump, Isco). Nitrogen was used to remove the residual oxygen contained in the additives aqueous solutions and in the initial reactor charge.

The rate of polymerization was monitored by calorimetry in both batch and semibatch modes. A redundant pressure drop measurement was also used in batch mode to validate the calorimetric measurement, and a mass flow rate was available during semi-batch reactors. The reactor temperature was regulated by a Proportional Integral Derivative (PID) controller.

An initial charge composed of deionized water, surfactant and wax was added into the reactor, then the reactor was sealed, and the 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  $83^{\circ}\text{C}$ ). During the heating up time of the reactor content, the residual oxygen was removed by purging with nitrogen

with the help of the dip tube. Monomer was added into the reactor via the diaphragm pump, and the inlet mass was monitored via the Coriolis mass-flowmeter. When the desired pressure was attained, aqueous solutions of chain transfer agent and initiator (oxygen-free) were introduced with the help of a syringe pump. The reaction was started by injecting the initiator. In batch polymerizations the reaction was left to proceed without monomer feed, while in semi-batch mode the monomer mass was continuously added throughout the reaction with the help of the diaphragm pump (manually controlled) in order to maintain a constant pressure. At the end of the polymerization the agitation speed was slowed down, the reactor was cooled down, and the remaining VDF was gently degassed. The reactor content was purged with nitrogen, and then the polymer was recovered from the reactor via a bottom valve. The exact recipe for the polymerization experiments cannot be shared here for secrecy reasons, but reference values of the levels of reactive components used in the given runs are given in Table 1.

**Table 1.** Range of literature values for emulsion polymerization formulations and reference value used in current work.

<b>Compound</b>	<b>Range of Values*</b>	<b>Reference</b>
VDF	0 < P < 100 bars	15
Paraffin	0-4 g/L	5,9,16-19
Temperature	60-90°C	9,20
CTA – Ethyl acetate	1.2-24 g/L	14,21
KPS	0.005-0.5 g/L	20
Surfactant	< 2 g/L	3,15,22

**Note:** All concentrations given in grams of active material per liter of pure water.

## 2.3 Polymer Characterization

### 2.3.1 Polymer Content and Rate of Polymerization

Gravimetric analysis was used to measure the solids content ( $SC$ ) of the final product of the solution polymerizations. A known amount of sample ( $m_{\text{Product}}$ ) in an aluminium dish was placed inside an oven at

60 °C over 4 hours. After solvent evaporation, the dried product was reweighed ( $m_{\text{Dried Product}}$ ). Finally, the  $PC$  was calculated by Equation 1. All polymer content calculation was made with triplicates.

$$SC = 100 \times \frac{m_{\text{Dried Product}}}{m_{\text{Product}}} \quad \text{Equation 1}$$

The overall rate of polymerization for the solution polymerizations ( $R_p - \text{mol.mL.s}^{-1}$ ) was estimated based on the work of Russo et. al.<sup>23</sup>, given by Equation 2.  $m_{\text{Polymer}}$  (total mass of polymer produced) was estimated through  $SC$  (Equation 3),  $V_s$  (total volume of solution –  $mL$ ) was estimated assuming entirety of solution is DMC ( $m_{\text{Total Solution}}$ ) (Equation 4) and  $t_p$  is the polymerization time in *seconds*.

$$R_p = \frac{10^6}{64.03} \times \frac{m_{\text{Polymer}}}{V_s \times t_p} \quad \text{Equation 2}$$

$$m_{\text{Polymer}} = \frac{\frac{SC}{100} \times (m_{\text{Luperox}} + m_{\text{CTA}} + m_{\text{DMC}})}{1 - \frac{SC}{100}} \quad \text{Equation 3}$$

$$V_s = \frac{m_{\text{Total Solution}}}{\rho_{\text{DMC}}} \quad \text{Equation 4}$$

### 2.3.2 Nuclear Magnetic Resonance

End chain analysis 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 samples of polymer 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).  $^1\text{H}$  NMR was to determine the polymers end chains and, in combination with  $^{19}\text{F}$  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).

### 2.3.3 Size Exclusion Chromatography

The molar mass distribution (MWD) was measured using Size Exclusion Chromatography (SEC), equipped with three porous columns – two 1000 Å and one 30 Å of Polyester copolymer (Gram column, PSS). Solutions of 5 g.L<sup>-1</sup> containing dried polymer samples into the previously described purified DMSO were prepared and maintained at 55 °C under constant stirring overnight. Then, the homogeneous solutions were filtered with a nylon 0.45 µm porous size filter. The experimental number-average ( $M_n$ ) and weight-average ( $M_w$ ) molar masses as well as the dispersity ( $D = M_w/M_n$ ) were derived from the RI signal determined using three PMMA samples (minimum of 831 Da and maximum of 1,430,000 Da) as standards.

### 2.3.4 Apparent Chain Transfer Activity ( $C_T^{\text{app}}$ ) Calculation

The apparent chain transfer activity ( $C_T^{\text{app}}$ ) is determined by a Mayo plot<sup>24,25</sup> of  $1/DP_n$  (cumulative) vs.  $[CTA]_0/[VDF]_0$ , in which  $DP_n = M_n/M_{VDF}$  ( $M_n$  – Number average molar mass of the polymer,  $M_{VDF}$  – VDF molar mass),  $[CTA]_0$  (CTA initial concentration) and  $[VDF]_0$  (VDF initial concentration). Since the Mayo method developed for low monomer conversions, the values of the chain transfer constants presented here must be considered as apparent values as the monomer concentration, and thus molar mass evolve during the polymerization. Nevertheless, these values provide comparison of the overall chain transfer performance of each CTA.

### 2.3.5 Particle Size and Particle Size Distribution

Dynamic Light Scattering (DLS) was employed to measure the particle size of the PVDF produced via emulsion polymerization. A Malvern Zetasizer Nano series ZS (Malvern Instruments) with the default

detection angle of 173° was utilized. The reported particle size corresponds to the average value of 3 measurements per sample. It was recognized that the DLS gives a reliable diameter, and that the sample is reasonably monodispersed when the Polydispersity Index was lower than 0.1. A disposable cell containing a high diluted solution of latex was placed inside the Zetasizer.

The required optical properties to perform the measurement were: a) Refractive index of the dispersed phase (PVDF latex particles) = 1.42<sup>26</sup>; Refractive index of the continuous phase (Water): 1.33 (Malvern database); Adsorption index of particles (PVDF particles): It was assumed around 0.001, this value was coherent with the Malvern data base typically reported for latex particles.

### 2.3.6 Number of particles

The particle size diameter determined from the DLS was used to compute the number of particles per volume ( $N_p$ ), as follows:

$$N'_p = \frac{V_{pol}}{v_p} = \frac{\frac{m_{Dried\ Product}}{1000}}{\frac{\rho_{PVDF}}{\frac{\pi}{6} \times (D_p \times 10^{-9})^3}}$$

$$N_p = \frac{N'_p}{V_{Sample}}$$

where  $\rho_{PVDF}$  is the density of PVDF polymer (1800 kg.m<sup>-3</sup>),  $D_p$  is the mean particle diameter,  $V_{Sample}$  is the volume of the measured sample.

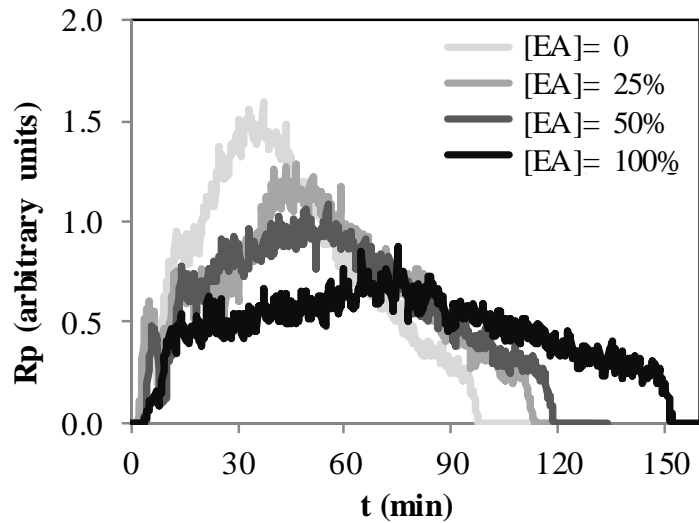
### 3 RESULTS AND DISCUSSION

#### 3.1 Emulsion Polymerization

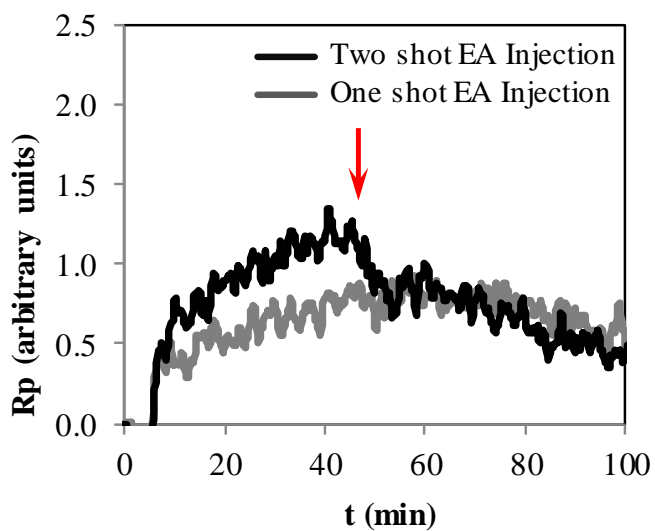
A summary of the final particle diameter and number for the emulsion polymerizations with different amounts of chain transfer agent is shown in Table 2, and the rates of polymerization are shown in Figures 1-3.

**Table 2.**  $D_P$  and  $N_P$  results of PVDF emulsion polymerizations.

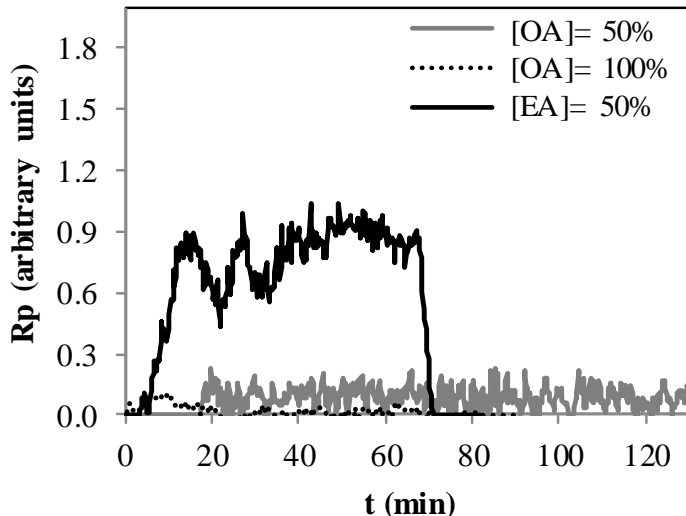
Reaction	$D_P$	$N_P$
	nm	$10^{19} m^{-3}$
[EA] = 0	215	2.80
[EA] = 25%	210	2.90
[EA] = 50%	190	3.90
[EA] = 100%	183	4.40
One Shot EA	186	4.40
Two Shot EA	189	4.60
[EA] = 50%	175	3.50
[OA] = 50%	89	7.20
[OA] = 100%	44	6.10



**Figure 1.** Polymerization rate profiles obtained at different concentrations of chain transfer agent in batch mode.



**Figure 2.** Influence of the chain transfer agent injection protocol on the polymerization rate profile, injected either all as one shot or in two shots of 50% of the maximum amount (red arrow indicates the time at which the second shot of CTA was injected). Reactions were carried out in semi-batch mode.



**Figure 3.** Polymerization rate profile obtained using Ethyl Acetate (EA) and Octyl Acetate (OA) as chain transfer agent. Reactions were carried out in batch mode. The concentration of EA and OA are given as the percentage of maximum number of moles.

All of the Figures show that as the amount of chain transfer agent increases, the maximum rate of polymerization decreases. If one considers Figure 1, it can be seen that the decrease in rate from 0% EA to 100% EA corresponds (roughly) to a proportional decrease in the maximum rate of polymerization. Note also from Figure 2 that as soon as the concentration of CTA was increased, the polymerization rate decreased.

In ideal free radical polymerizations, it is usually assumed that the chain transfer agent controls the molar mass of the produced polymer without affecting the rate of polymerization. This is based on the implicit assumption that free radicals created by a CT event to CTA have essentially the same reactivity as free radicals created by the reaction of an initiator fragment and the monomer. But, as we have just pointed out, increasing the amount of CTA leads to a proportional decrease in the rate of polymerization. There are different possible explanations for this, and two of the most likely include:

- I. Pladis et al.<sup>14</sup> proposed that radical desorption due to chain transfer to a slightly hydrophilic CTA leads to a decrease in the polymerization rate due to radical depletion in the particles. They set different values of transfer to CTA constants in their model of VDF emulsion polymerization and showed that increasing the CTA concentration can lead to a decrease in the rate if this hypothesis is correct.
  
- II. It is also possible that the assumption that CTA-terminated radicals are as active as monomer-terminated radicals is false. In this case, referred to as degradative chain transfer, a free radical transfers from a growing PVDF chain to a CTA, the reaction will slow down because the CTA-terminated radical is far more stable (i.e. less reactive) than the VDF-based radical.

We can test the validity of the first hypothesis by using a more hydrophobic CTA. The first set of emulsion polymerizations were carried using Ethyl Acetate (EA) as the CTA. As EA is relatively hydrosoluble ( $9.42 \cdot 10^{-1}$  M), using a CTA such as octyl acetate (OA) (water solubility of  $1.04 \cdot 10^{-3}$  M) would lead to a lower tendency of radicals formed from a CT event to desorb from the particles. From Figure 3, it can be seen that at equivalent molar concentration, reactions performed with octyl acetate proceeded extremely slowly, and after almost 100 minutes just 2 % of the monomer was consumed. Even after reducing the molar concentration of OA to half of its initial value, the reaction rate is still much lower than the reaction obtained with as equivalent amount of EA. So eliminating the possibility of desorption of radicals with OA actually leads to a decrease of the polymerization rate, rather than an increase. This suggests that the reduction in rate due to the presence of a CTA not due to desorption, but rather to degradative chain transfer. This would also explain the roughly linear decrease in rate as a function of the CTA concentration. Note that changing the amount of CTA also leads to a slight increase in the number of particles, so the rate increase with CTA concentration is not exactly linear.

### 3.2 Solution Polymerization

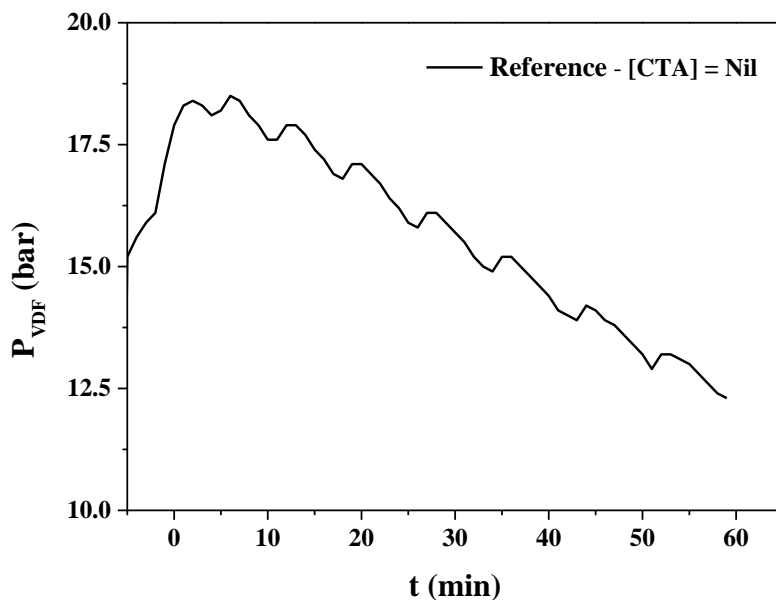
In order to test this last hypothesis, we performed VDF solution polymerization in DMC (which acts as both solvent and CTA) using various quantities and types of CTA (Ethyl Acetate – “EA”, Octyl Acetate – “OA” and Isopropyl Alcohol – “IPA”). The idea here of course is that if the polymerization takes place in one phase, then one can eliminate desorption of radicals, and perhaps isolate the CTA effect.

A reference experiment, shown in Table 3 was first run in order to compare polymerizations with, and without different types of CTA. As explained in the materials section, total mass of liquid inside the reactor was always 33g, the initial VDF pressure (PVDF) was 15 bar at a reaction temperature of 70 °C, the agitation rate was set at 350 rpm, and the initiator concentration was 0.1 wt% with respect to total liquids.

**Table 3.** Reference experimental conditions

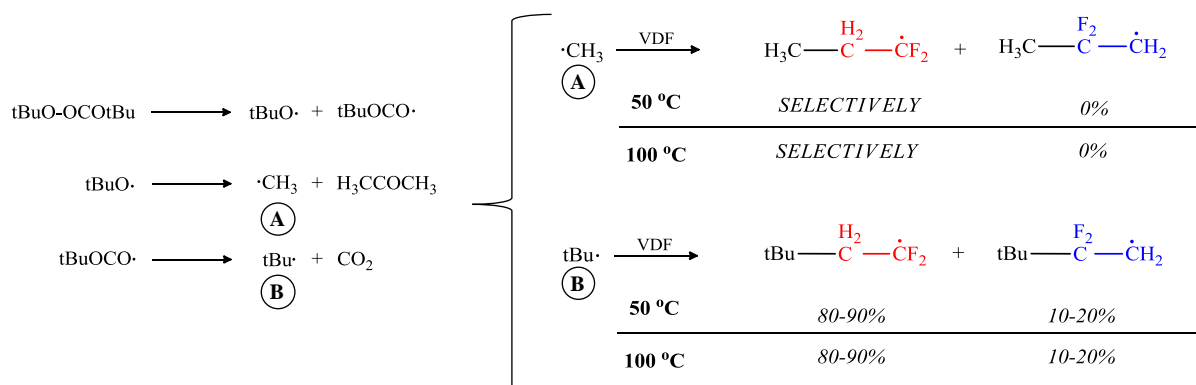
	$P_{\text{VDF}}$	$T_{\text{R}}$	N	$m_{\text{TOTAL}}$	[TBPP]	[CTA]
	<i>bar</i>	<i>°C</i>	<i>rpm</i>	<i>g</i>	<i>wt%</i>	<i>wt%</i>
<b>Reference</b>	15	70	350	33	0.1	Nil

The product of solution polymerization is a dispersion containing a white, insoluble PVDF dispersed in DMC with a calculated 9.25% solids content (SC) and estimated overall average rate of polymerization ( $R_p$ ) of  $0.47 \text{ mol}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$ . The pressure profile of the polymerization is given by Figure 4. Throughout the reaction there are intervals of sudden  $P_{\text{VDF}}$  increase followed by a decrease, this is due to an equilibrium that occurs throughout batch VDF solution polymerization in DMC. In this equilibrium, as VDF units dissolve into DMC, a slight increase of temperature causes the pressure inside the reactor to increase. Simultaneously, as the dissolved VDF monomer is consumed, additional VDF monomer located in the reactor’s overhead space is solubilized into the DMC.



**Figure 4.** Pressure profile of Reference VDF solution polymerization in DMC initiated by TBPP.

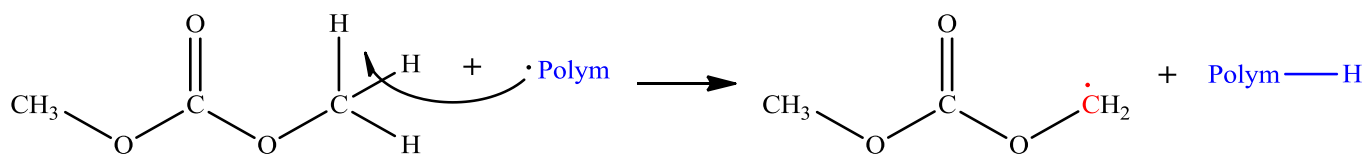
The initiation mechanism of TBPP in VDF solution polymerization in acetonitrile at 50 °C and 100 °C was studied by Guiot et. al.<sup>27</sup>. These studies showed that TBPP has the potential to decompose into 4 types of radicals, but that the two shown in Figure 5 are the most likely to participate in VDF polymerization. tBu was the primary source of initiation for VDF polymerization while the CH<sub>3</sub> radical might also selectively initiate the polymerization.



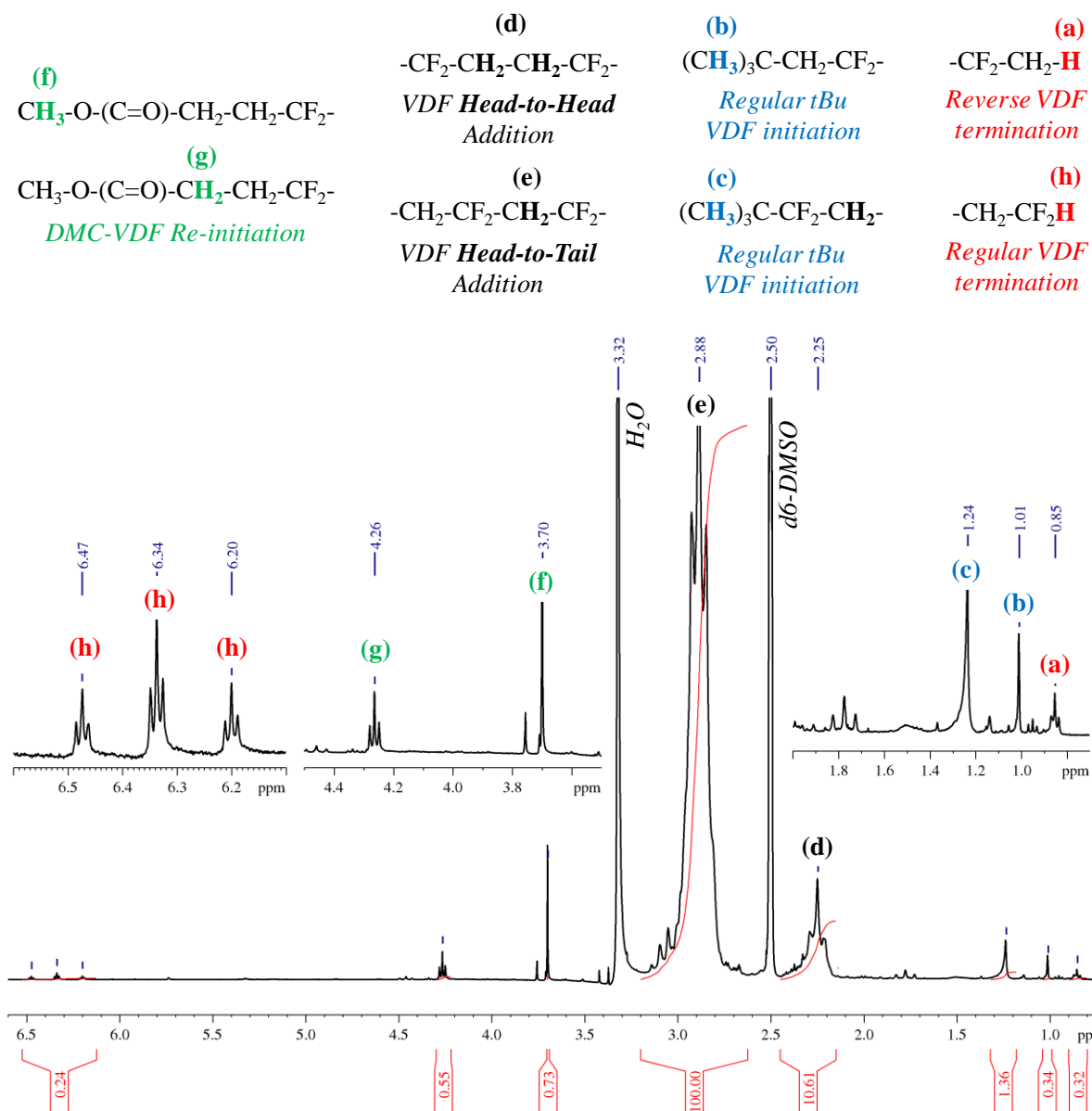
**Figure 5.** Decomposition of TBPP initiator on Acetonitrile for VDF solution polymerization (adapted from Guiot et al.<sup>27</sup>).



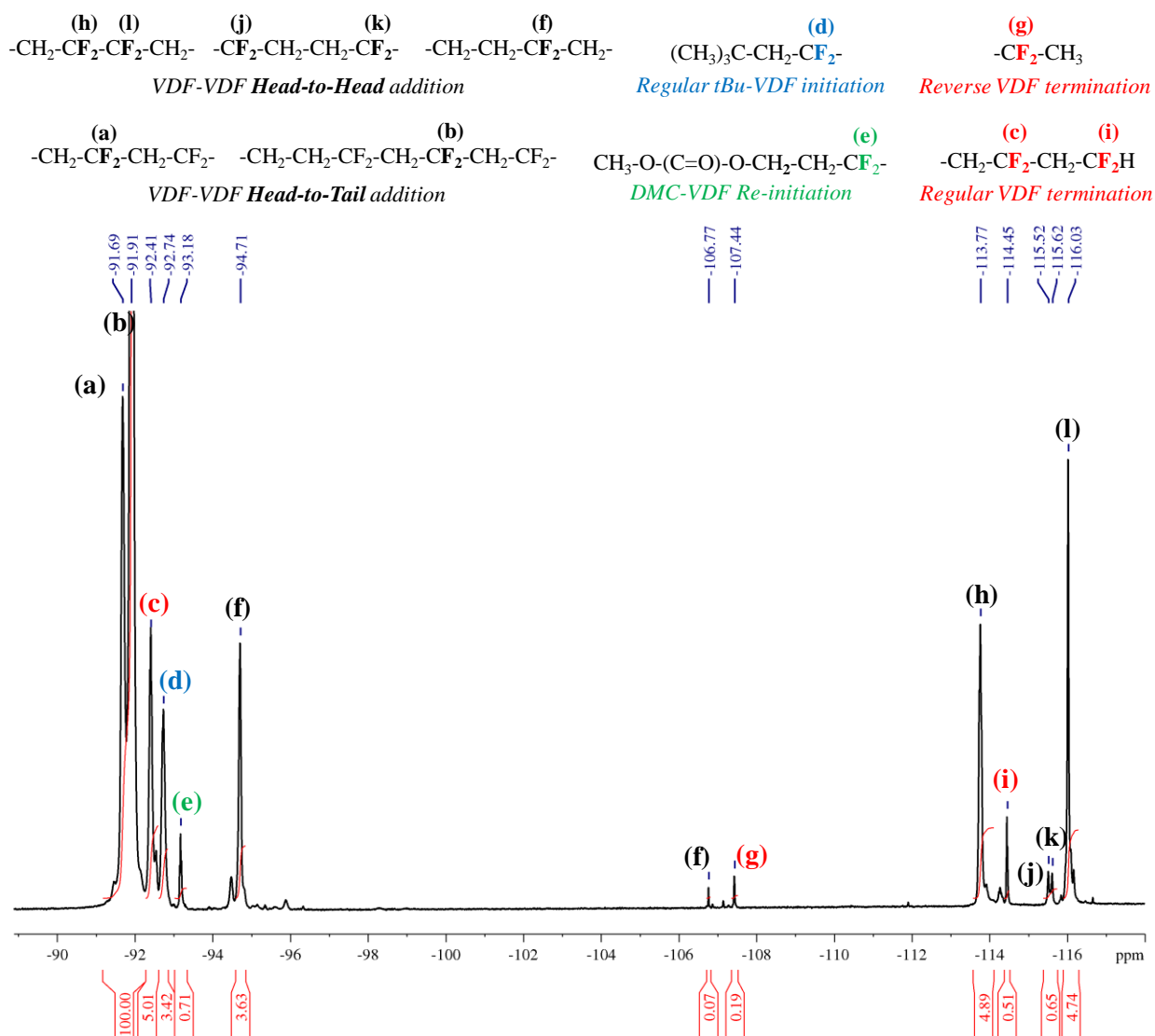
In this work, VDF polymerizations were carried in DMC, which will act as a chain transfer agent (CTA). The mechanism chain transfer to DMC is given by Figure 6. Baseline assignments for  $^{19}\text{F}$  and  $^1\text{H}$  NMR chemical shifts in PVDF polymer synthesized in REF, taking into consideration the type of initiation and chain transfer to DMC are shown in Figure 7 and Figure 8. The signals at 2.5 and 3.3 ppm refer to solvent DMSO and traces of water. The following peaks were assigned to the PVDF polymers<sup>28,29</sup>:  $^1\text{H}$  NMR peak assignments (400 MHz DMSO, chemical shift [ppm]): 0.85-0.91 (t,  $-\text{CF}_2-\text{CH}_2-\mathbf{H}$ , VDF Reverse Termination), 1.05 ( $(\text{CH}_3)_3\text{C}-\text{CH}_2-\text{CF}_2-$ , Regular tBu-VDF initiation), 1.20 ( $(\text{CH}_3)_3\text{C}-\text{CF}_2-\mathbf{CH}_2-$ , Reverse tBu-VDF initiation) 2.28-2.43 (m,  $-\text{CF}_2-\mathbf{CH}_2-\mathbf{CH}_2-\text{CF}_2-$ , VDF-VDF Head-to-Head Addition), 2.70-3.19 (t,  $-\text{CH}_2-\text{CF}_2-\mathbf{CH}_2-\text{CF}_2-$ , VDF-VDF Head-to-Tail Addition), 3.67-3.73 ( $\text{CH}_3-\text{O}-(\text{C}=\text{O})-\text{CH}_2-\text{CH}_2-\text{CF}_2-$ , DMC-VDF Re-initiation), 4.22-4.30 ( $\text{CH}_3-\text{O}-(\text{C}=\text{O})-\mathbf{CH}_2-\text{CH}_2-\text{CF}_2-$ , DMC-VDF Re-initiation), 6.15-6.55 ( $-\text{CH}_2-\text{CF}_2\mathbf{H}$ , VDF Regular Termination).  $^{19}\text{F}$  NMR peak assignments (400 MHz DMSO, chemical shift [ppm]): -91.70 ( $-\text{CH}_2-\mathbf{CF}_2-\text{CH}_2-\text{CF}_2-$ , VDF-VDF Head-to-Tail Addition), -91.90 ( $-\text{CH}_2-\text{CH}_2-\text{CF}_2-\text{CH}_2-\mathbf{CF}_2-\text{CH}_2-\text{CF}_2-$ , VDF-VDF Head-to-Tail Addition) -92.40 ( $-\text{CH}_2-\mathbf{CF}_2-\text{CH}_2-\text{CF}_2\mathbf{H}$ , VDF Regular Termination), -92.70 ( $(\text{CH}_3)_3\text{C}-\text{CH}_2-\mathbf{CF}_2-$ , Regular tBu-VDF initiation), -93.20 ( $\text{CH}_3-\text{O}-(\text{C}=\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\mathbf{CF}_2-$ , DMC-VDF Re-initiation), -94.70 ( $-\text{CH}_2-\text{CH}_2-\mathbf{CF}_2-\text{CH}_2-$  VDF-VDF Tail-to-Tail Addition), -106.80 ( $(\text{CH}_3)_3\text{C}-\mathbf{CF}_2-\text{CH}_2-$ , Reverse tBu-VDF initiation), -107.40 ( $-\mathbf{CF}_2-\text{CH}_3$ , VDF Reverse Termination), -113.80 ( $-\text{CH}_2-\mathbf{CF}_2-\text{CF}_2-\text{CH}_2-$ , VDF-VDF Head-to-Head Addition), -114.50 ( $-\text{CH}_2-\mathbf{CF}_2\mathbf{H}$ , VDF Regular Termination), -115.50 ( $-\mathbf{CF}_2-\text{CH}_2-\text{CH}_2-\text{CF}_2-$ , VDF-VDF Head-to-Head Addition), -115.60 ( $-\text{CF}_2-\text{CH}_2-\text{CH}_2-\mathbf{CF}_2-$ , VDF-VDF Head-to-Head Addition), -116.00 ( $-\text{CH}_2-\text{CF}_2-\mathbf{CF}_2-\text{CH}_2-$ , VDF-VDF Head-to-Head Addition).



**Figure 6.** Chain transfer mechanism of DMC throughout the VDF solution polymerization. (Legend: Polym = PVDF).



**Figure 7.** Expansion of the 0.7-6.6 ppm region of the  $^1\text{H}$  NMR spectra of Reference VDF solution polymerization in DMC initiated by TBPP.



**Figure 8.** Expansion of the  $-88.00 \rightarrow -117.0$  ppm region of the  $^{19}\text{F}$  NMR of Reference VDF solution polymerization in DMC initiated by TBPP.

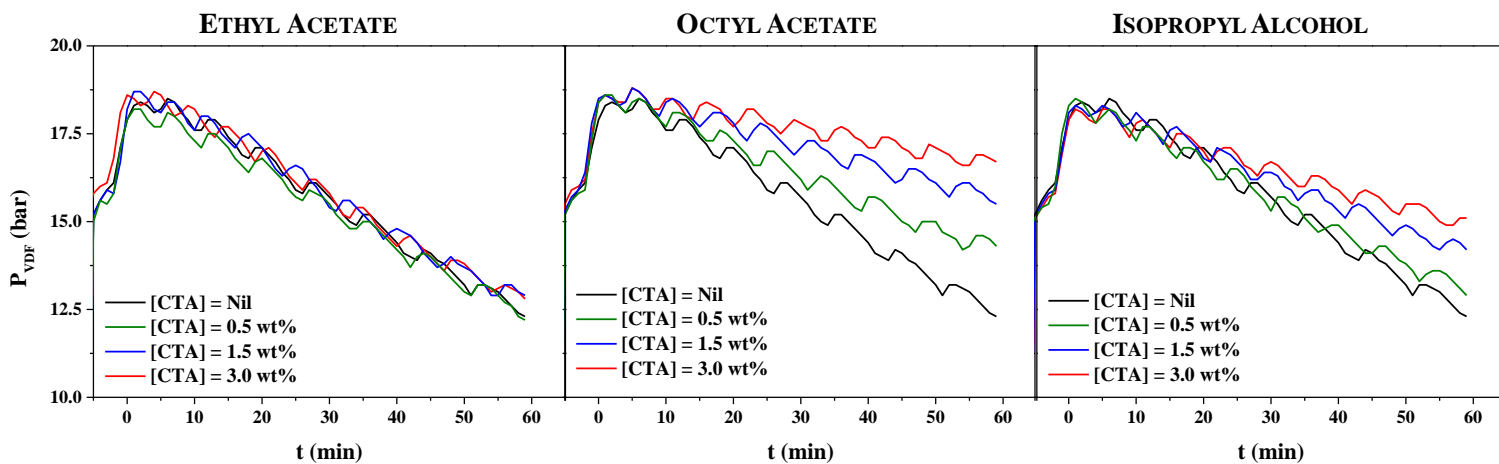
To elucidate the mechanism effects of CTA on VDF emulsion polymerization, sets of experiments containing 3 different CTA (EA, OA and IPA) at 3 increasing concentrations (0.5, 1.5 and 3.0 wt% of total mass of liquid inside de reactor) were carried. Conditions and results from the polymerizations, containing data from SC,  $R_p$ ,  $C_T^{app}$  (Figure 11)  $M_w$  and  $\bar{D}$  are listed on Table 4.  $^1H$  and  $^{19}F$  NMR spectra of all experiments were assessed and utilized to understand the structure of the final products synthesized. Pressure profiles of all experiments are presented on Figure 9, SEC chromatograms for all reactions are presented on Figure 10.

**Table 4.** Conditions and results of PVDF solution polymerizations in DMC in the presence of of CTA (EA, OA, IPA), initiated by TBPP.

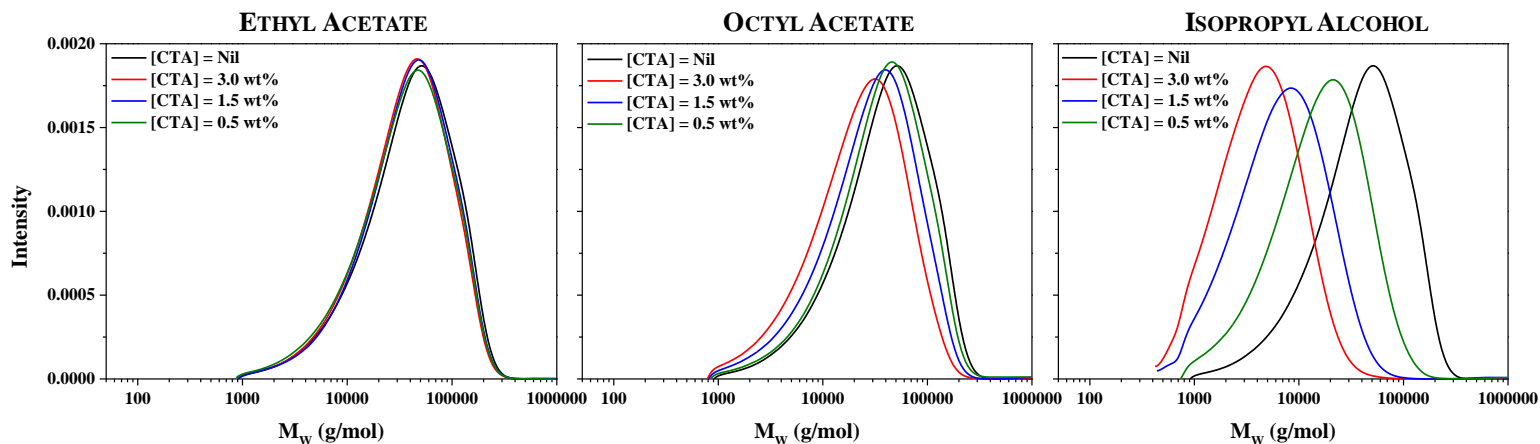
	CTA	[TBPP]	[CTA]	SC	$R_p$	$C_T^{app}$	$M_w$	$\bar{D}$
		wt%	wt%	%	$mol.mL.s^{-1}$	$10^{-3}$	$10^4 g.mol^{-1}$	-
<b>Reference</b>		0.11	0.00	9.25	0.47	-	5.69	2.72
<b>EA1</b>	Ethyl Acetate	0.11	3.03	7.81	0.39	0.02	5.16	2.62
<b>EA2</b>		0.11	1.52	8.08	0.41		5.41	2.61
<b>EA3</b>		0.11	0.50	8.26	0.42		5.25	2.78
<b>OA1</b>	Octyl Acetate	0.11	3.04	3.16	0.15	0.34	3.36	2.82
<b>OA2</b>		0.11	1.50	4.34	0.21		4.26	2.85
<b>OA3</b>		0.11	0.51	6.13	0.30		5.23	2.79
<b>IPA1</b>	Isopropyl Alcohol	0.11	3.01	4.65	0.23	4.32	0.64	2.28
<b>IPA2</b>		0.11	1.52	5.94	0.29		1.12	2.69
<b>IPA3</b>		0.11	0.52	7.23	0.36		2.44	2.69

The pressure profiles (Figure 9) and  $R_p$  information (Table 4) showed that OA had the most significant degradative effect on the VDF consumption throughout the polymerization process. All PVDF polymers

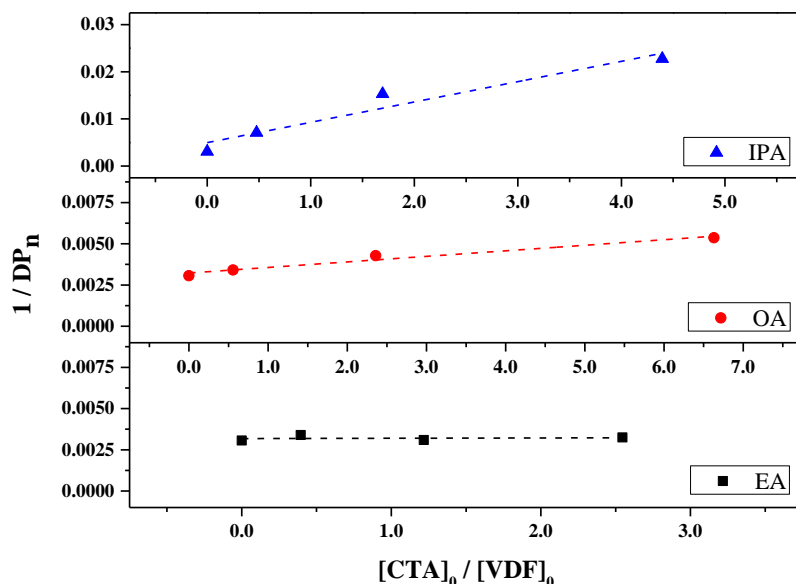
synthesized presented have monomodal distributions (Figure 10). The effect of both types and concentration of additional CTA into the reaction media were clear. The increase of CTA concentration lead to the decrease of molar mass, which was expected. EA and OA, did not influence molar masses as much as IPA, evidenced by lowest  $M_w$  values of 51607, 33649 and 6412  $\text{g}\cdot\text{mol}^{-1}$  for 3 wt% of EA, OA and IPA, respectively. Note that it is possible that the fact that DMC can also act as a chain transfer agent might mask the impact of EA in this type of polymerization experiment, as it is known in the patent literature that EA does indeed have an impact on the molar mass distribution in emulsion polymerization experiments.



**Figure 9.** Pressure profiles VDF solution polymerization with CTA's Ethyl Acetate, Octyl Acetate and Isopropyl Alcohol.



**Figure 10.** Normalized SEC traces of VDF solution polymerization with CTA's Ethyl Acetate, Octyl Acetate and Isopropyl Alcohol.



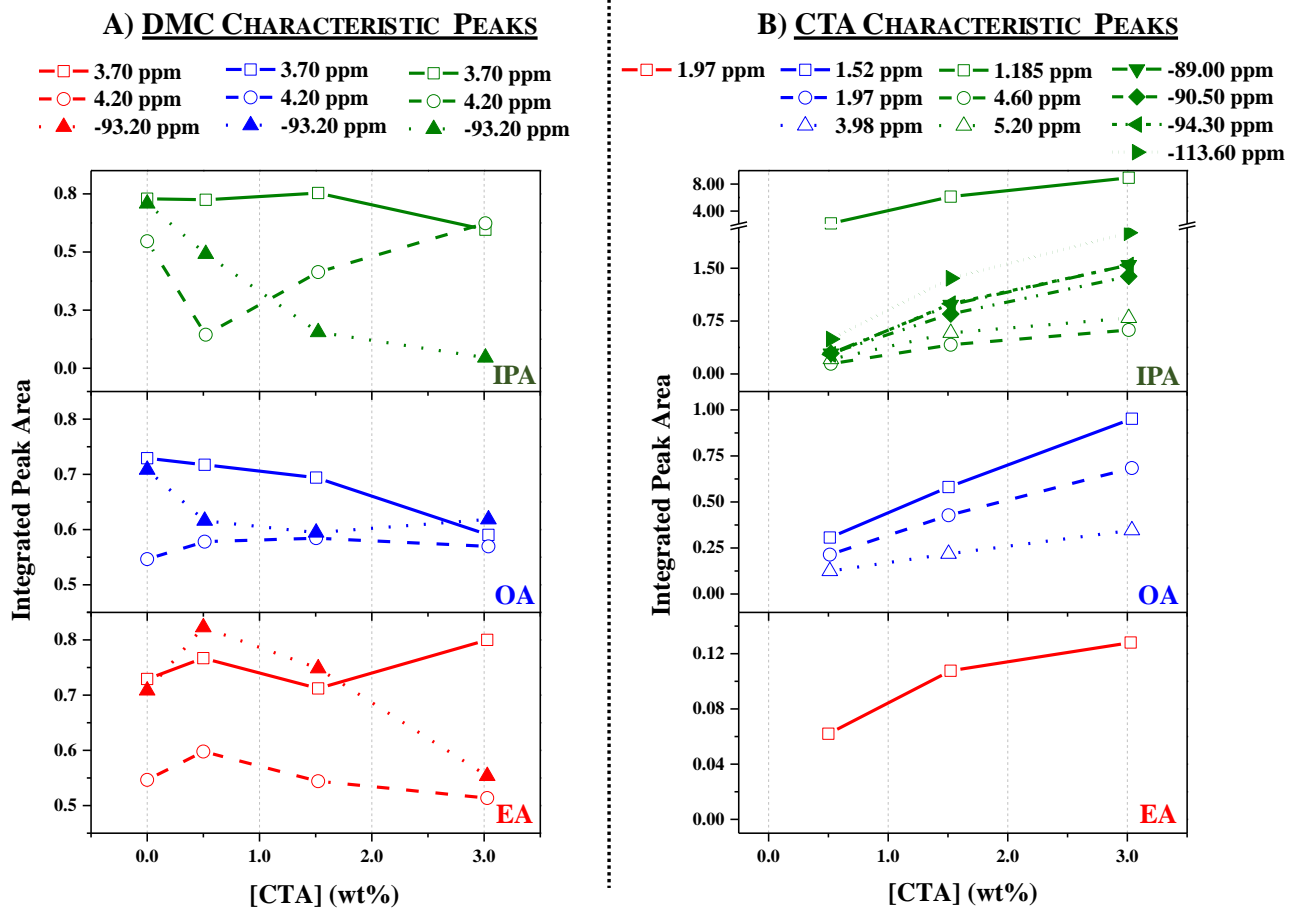
**Figure 11.** Cumulative  $DP_n^{-1}$  as a function of  $[CTA]_0/[VDF]_0$  for PVDF solution polymerizations in DMC in the presence of different concentrations of CTA (EA, OA, IPA), initiated by TBPP.

The previously established baseline assignments for  $^1H$  and  $^{19}F$  NMR of VDF head-to-head addition and VDF head-to-tail addition, VDF reverse and regular termination, and finally reverse and regular tBu-VDF initiation were found in all experiments containing EA, OA and IPA. Additionally, despite the

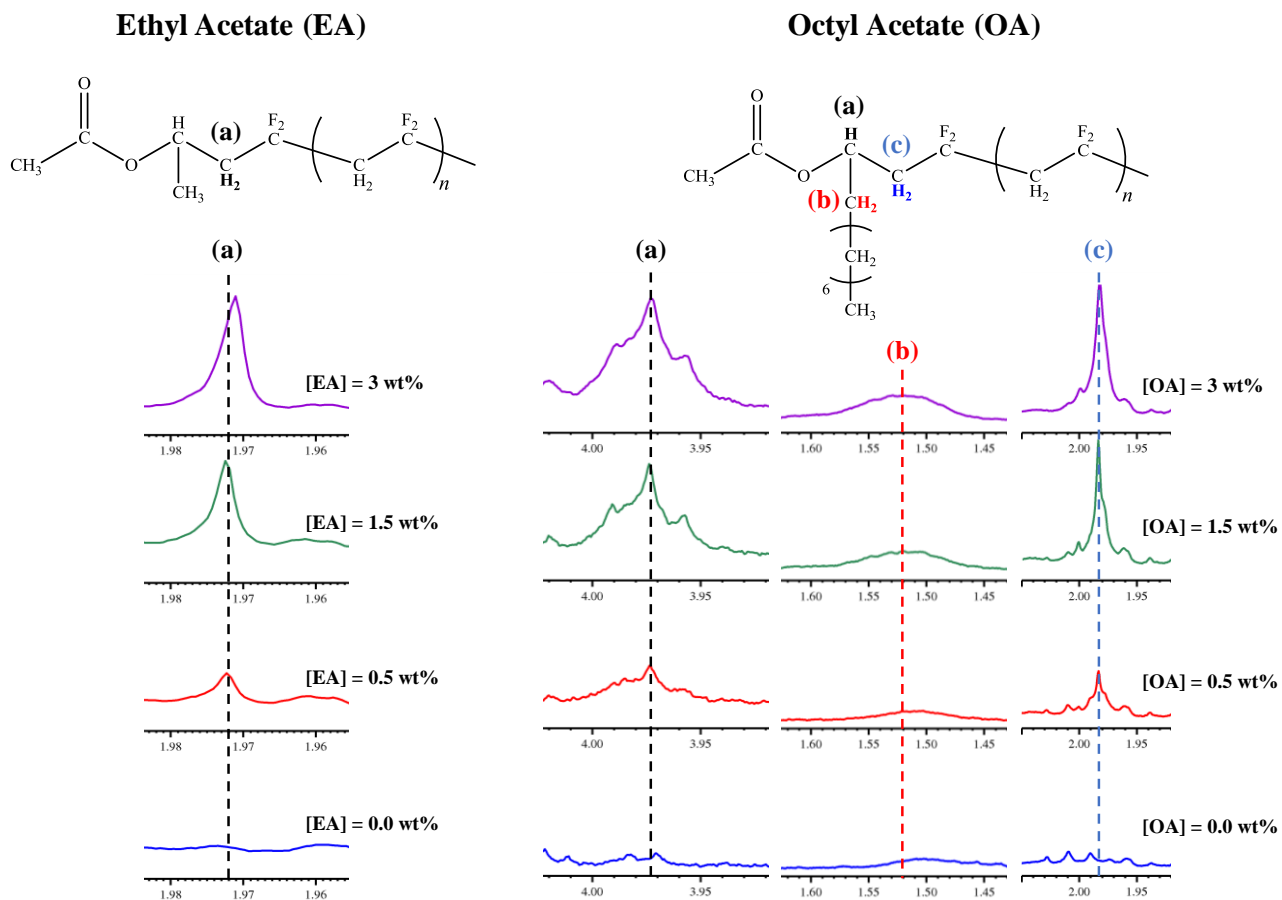
presence of end-chain groups pertaining to the CTA studied, chain transfer due to DMC was identified from the distinct peaks at 4.26 ppm and 3.70 ppm in  $^1\text{H}$  NMR and -93.20 ppm in  $^{19}\text{F}$  NMR spectra (Figure 12A).

EA-containing polymerization processes presented distinct peak at 1.97 ppm on  $^1\text{H}$  NMR spectra (Figure 13) with relatively low intensities and variation, regardless of concentration indicated by the integrated peak areas (Figure 12B). In agreement with SEC analysis, small  $M_w$  variations were noticed. It appears that most chain transfer reactions occur with DMC with the EA concentrations used in this particular system, complementary of the lowest  $C_T^{\text{app}}$  values. In contrast, OA chain transfer activity is not masked by DMC.  $^1\text{H}$  NMR characteristic peaks at 1.52, 1.97 and 3.98 ppm (Figure 13) presented higher intensities (Figure 12B) and higher  $M_w$  variation as concentration increases when OA was used as the CTA. In accordance, OA possesses  $C_{T\text{app}}$  value 17 times higher than EA.

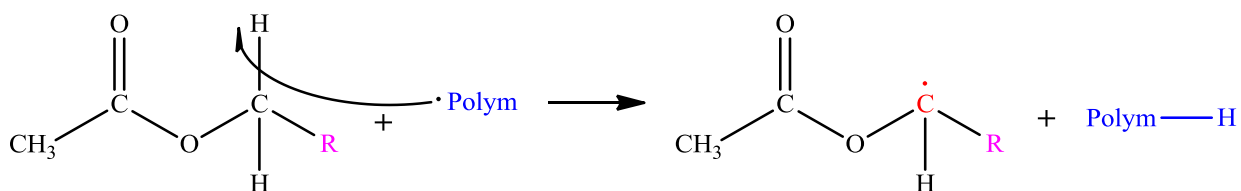
The rate of chain transfer rate of free radicals to an acetate-based CTA chain transfer activity, and reactivity of the resulting CTA-terminated radicals toward VDF depend on the length of their alkyl chain. Based on mechanism of chain transfer in Figure 14, it is noticeable that the chain transfer reaction occurs at the  $\beta$ -carbon, and therefore higher chain transfer activity will occur in the species with a stronger dipole. OA has 7 carbons, thus creating a stronger dipole in the  $\beta$ -carbon than EA, leading to higher chain transfer activity. However, steric hindrance of VDF units being added to the CTA-reinitiated polymer chains will occur as alkyl chain length increases. Therefore, the long, stable octyl chains of OA-reinitiated polymer chains will hinder further propagation, whereas EA, containing a much smaller alkyl chain length of 2 carbons, hindrance will be less significant (Figure 9).







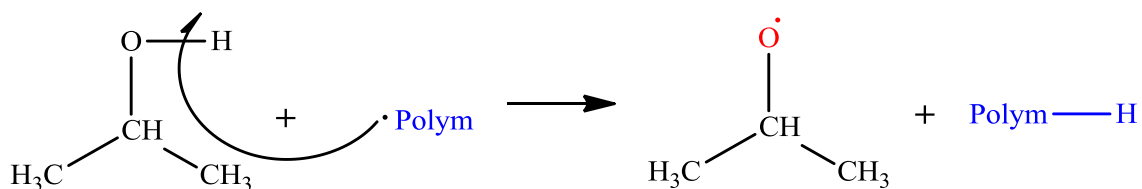
**Figure 13.** Comparison of the  $^1\text{H}$  NMR characteristic peaks of EA and OA for PVDF solution polymerizations in DMC with addition of different concentrations of CTA's EA and OA, initiated by TBPP.



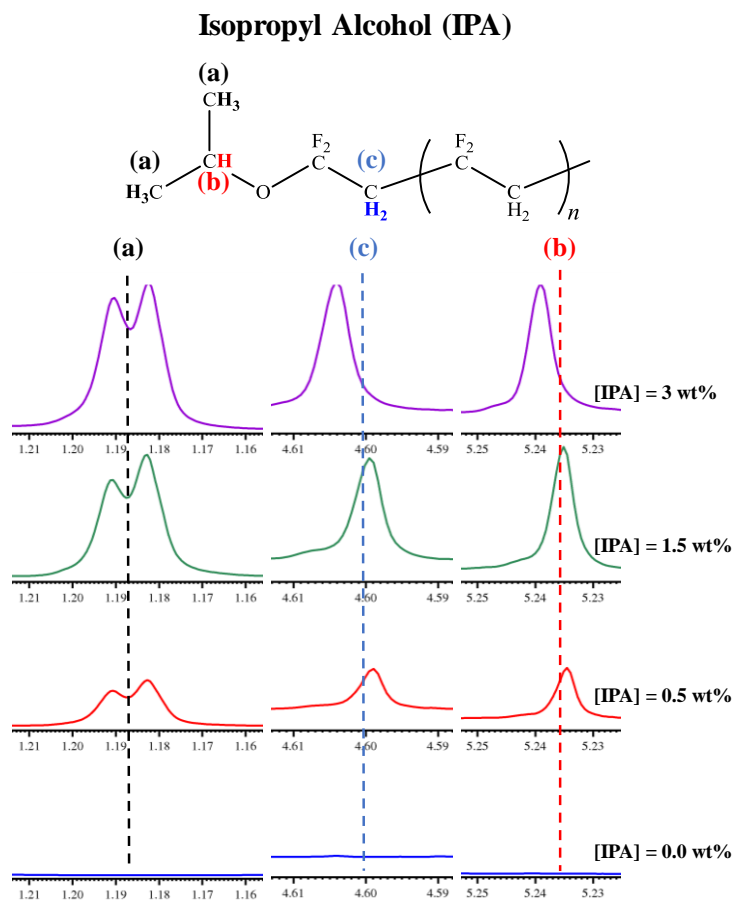
**Figure 14.** Chain transfer mechanism of Acetate-base CTA throughout the VDF solution polymerization.

Ethyl Acetate,  $\text{R} = -\text{CH}_3$ ; Octyl Acetate,  $\text{R} = -(\text{CH}_2)_6-\text{CH}_3$  (Legend: Polym = PVDF).

IPA displayed the biggest influence on molar mass on the PVDF solution polymerizations. Both  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra showed distinct peaks at 1.185, 4.60 and 5.20, -89.00, -90.50, -94.30 and -113.60 ppm and their integrated peak areas are the highest recorded, indicative of high chain transfer activity (Figure 12B). Indeed, the highest calculated  $C_T^{\text{app}}$  of  $4.32 \cdot 10^{-3}$  (13 times higher than OA and 215 times higher than EA) was of IPA due to the strongest dipole in the hydroxyl group combined with the reverse addition of a VDF unit which led to the most substantial decreases of  $M_w$  values (Table 4). However, IPA has an intermediate effect compared to the acetate-based CTA concerning the reactivity of the resulting IPA-terminated radicals toward VDF. Addition of VDF units are, in fact, more hindered when compared to EA, but less than OA. By confirming the IPA chain transfer mechanism (Figure 16) established by Bhattacharyya and Nandi<sup>30</sup> through  $^1\text{H}$  NMR (Figure 15), the intermediate reactivity of IPA-terminated radicals is postulated to occur due to the equilibrium between steric hindrance of two methyl groups surrounding the strong dipole in the hydroxyl group which re-initiates the VDF polymerization.



**Figure 15.** Chain transfer mechanism of IPA throughout the VDF solution polymerization. (Legend: Polym = PVDF).



**Figure 16.** Comparison of the  $^1\text{H}$  NMR characteristic peaks of IPA for PVDF solution polymerizations in DMC with addition of different concentrations of IPA, initiated by TBPP.

#### 4 CONCLUSION

A series of PVDF polymers were synthesized in both emulsion and solution polymerizations with various CTA. In the emulsion polymerizations, it was observed that increasing the hydrophobicity of the CTA lead to significant reductions in the observed rate of reaction. This results strongly suggests that a mechanism other than enhanced radical desorption is at the origin of the effect of CTA on the polymerization. In order to confirm this point, several solution polymerizations were subsequently run. The choice of solution polymerization was to eliminate the possibility of radical exit, and this would allow us to study more directly the role of the CTA.

All experiments containing CTA presented expected values of  $SC$ ,  $R_p$ ,  $M_w$  and  $D$  with the reference experiment containing nil CTA. Furthermore, all baseline assignments for  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectroscopy were found for independently of CTA type. Additionally, DMC (the solvent used for the solution experiments) was identified as a chain transfer agent due to distinct peaks at 4.26 and 3.70 ppm ( $^1\text{H}$  NMR) and -93.20 ppm ( $^{19}\text{F}$  NMR). The chain transfer mechanism proposed remained the same for all CTA-containing polymerizations.

Distinct  $^1\text{H}$  and  $^{19}\text{F}$  NMR peaks confirming the chain transfer reaction of EA, OA and IPA throughout the PVDF solution polymerization were found and a chain transfer mechanism for each CTA was proposed. Combined with SEC analysis and  $C_T^{\text{app}}$  calculations, it was definitive that the descending order chain transfer activity for the CTA studied is  $\text{IPA} > \text{OA} > \text{EA}$ . Degradative chain transfer was noticed due to stability of each CTA-born radicals. Acetate-derived CTA will affect the consumption rate of VDF depending on the length of the alkyl chain. It is postulated that the increasing number of carbons in the alkyl chain will increase the stability of acetate-based CTA-born and hinder VDF consumption. Finally, the stability of IPA-born radicals is provided from the steric hindrance of methyl groups surrounding the hydroxyl group taking part in the chain transfer mechanism.

## **ASSOCIATED CONTENT**

### **Supporting Information**

$^1\text{H}$  and  $^{19}\text{F}$  NMR spectra of all VDF solution polymerizations containing various concentrations of EA, OA and IPA are available in the Supporting Information.

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